# METALLOENZYME & THEIR RELATIONSHIP WITH CANCER, DIABETES & CARDIOVASCULAR DISEASE

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# DECLARATION

I hereby declare that this dissertation entitled "METALLOENZYME & THEIR RELATIONSHIP WITH CANCER , DIABETES & CARDIOVASCULAR DISEASE" submitted as part of Semester-VI-DSE-B4 for the B.Sc. Semester VI Honours Examination, 2025, is a review work carried out by me under the supervision of a faculty member of the Department of Chemistry, St.Paul's Cathedral Mission college. This dissertation has been prepared solely for the purpose of the DSE-B4 examination of Semester 6 (under CBCS) of the University of Calcutta and has not been submitted for any other degree nor used for any other purpose in any university or institute.

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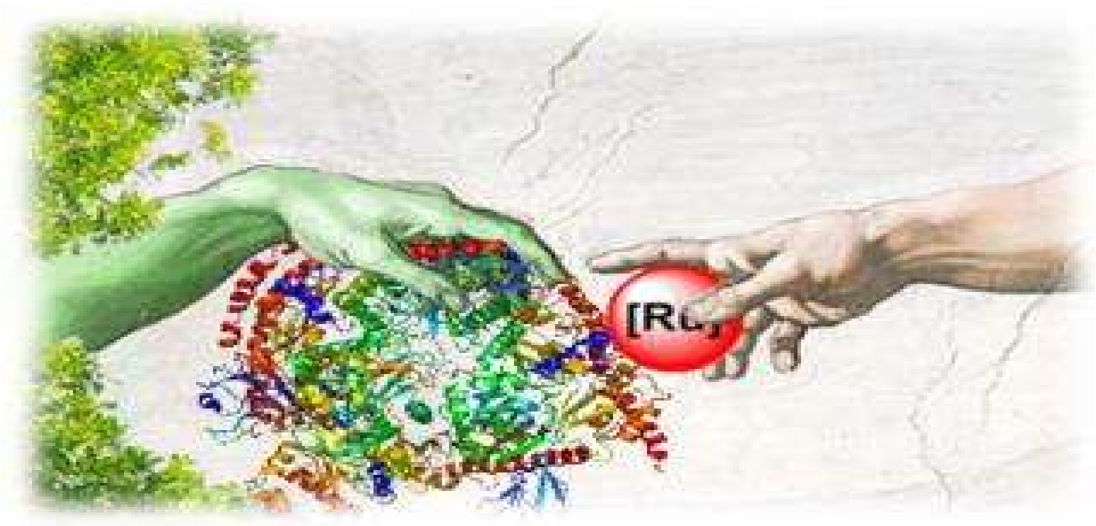
# ABSTRACT

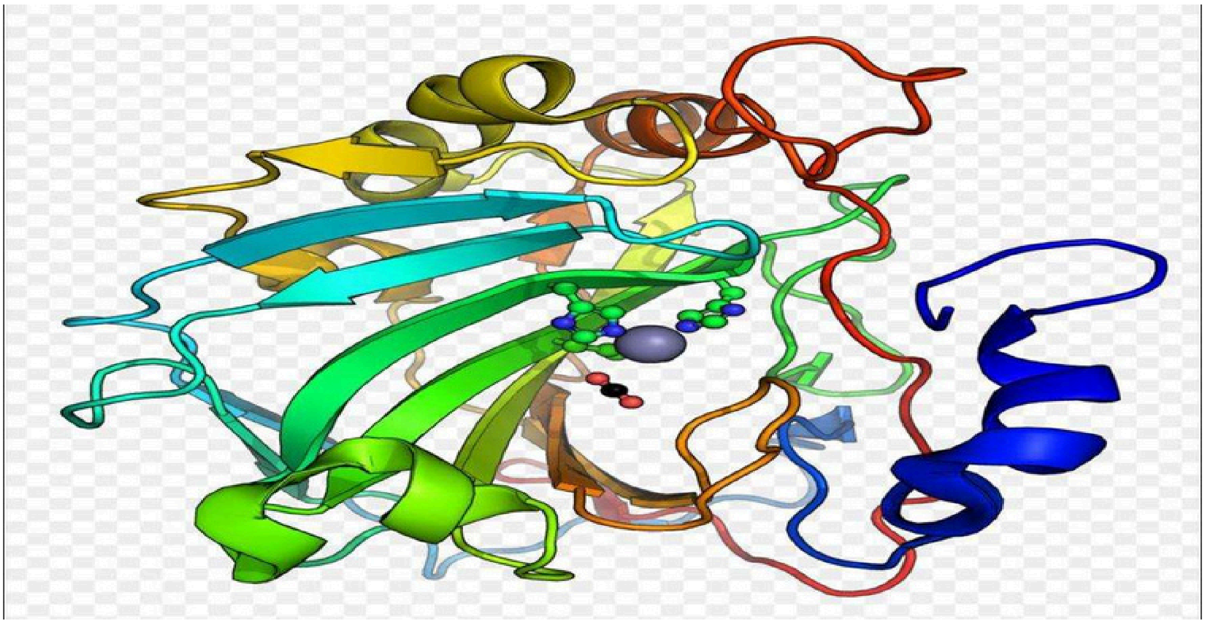
Metalloenzymes are a class of enzymes that contain one or more tightly bound metal ions, such as zinc, iron, copper, or manganese, which are essential for their catalytic activity. These metal ions play a critical role in the enzyme's function by stabilizing reaction intermediates, facilitating electron transfer, or activating substrates like water or molecular oxygen. The metal ions are typically coordinated by amino acid residues within the protein's active site, precisely positioning them to participate directly in the enzyme's biochemical reactions. Metalloenzymes are indispensable to a wide range of vital biological processes, including cellular respiration, antioxidant defense, DNA synthesis, and various metabolic pathways, making them key targets of study in biochemistry and medicine.



# CONTENTS

# What is METALLOENZYME

**Metalloenzymes** are a subclass of the metalloproteines which shows specific enzymatic activity in biological systems & the enzymes strongly bind one or more metal ions which serve as the active sites during their function. These metal ions are essential for the enzyme's catalytic function, as they can directly participate in chemical reactions by facilitating electron transfer, stabilizing charged reaction intermediates, or activating small molecules like water or oxygen. The metal ions are usually coordinated by specific amino acid side chains, such as histidine, cysteine, aspartate, or glutamate, which help position the metal precisely for its role in catalysis. Metalloenzymes are crucial in many fundamental biological processes, including respiration, photosynthesis, DNA synthesis and repair, detoxification of reactive oxygen species, and metabolism of various biomolecules.



## *Key Features:*

**Metal Ions Involved**: Common metals include **zinc ($Zn^{2+}$), iron ($Fe^{2+}/Fe^{3+}$), copper ($Cu^{+}/Cu^{2+}$), manganese ($Mn^{2+}$) and magnesium ($Mg^{2+}$).**

### Functions of Metal

a. Participate directly in catalysis.

b. Stabilize negative charges on reaction intermediates.

c. Help in substrate binding and positioning.

d. Participate in redox (electron transfer) reactions.

# Metalloenzyme & Their Consisting Metal

| **Metalloenzyme** | **Metal Centre** |
|---|---|
| Carbonic Anhydrase | $Zn^{2+}$ |
| Cytochrome C oxidase | $Fe^{2+}/Fe^{3+}$ & Cu+/$Cu^{2+}$ |
| Superoxide dismutase(SOD1) | $Cu^{2+}$ & $Zn^{2+}$ |
| Superoxide dismutase(SOD2) | $Mn^{2+}$ |
| Nitrogenase | FeMo-cofactor |
| Alcohol dehydrogenase | $Zn^{2+}$ |
| Catalase | $Fe^{3+}$(heme) |
| Glucothione peroxidase | Se (selenocysteine) |

# Carbonic Anhydrase & its Active Site

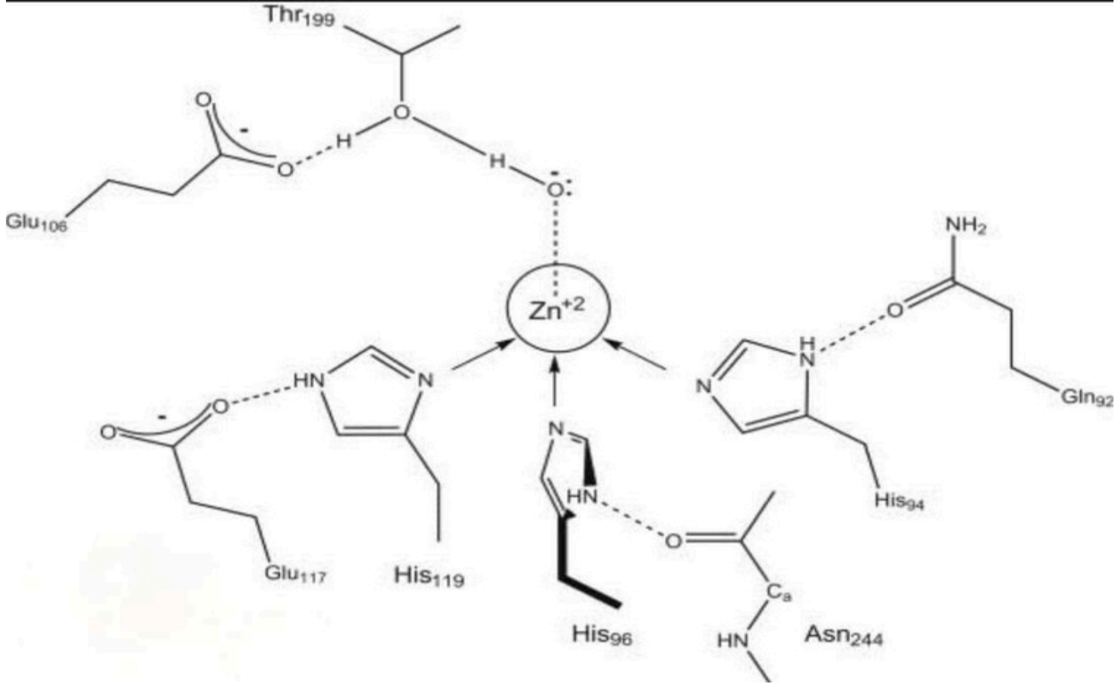
Carbonic anhydrase is an enzyme that plays a crucial role in various physiological processes. Here's a brief overview:

$H_2O+CO_2 \Longleftrightarrow H_2CO_3 \longleftrightarrow H^++CO_3^-$

In the erythrosites the hydration of $CO_2$ occurs during uptake of $CO_2$ by blood in tissue whereas the dehydration reaction of $H_2CO_3$ leading to release of $CO_2$ in the lungs. The carbonic anhydrase increases the rate of this equilibrium the significant.

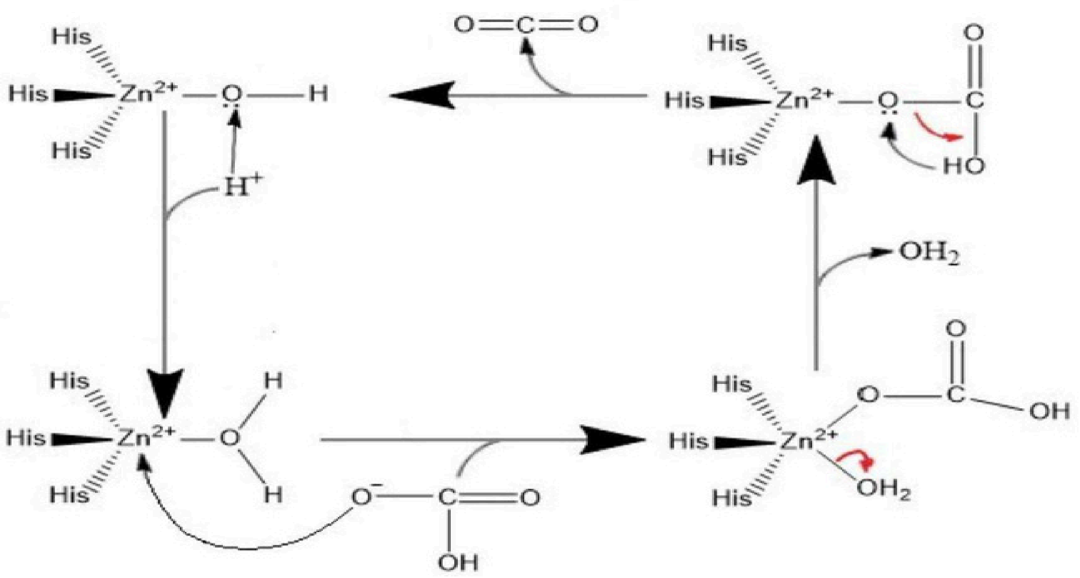
## ACTIVE SITE

The metalloprotein consists of 960 AA and contains $Zn^{2+}$ ion bound by three histidine residue. The td coordination sphere is completed by a $H_2O$ molecule. Near the $Zn^{2+}$ there is a hydrophobic pocket which captures $CO_2$.



Active site of carbonic anhydrase

## Mechanism of carbonic Anhydrase



### Step 1: Activation of water at the active site

The active site of carbonic anhydrase contains a zinc ion ($Zn^{2+}$) that is coordinated by three histidine residues and a water molecule. The positive charge of $Zn^{2+}$ attracts electrons from the bound water, which greatly lowers its pKa. This causes the water molecule to release a proton ($H^+$), resulting in the formation of a zinc-bound hydroxide ion ($Zn–OH^-$). This $Zn–OH^-$ acts as a powerful nucleophile that is essential for the enzyme's catalytic activity.

### Step 2: Binding and positioning of carbon dioxide ($CO_2$)

Carbon dioxide, produced as a metabolic waste product, diffuses into the enzyme's active site. The structure of the active site contains a hydrophobic pocket that helps trap and orient $CO_2$ in an ideal position next to the reactive $Zn–OH^-$. This precise positioning ensures that the nucleophilic attack can occur quickly and efficiently. Amino acid residues near the active site, such as Val121 and Thr199, help stabilize $CO_2$ in the correct orientation for the reaction.

## Step 3: Conversion of $CO_2$ to bicarbonate ($HCO_3^-$)

Once $CO_2$ is correctly positioned, the Zn-bound hydroxide ion carries out a nucleophilic attack on the carbon atom of $CO_2$. This results in the rapid formation of a zinc-bound bicarbonate intermediate. The bicarbonate is initially still coordinated to the zinc ion, which stabilizes the negative charge and facilitates the conversion of the gaseous $CO_2$ into a soluble, transportable form ($HCO_3^-$). This step is extremely fast and is the central chemical transformation catalyzed by carbonic anhydrase.

## Step 4: Release of bicarbonate and regeneration of the active site

After bicarbonate is formed, a fresh water molecule enters the active site and displaces the bicarbonate ion from the zinc, releasing $HCO_3^-$ into the surrounding solution. Meanwhile, the proton released in Step 1 is transported away from the active site by a special amino acid, usually His64, which acts as a proton shuttle. His64 passes the proton to the surrounding solvent, clearing the active site of excess protons. This step regenerates the $Zn–OH^-$ nucleophile, allowing the enzyme to immediately start another catalytic cycle with a new $CO_2$ molecule.

# Function Of Carbonic Anhydrase

1. **Catalyzes $CO_2$ hydration**: Carbonic anhydrase facilitates the reversible reaction of carbon dioxide ($CO_2$) and water ($H_2O$) to form bicarbonate ($HCO_3^-$) and protons ($H^+$).

$$CO_2 + H_2O \Longleftrightarrow H_2CO_3 \Longleftrightarrow H^+ + HCO_3^-$$

2. **Regulates pH and ion balance**: This enzyme helps maintain acid-base balance and ion homeostasis in various tissues, including the kidneys, lungs, and eyes.

## Importance

1. **Respiratory function**: Carbonic anhydrase aids in $CO_2$ transport and exchange in the lungs.

2. **Kidney function**: It helps regulate electrolyte balance and acid-base homeostasis in the kidneys.

3. **Ocular health**: Carbonic anhydrase is involved in maintaining the eye's fluid and electrolyte balance.

## Inhibitors and applications

1. **Diuretics and glaucoma treatment** : Carbonic anhydrase inhibitors are used to treat conditions like glaucoma and edema.

2. **Research and development** : Understanding carbonic anhydrase's role in various diseases has led to research on potential therapeutic applications.

Carbonic anhydrase is a vital enzyme with significant implications for human health and disease.

# METALLOENZYMES IN CANCER PREVENTION

**Zinc ($Zn^{2+}$)**– stabilizes protein structures and acts as a Lewis acid.

**Iron ($Fe^{2+}/Fe^{3+}$)** – common in redox reactions like oxygen transfer.

**Copper ($Cu^{2+}$)** – also involved in redox reactions.

These enzymes are involved in metabolism, DNA repair, detoxification, and antioxidant defence

## Antioxidant Defence

Cells constantly produce **reactive oxygen species (ROS)** like **superoxide ($O_2•^-$)** and **hydrogen peroxide ($H_2O_2$)**, which can damage DNA and proteins.

### Metalloenzymes neutralize ROS:

**SOD (Superoxide Dismutase)**: Uses $Cu^{2+}/Zn^{2+}$ or $Mn^{2+}$ to convert harmful superoxide into less reactive $H_2O_2$.

$$2O_2^{\cdot-}+2H^+ \Longrightarrow O_2+H_2O_2$$

**Catalase (Fe-based)**: Breaks $H_2O_2$ into water and oxygen.

$$2H_2O_2 \Longrightarrow 2H_2O+O_2$$

These reactions prevent ROS-induced mutations and damage that can lead to cancer.

## DNA Repair

DNA is constantly under attack from radiation, chemicals, and oxidative damage.

**Zinc-finger enzymes** use $Zn^{2+}$ to stabilize their structure and bind DNA accurately, guiding repair.

**PARP (Poly ADP-Ribose Polymerase)**: A $Zn^{2+}$-dependent enzyme that detects DNA single-strand , breaks & strangle repair system

Without such enzymes, DNA damage can accumulate and trigger mutations.

## Cell Cycle & Apoptosis Regulation

Cancer results from uncontrolled cell growth.

**p53**, a key tumor suppressor protein, requires **$Zn^{2+}$** to maintain its shape and bind DNA. It stops the cell cycle when damage is detected, or it initiates **apoptosis** (programmed cell death).

* If **$Zn^{2+}$** is missing or mutated in **p53**, it can't function properly, leading to unchecked cell division and cancer.

## Detoxification

The liver detoxifies harmful chemicals using **cytochrome P450 enzymes**.

These enzymes contain a **heme group with $Fe^{2+}$** that helps insert oxygen into toxins (hydroxylation), making them water-soluble for excretion.

$$RH+O_2+NADPH+H^+ \Longrightarrow ROH+H_2O+NADP^+$$

This prevents carcinogens (like those in tobacco or pollutants) from accumulating and damaging DNA.

## Immune Function Support

The immune system helps detect and destroy abnormal or cancerous cells:

**Myeloperoxidase (MPO)** uses $Fe^{3+}$ in heme to make hypochlorous acid (HOCl), a toxic substance that kills pathogens.

**Zinc-dependent enzymes** aid in proper immune signaling (e.g., cytokines).

A well-functioning immune system reduces cancer risk by catching mutated cells early.

## Summary

Metalloenzymes are **key defenders against cancer** through their chemistry:

1. Redox reactions with Cu, Fe, Mn combat oxidative damage.
2. Zn supports structural proteins for DNA binding and repair.
3. Fe enables detoxification of potential carcinogens.
4. Enzyme malfunction or metal deficiency can lead to **mutations, immune failure, or uncontrolled cell growth.**

# METALLOENZYME IN CARDIOVASCULAR DISEASE PREVENTION

## 1. Neutralizing Reactive Oxygen Species (ROS)

In the bloodstream and vascular tissues, ROS such as **superoxide ($O_2^{\bullet -}$)** and **hydrogen peroxide ($H_2O_2$) are produced during metabolism and inflammation. Excess ROS damages blood vessels,** oxidizes LDL cholesterol, and triggers plaque formation.

Metalloenzymes protect against this:

### Superoxide Dismutase (SOD):

Uses **copper ($Cu^{2+}$)** and **zinc ($Zn^{2+}$)**or **manganese ($Mn^{2+}$)** at the active site to catalyze:

$$2O_2^{\cdot -} + 2H^+ \Longrightarrow H_2O_2 + O_2$$

This reaction prevents superoxide from reacting with nitric oxide (NO) to form toxic peroxynitrite ($ONOO^-$).

### Catalase (Fe-heme enzyme):

Converts $H_2O_2$ to water and oxygen:

$$2H_2O_2 \Longrightarrow 2H_2o + O_2$$

Catalase contains **iron** in a heme group, which cycles between $Fe^{3+}$ and $Fe^{4+}$ during the reaction.

## 2. Protecting Nitric Oxide (NO) and Vascular Tone

Nitric Oxide Synthase (NOS) enzymes are **$Zn^{2+}$- and Fe-dependent** and synthesize NO from **L-arginine**:

$$\text{L-arginine} + O_2 \xrightarrow{NADPH} \text{L-citrulline} + NO + NADP^+$$

NO is a vasodilator—it relaxes smooth muscle cells in blood vessels, lowers blood pressure, and inhibits platelet aggregation.

However, ROS like superoxide ($O_2^{\bullet-}$) can react with NO to form **peroxynitrite ($ONOO^-$),** which is toxic and reduces NO availability. By removing ROS, metalloenzymes protect NO levels and maintain healthy vascular function.

## 3. **Controlling Inflammation**

During immune responses, **myeloperoxidase (MPO)**—a Fe-heme metalloenzyme—produces **hypochlorous acid (HOCl)** from $H_2O_2$ and chloride ions:

$$H_2O_2 + Cl^- \rightarrow HOCl + H_2O$$

While HOCl kills pathogens, excess production can oxidize LDL and damage endothelial cells. Antioxidant metalloenzymes help modulate and limit this inflammatory response.

## 4. **Preventing Lipid Oxidation and Plaque Formation**

Oxidized low-density lipoprotein (ox-LDL) is a key driver of atherosclerosis. **Glutathione peroxidase**, by reducing lipid peroxides (ROOH), prevents:

* Oxidation of cholesterol

* Foam cell formation

* Arterial plaque buildup

The chemistry involves electron transfer from glutathione (GSH) to lipid peroxides, catalyzed by a **selenocysteine residue** at the enzyme's active site.

## 5. **Maintaining Metal Ion Homeostasis**

Transition metals like **$Fe^{2+}$** and **$Cu^{+}$** can catalyze ROS formation via the **Fenton reaction**:

$Fe^{2+} + H_2O_2 \Longrightarrow Fe^{3+} + OH^{-} + .OH$

Metalloenzymes, such as ferritin and ceruloplasmin **bind excess metal ions** to prevent them from engaging in these damaging reactions.

Metalloenzymes use their metal cofactors (Cu, Zn, Fe, Mn, Se) to:

* Catalyze antioxidant reactions (neutralizing $O_2{\bullet}^{-}$ and $H_2O_2$)

* Produce and preserve **nitric oxide (NO)** for vasodilation

* Detoxify lipid peroxides

* Control inflammation via redox chemistry

* Regulate free metal ions to prevent toxic reactions

These biochemical processes **protect blood vessels** from oxidative damage, inflammation, and plaque buildup—key factors in cardiovascular disease.

| Metalloenzyme | Metal(s) | Function | Role in CVD prevention |
|---|---|---|---|
| SOD | Cu/Zn, Mn, Fe | Antioxidant defence | Reduces oxidative stress |
| NOS | Fe(heme) ,Zn | Produces NO | Maintains blood pressure and vessel health |
| ACE | $Zn^{2+}$ | Forms angiotensin II | Target for blood pressure control |
| Cytochrome P450 | Fe(heme) | Lipid metabolism | Balances cholesterol |
| MMPs | $Zn^{2+}$,$Ca^{2+}$ | ECM remodeling | Prevents plaque rupture |

# METALLOENZYME IN DIABETES PREVENTION

## 1. Superoxide Dismutase (SOD) – Oxidative Stress Control

### Metal Centers:

Cu/Zn SOD: $Cu^{2+}/Cu^{+}$ (catalytic), $Zn^{2+}$ (structural)

Mn SOD: $Mn^{3+}/Mn^{2+}$ (mitochondrial)

Fe SOD: $Fe^{3+}/Fe^{2+}$ (in some bacteria)

### 1.Chemical Reaction:

$2\,O_2^{-} + 2\,H^{+} \xrightarrow{SOD} H_2O_2 + O_2$

### Mechanism:

2. $Cu^{2+}$ accepts an electron from **superoxide ($O_2^{-}$)** → $Cu^{+}$

3. $Cu^{+}$ donates the electron to another $O_2^{-}$ to form $O_2$ and regenerate $Cu^{2+}$

4. $Zn^{2+}$ stabilizes the structure and maintains proper geometry

### Diabetes Role:

1. **β-cells** are sensitive to ROS due to low endogenous antioxidant enzymes

2.**SOD** minimizes oxidative damage, preserving **insulin-producing β-cells**

## 2. Catalase – Hydrogen Peroxide Detoxification

### Metal Center:

Fe (heme) coordinated to a porphyrin ring

### Reaction:

$2\,H_2O_2 \xrightarrow{Catalase} 2\,H_2O + O_2$

### Mechanism:

$Fe^{3+}$ in the heme reacts with $H_2O_2$ → forms Compound I ($Fe^{4+}=O$)

Another $H_2O_2$ molecule reduces it back to $Fe^{3+}$, releasing water and $O_2$

### Diabetes Role:

Prevents $H_2O_2$ accumulation → protects pancreatic and vascular cells from oxidative stress linked to **insulin resistance** and **β-cell apoptosis**

## 3. Glutathione Peroxidase (GPx) – Lipid Peroxide Removal

### Metal Involvement:

Core enzyme uses **selenocysteine (Se)**

**$Zn^{2+}$** is required indirectly for **GPx gene expression and activation**

### Reaction:

$ROOH + 2\,GSH \xrightarrow{GPx} ROH + GSSG + H_2O$

### Mechanism:

**$Se^-$** in selenocysteine attacks peroxide (ROOH)

Forms selenenic acid intermediate, reduced back by GSH (glutathione)

### Diabetes Role:

Reduces **lipid peroxides**, inflammatory mediators that impair **insulin signaling**

Helps prevent or delay **insulin resistance**

## 4. Protein Tyrosine Phosphatase 1B (PTP1B) – Insulin Signaling Regulation

### Metal Involvement:

$Zn^{2+}$ is important for **stability** and **folding** of PTP family enzymes

### Function:

Dephosphorylates tyrosine residues on **insulin receptor (IR)**

$\text{IR-P} \xrightarrow{\text{PTP1B}} \text{IR+ Pi}$

### Mechanism:

1. Catalytic cysteine attacks phosphate ester, forming **phospho-cysteine intermediate**
2. Hydrolyzed to release phosphate and regenerate the enzyme

### Diabetes Role:

1. Overactive PTP1B → decreased insulin signaling → insulin resistance
2. PTP1B inhibitors (some metal-based) are being developed to improve glucose uptake

## 5. Carbonic Anhydrase (CA) – pH Regulation & Insulin Secretion

### Metal Center:

**$Zn^{2+}$** tetrahedrally coordinated to 3 His residues + 1 $H_2O/OH^-$

### Reaction:

$CO_2 + H_2O \xrightarrow{CA} HCO_3^- + H^+$

### Mechanism:

1. $Zn^{2+}$-bound $OH^-$ nucleophilically attacks $CO_2 \rightarrow HCO_3^-$

2.Proton is shuttled away via histidine or buffer

### Diabetes Role:

1. Maintains **intracellular pH** and **$CO_2$ buffering,** which affects:

2.Insulin granule exocytosis

3.Glucose transporters (e.g., GLUT4)

## 6. Metallothionein – Antioxidant and Metal Buffer

### Metal Binding:

Binds multiple $Zn^{2+}$ and $Cu^{+}$ via thiolate (–SH) groups on cysteines

### Function:

Scavenges ROS via thiol redox chemistry

Regulates intracellular levels of $Zn^{2+}$ and $Cu^{+}$ needed for other enzymes

### Diabetes Role:

Reduces oxidative/inflammatory damage to β-cells

$Zn^{2+}$ release helps regulate insulin storage and release.

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UNIVERSITY OF CALCUTTA

**B.Sc. Chemistry (Honours) Semester - VI (Under CBCS)**
**Examination, 2025**

**Course: CEMA DSE-B4 (Dissertation)**

# Topic: Chemical Explosives

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# Contents

# Chemical Explosives: History,Composition, Effects, and Applications :

## Abstract

Chemical explosives have been pivotal to human advancement, playing essential roles in mining, construction, warfare, and space exploration. This dissertation investigates the fundamental chemistry, classifications, mechanisms, synthesis, and applications of chemical explosives. Additionally, it addresses the safety concerns, environmental impact, and future directions of explosive materials research.

## 1: Introduction

### WHAT IS CHEMICAL EXPLOSIVE?

Chemical explosives are substances capable of rapid chemical reactions that release energy, producing heat, light, sound, and pressure waves. Their utility stems from their ability to release massive amounts of energy in extremely short periods, enabling applications from engineering demolitions to propulsion in rocketry. Understanding the chemistry and mechanics of explosives is vital for their safe and effective use.

### 1.1 Definition

An explosive is a reactive substance containing a significant amount of potential energy that can produce an explosion if released suddenly, usually accompanied by the production of light, heat, sound, and pressure.

### 1.2 Historical Overview

The history of explosives dates back to the invention of gunpowder in 9th-century China. Subsequent centuries saw the evolution of explosives, culminating in the development of nitroglycerin, dynamite, TNT, RDX, and modern nuclear explosives.

Ancient Times

- Around 9th century  (Tang Dynasty, China):
  The first explosive “Greek Fire” or gunpowder was invented. It’s a mix of saltpeter (potassium nitrate), sulfur and charcoal.

17th–18th Century

- Refined Gunpowder Use:
  During this time, the formulation and manufacturing of gunpowder became more precise.
- Military Engineering:
  Explosives were used for warfare, mining, and blasting operations.

## 19th Century: The Era of Modern Explosives

- 1847 – Nitroglycerin:
  Italian chemist Ascanio Sobrero discovered nitroglycerin, a highly sensitive and powerful explosive.
- 1867 – Dynamite:
  Alfred Nobel stabilized nitroglycerin by absorbing it into an inert substance (diatomaceous earth) to create dynamite—much safer to handle.
- Military and Industrial Boom:
  Dynamite revolutionized mining, construction, and warfare.

## Late 19th to Early 20th Century

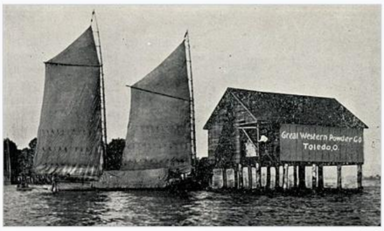
- Development of Smokeless Powders:
  Chemicals like nitrocellulose (guncotton) led to smokeless powders, replacing black powder in firearms and artillery.
- High Explosives:
  Compounds like TNT (trinitrotoluene, discovered 1863) became widespread due to their stability and power.

## 20th Century

- World Wars:
  Massive development and production of new explosives like RDX (Research Department Explosive), PETN, powerful bombs, for military use.
- Plastic Explosives:
  Easily moldable and very powerful, used in demolition and sabotage.

## Modern Times

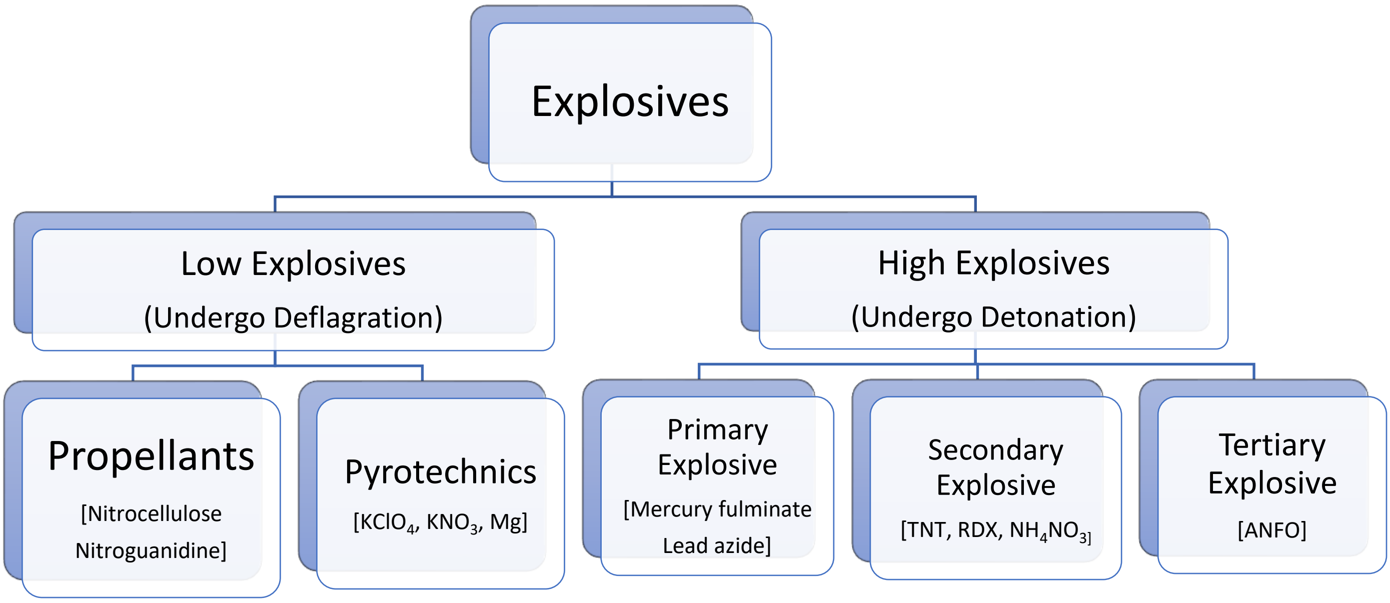
- Advanced Explosives:
  Scientists have developed high-performance explosives like HMX, CL-20, and insensitive munitions (which don't easily detonate by accident).
- Controlled Demolition & Special Applications:
  Explosives are used not just in weapons but in mining, construction, aerospace (e.g., separation charges), and even airbags in cars.



The Great Western Powder Company of Toledo, Ohio, a producer of explosives, seen in 1905

## 2: Classification

Chemical explosives are broadly classified based on their physical behavior and chemical structure. But the most common classification is based upon sensitivity of explosives –



Deflagration and detonation are two terms often used in association with explosives. ***Deflagration*** involves subsonic flame propagation velocity, typically below 100 m/s, and relatively modest overpressures, below 0.5 bar.

***Detonation***, on the other hand, is featured by supersonic flame propagation velocities, often up to 2000 m/s, and highover pressures of gases released up to 20 bars. Being very fast reactions, these explosions create a high-pressure shock wave that causes significant damage at large distances from the site of the blast. Detonation is unique in the rapid rate at which energy is released. A detonating high explosive creates a tremendous *power density* compared to deflagration materials: Burning acetylene 102 (W/cm3) Deflagrating propellant 106 (W/cm3) Detonating high explosive 1010 (W/cm3). The shock waves in high explosives travel at speeds in the range 5000-9000 m/s, compared to gun powder, a low explosive, at ~100 m/s.

### 2.1 Low explosives :

Those substances which do not explodes suddenly and their shock wave travels with slower rate are known as low explosive. The chemical reaction of such explosives starts at surface of material and travels inside at rate of 20-25 cm sec-$^{1}$. The gases produces during burning disperse readily without building high pressure, therefore such explosive can be controlled easily. Such materials are commonly used as missile, rocket propellants and in fire work.

- Examples: Gun powder, colloidal nitrocellulose etc.

### 2.2 High explosives :

A material which detonates and the shock wave passes through the material at a supersonic sound is known as a high explosive. They explodes with explosive velocity ranging from 3 to 9 km sec-1. They are commonly used in mining demoelition, military applications etc

- Examples: Trinitrotoluene (TNT), Research development explosive (RDX), High melting explosive (HMX), Pentaery Thritol tetranitrate (PETN) etc.

#### (1) Primary explosives :

Those explosives which are extremely sensitive to the action of heat, pressure, friction, static electricity are known as primary explosive. They are commonly used as detonators or to trigger large explosives.

- Examples: Acetone peroxide, Ethyl azide, Halogen azides, nitroglycerine, peroxy acids etc.

#### (2) Secondary explosives :

These are less sensitive than primary explosive and require relatively are impact of heat, pressure friction, radiation etc to initiate explosive. Because of lesser sensitivity they are usable in a wide vareity of application and are safe to handle and store. They are used in large quantities in a explosive train and are initiated by a smaller quantity of primary explosive.

- Examples: Trinitrotoluene (TNT), Research Development explosive (RDX) or cyclontite etc.

#### (3) Tertiary explosives :

These are least sensitive to the action of heat, pressure, friction, radiations etc. They are so insensitive to shock that they cannot be detonated by practical Quantities of primary explosives and instead, they require explosive booster of secondary explosive. They are used as blasting agents in large scale mining and construction operations.

- Examples: ANFO (ammonium nitrate fuel oil)

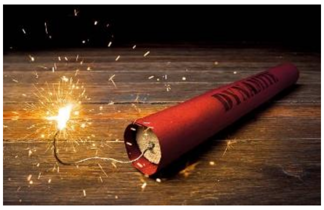
## High explosives are further divided into following four categories:

- **Single Compound Explosives:** These explosives contain only one compound in them. Ex-amples, TNT, PETN, RDX, picric acid etc.

- **Binary Explosives**: These explosives contain only one compound in them. Ex-amples, TNT, PETN, RDX, Picric acid etc.

- **Plastic Explosives**: Those explosives which are in plastic state and can be hand moulded into various shapes without any serious risk are known as plastic explosives. Such explosives usually contain TNT in them.

- **Dynamites:** Those explosives which contain Nitroglycerin (NG) as the principal ingredient in them are known as dynamite. Blasting gelatin-Dynamine, Gun cotton cordite, gelignite straight dynamite etc are the exemples of dynamite.



## 3: Synthesis and Preparation

### Lead azide $Pb(N_3)_2$

Lead azide is commonly prepared by treating sodium azide with lead acetate or lead nitrate. Sodium azide itself can be obtained by the reaction of sodium amide with nitrous oxide.

| $NaNH_2$ | + | $N_2O$ | → | $N_aN_3$ |
|---|---|---|---|---|
| **Sodium amide** | | **Nitrous Oxide** | | **Sodium azide** |

| $2\ NaN_3$ | + | $Pb(CH_3COO)_2$ | → | $Pb(N_3)_2$ | + | $2CH_3COONa$ |
|---|---|---|---|---|---|---|
| **Sodium azide** | | **Lead acetate** | | **Lead azide** | | **Sodium acetate** |

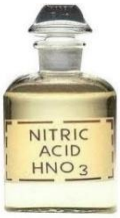
Alternatively, lead azide can also be obtained by the reaction of sodium azide with lead nitrate.

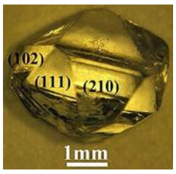
| $2\ NaN_3$ | + | $Pb(NO3)_2$ | → | $Pb(N_3)_2$ | + | $2\ NaNO_3$ |
|---|---|---|---|---|---|---|
| **Sodium azide** | | **Lead nitrate** | | **Lead azide** | | **Sodium nitrate** |

- **RDX $(CH_2NNO_2)_3$**

Hale's method: RDX is obtained by the destructive nitration of hexamethylene tetramine with conc, HNO3.

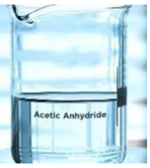
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $(CH_2)_6 N_4$ | + | $4\ HNO_3$ | → | $(CH_2NNO_2)_3$ | + | $NH_4 NO_3$ | + | $3\ HCHO$ |
| **Hexamethylediamine** | | **Nitric acid** | | **RDX** | | **Ammonium Nitrate** | | **Formaldehyde** |

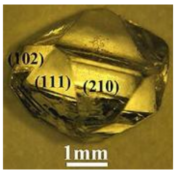






Ebele-Schiessler Ross method: RDX can be prepared by the addition of paraformaldehyde and ammonium nitrate to acetic anhydride at 70°C.

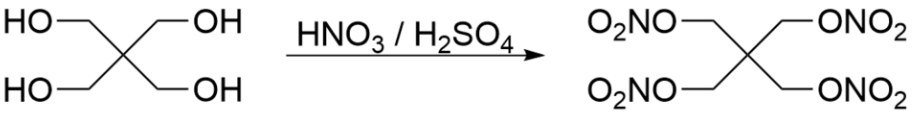
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $3\ HCHO$ | + | $3NH_4NO_3$ | + | $6\ (CH_3CO)_2O$ | → | $(CH_2NNO_2)_3$ | + | $12\ CH_3COOH$ |
| **Formaldehyde** | | **Ammonium Nitrate** | | **Acetic anhydride** | | **RDX** | | **Acetic acid** |



- **PETN [Pentaerythritol tetranitrate]**

- **IUPC Name - *2,2-Bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate***



**Pentaerythirtol** **Pentaerythirtol tetranitrate (PETN)**


## 4: Oxygen Balance

Oxygen balance (OB) provides insights into the oxygen content of an explosive compound relative to the amount needed for complete combustion. Here’s what positive and negative oxygen balances mean:

### 4.1 Positive Oxygen Balance:

A positive OB indicates the compound contains excess oxygen beyond what is required for complete combustion of carbon and hydrogen.

Implications:

- Complete Oxidation: A positive OB allows all carbon and hydrogen in the compound to be fully oxidized to $CO_2$ and $H_2O$.
- Potential Oxidizer: Compounds with a positive OB, such as ammonium nitrate, can act as oxidizing agents in mixtures, supplying oxygen to other fuel-rich compounds.

- Example: Ammonium nitrate ($NH_4NO_3$) has a positive OB of +20%, meaning it has more oxygen than it needs, which is why it’s commonly used as an oxidizer in explosive formulations.

### 4.2 Negative Oxygen Balance:

A negative OB means there is insufficient oxygen within the compound to completely oxidize all the carbon to carbon dioxide ($CO_2$) and hydrogen to water ($H_2O$) during combustion or detonation.

Implications:

- Incomplete Combustion: Since there isn’t enough oxygen in the molecule, it produces partially oxidized gases such as carbon monoxide (CO) and sometimes even elemental carbon (soot) upon detonation.
- High Energy Explosives: Many powerful explosives, like TNT, have a negative OB, often making them more fuel-rich, which can contribute to the explosive's power as external oxygen (like from the air) aids in complete combustion.

- Example: TNT ($C_7H_5N_3O_6$) has a significantly negative oxygen balance of -74%, meaning it lacks enough internal oxygen, resulting in products like CO and other incompletely oxidized gases.

$$\text{OB} = \frac{\left(x-2y-\frac{z}{2}\right)1600}{\text{Molar Mass of Compound}}$$

Where x is the number of oxygen atms, y is the number of carbon atoms and z is the number of hydrogen atoms.

## 4.3 Oxygen balance for PETN

$$C_5H_8N_4O_{12} \rightarrow 4CO_2 + 4H_2O + 2N_2 + C$$

Molecular wt for $C_5H_8N_4O_{12}$ = 5(12)+ 8(1)+ 4(14)+ 12(16) = 316 gm/mole

Here x(o) =12, y(C) =5, z(H) =8

$$\text{OB} = \frac{\left(12-2(5)-\frac{8}{2}\right)1600}{316} = -10.13\%$$

## 4.4 Oxygen balance for RDX

$$C_3H_6N_6O_6 \rightarrow 3CO + 3H_2O + 3N_2$$

Molecular wt for $C_5H_8N_4O_{12}$ = 3(12)+ 6(1)+ 6(14)+ 6(16) = 222 gm/mole

Here x(o) =6, y(C) =3, z(H) =6

$$\text{OB} = \frac{\left(6-2(3)-\frac{6}{2}\right)1600}{222} = -21.62\%$$

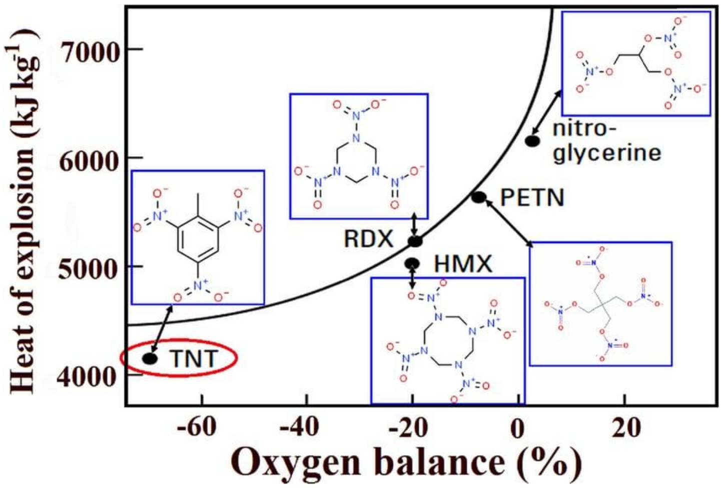
## 4.5 Oxygen balance for Lead azide $Pb(N_3)_2$

$$Pb(N_3)_2 \rightarrow Pb + 3N_2 \uparrow$$

$$\text{OB} = \frac{\left(x-2y-\frac{z}{2}\right)1600}{\text{Molar Mass of Compound}}$$

Where x is the number of oxygen atms, y is the number of carbon atoms and z is the number of hydrogen atoms.

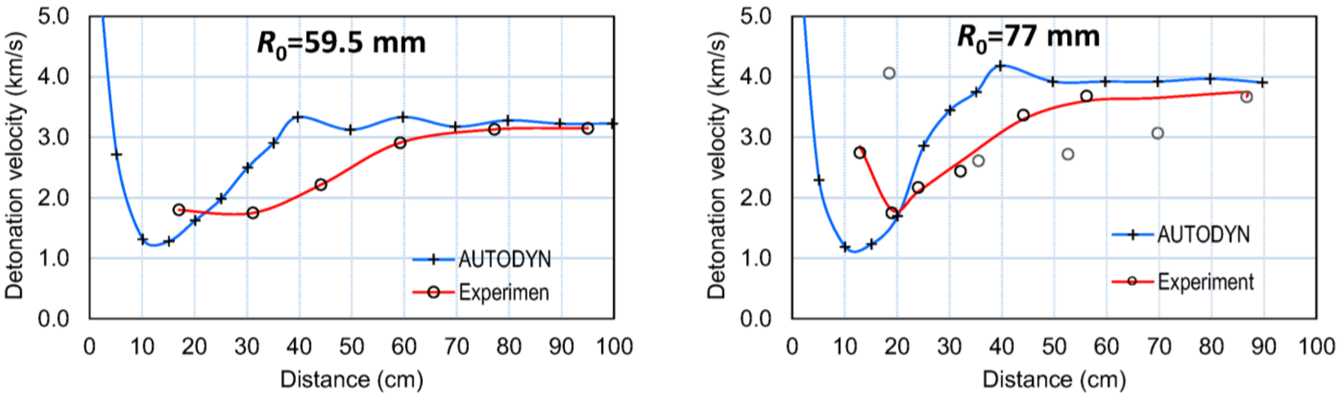
Oxygen balance = 0 (as x=0, y=0 and z=0)



## 5: Applications of Explosive

### 5.1 Civil Applications

- **Mining and Quarrying:** Use of ANFO (ammonium nitrate-fuel oil) for blasting.
- **Construction:** Demolition of buildings and tunnels.



**Shock Initiation and Propagation of Detonation in ANFO**

### 5.2 Military Applications

- **Weapons:** Use in bombs, grenades, and artillery shells.
- **Propellants:** For missiles and rocket engines.

### 5.3 Aerospace

- **Solid rocket propellants:** Such as ammonium perchlorate composite propellant (APCP).
- **Liquid rocket propellant:** Liquid propellants are widely used in rocket engines because they offer several distinct advantages.

#### Advantages

- Higher Efficiency: Liquid propellants generally have a higher specific impulse (a measure of fuel efficiency) than solid propellants, allowing rockets to achieve greater thrust with less fuel.
- Thrust Control: Liquid fuel engines can be throttled, shut down, and even restarted mid-flight, providing precise control over thrust levels. This is especially useful for stages that need precise maneuvering, such as those in orbit.

#### Disadvantages

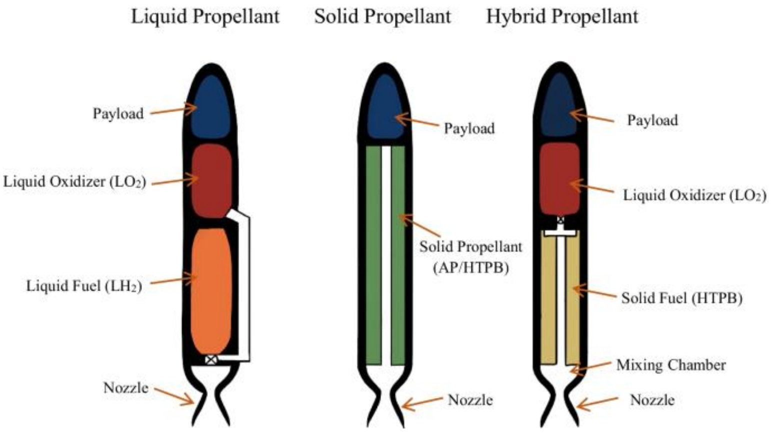
- Complexity and Cost: Liquid propellant systems are more complex to design and maintain. They require precise pumps, tanks, and plumbing, which increases cost and the risk of mechanical failure.

- Storage and Handling: Many liquid propellants, such as cryogenic fuels (like liquid hydrogen and oxygen), must be stored at extremely low temperatures. This makes handling, transport, and storage more challenging and costly, particularly for long-duration missions.

- Safety Concerns: Some liquid propellants are highly reactive and toxic (e.g., hydrazine-based fuels), requiring special precautions and increasing safety risks during fueling and handling.

## 6. Propellant :

Propellant is the chemical mixture burned to produce thrust in rockets and consists of a fuel and an oxidizer. A fuel is a substance which burns when combined with oxygen producing gas for propulsion.



An oxidizer is an agent that releases oxygen for combination with a fuel. Propellants are classified according to their state - liquid, solid, or hybrid.

## 7: Environmental and Health Impact

**Pollution**

- Residual explosives can contaminate soil and water sources, causing ecological harm.

**Toxicity**

- Exposure to explosive residues, such as TNT, can have carcinogenic and mutagenic effects.

**Remediation Strategies**

- Bioremediation using bacteria capable of metabolizing explosives is an emerging field.

## 8: Precautions needed for the storage of explosives

- Storing explosives safely requires strict adherence to regulations and specific precautions due to their sensitivity to environmental factors and handling. Here are some major precautions:

- **Controlled Environment**
  Explosives should be stored in a cool, dry environment to prevent deterioration. High temperatures or fluctuating conditions can make explosives unstable. Proper ventilation is essential to dissipate any gases that may be emitted from certain types of explosives over time.

- **Distance and Isolation**
  Storage facilities must be located at a safe distance from populated areas, other buildings, and transportation routes to minimize risk in case of accidental detonation. Explosives are stored separately from other materials, especially incompatible substances like flammables, corrosives, and reactive chemicals, which could exacerbate an accident.

- **Labeling and Inventory Management**
  Each type of explosive should be clearly labeled, and storage areas must have signage indicating the presence of hazardous materials. Precise records of the quantity, type, and condition of stored explosives should be maintained to monitor usage and shelf-life.

- **Protection from Ignition Sources**
  Static electricity, sparks, and open flames are strictly prohibited near explosives. Storage areas must be free from electrical equipment that could generate sparks. Tools used in the storage area should be made from non-sparking materials like brass or wood.

## 9: Future Perspectives

**Green Explosives**

- Development of environmentally benign explosives with minimal toxic byproducts.

**Smart Explosives**

- Integration of sensors to enable controlled or programmable detonations.

**Alternative Energetic Materials**

Research into ionic liquids and high-energy polymers aims to find safer alternatives.

## 10: Conclusion

Chemical explosives have revolutionized industries and warfare, yet their hazardous nature necessitates careful management. Advances in green chemistry, materials science, and safety engineering will shape the future of explosives, balancing efficacy with environmental stewardship and human safety.

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------------------------------------------------------------
Signature
Associate professor of St. Paul's CM College
Department of Chemistry

# B.Sc. Chemistry(H)Semester- VI (Under CBCS) Examination,2025

COURSE: CEMA DSE-B4

## CU ROLL NO: 223114-11-0048
## CU REGISTRATION NO: 114-1214-0226-22

# CERTIFICATE

This is to certify that the dissertation entitled 'ALL ABOUT ACID IONIZATION CONSTANT ($pK_a$)",submitted to the Department of Chemistry, St. Paul's C. M. College, Kolkata in partial fulfilment for the award of the degree of SEM-VI, DSE-B4 (under CBCS) in the B.Sc. Sem- VI, CEMA Examination 2025, CU, is a record of bona fide work carried out by Mrs. "Taniya Parvin", CU Roll No. 223114-11-0048 (CU Reg No: 114-1214-0226-22), under supervision and guidance.

This is a review work and has not been submitted to receive any other degree. All help received by him front various sources have been duly acknowledged.

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3. COMPARING ACIDIC BASIC STRENGTH
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7. NATURE OF ACTIVATING AND DEACTIVATING GROUP
8. CONCLUSION
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# ALL ABOUT ACID IONIZATION CONSTANT( p$K_a$)

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**Department Of Chemistry, St. Pauls Cathedral Mission College, Kolkata, India**

## ABSTRACT

The transition from first-year general chemistry a daunting task to second year organic chemistry is found by many students. There are many reasons for this, not the least of which is their lack of a solid understanding and appreciation of the importance of some basic Concepts and principles from general chemistry that plays an extremely crucial role in organic chem. one of the such Concept is logarithm value of acid ionization constant Such -log of $K_a$. And the other Such Concept is the solvent dependent like aqueous and org solvent (DMSO) is calculated at quantum Chemical level. For aqueous solvent short-range Solvation effect are considered by adding circumstantial water molecules as the first solvent Shell. And the Other side is the absence of $H_2O$; Corresponding organic solvent directly is used as the proton Capture and the resulted p$K_a$ are quite comparable

**KEYWORDS :** Ionization, Acid-Base, Gibbs – Energy, Nucleophilic strength

## INTRODUCTION

The concept of Bronsted acid base theory plays the vital role in organic chemistry. Generally organic chemistry uses the p$K_a$ values to predict chemical and physical property to plan experiments, to design reaction and to understand their mechanism. The p$K_a$ value of acid describes the equilibrium position of a specific reversible reaction: acid ionisation (sometimes it is called dissociation) like any other chemical equilibrium the position of minimized free energy and therefore the equilibrium constant depends on all of the characteristic of the reaction system, including temperature, pressure and the presence of other participating species specially solvents[1]. During the measurement the most common being in gas phase, dimethyl sulfoxide (DMSO) or $H_2O$. Chemistry in aqueous medium is a major thrust for health science related (biology, paramedical, pharmacy etc). One of the most important physical constants for a Bronsted acid is its $pK_a$. The equilibrium of acid ionization into the proton and the associated conjugate base can be simply described by the following way:

$$HA\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-\,(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

pka is the defined by $pka = -\log_{10} k_a$

Where HA denotes the parent acid, $A^-$ is the conjugate base and $H^+$ is the proton.

$K_a$ is the reflection of the strength of the acid. Weak acid with relatively higher $K\alpha$ values is stronger than acids with relatively lower $k_a$ values. Because strong acid is essentially 100% ionized, the concentration of the acid in the demonstration is nearly zero and the $k_a$ value approaches infinity. For this Type equation here.reason , $K_a$ values are generally reported for weak acids only. Here table of acid ionization constant for several acid .[2]

$H_2SO_4 \leftrightharpoons H^+ + HSO_4^-$ ; $HSO_4^- \leftrightharpoons H^+ + SO_4^{2-}$ $\underline{(pK_a = 1.3\times10^{-2})}$

$\underline{C_6H_5COOH \leftrightharpoons H^+ + C_6H_5COO^- \quad (pK_a=6.5\times10^{-5})}$

## DISCUSSION

### (1) COMPARING ACIDIC AND BASIC STRENGTH

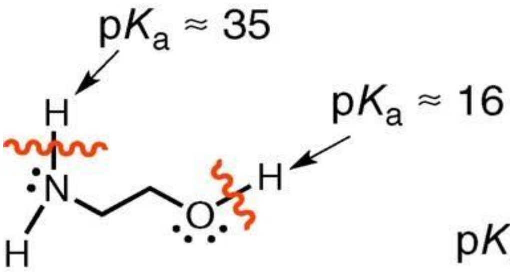
$pK_a$ value is used to predict which is the more strongly acid and base. $pK_a$ tell us different acid and basic property of substance.[3]

## FOR ACIDIC

we can also apply the concept of $pK_a$ on the polyprotic organic molecules to predict which protons will be lost in reaction with base.

Polyprotic amino alcohol contains two main sites for possible reaction with a base. There are two types of H (1) alcohol H, (2) Amino H, is low the reaction will take place this side, especially the H on oxygen. Likewise, the alkyne of the three potential c-H sites for base attack. The preferred reaction site is that of the terminal alkyne, possessing H attached to c that is sp hybridized thereby having a lower pka by some 19 orders magnitude compared to a vinyl hydrogen[5]

## EXAMPLE: 01



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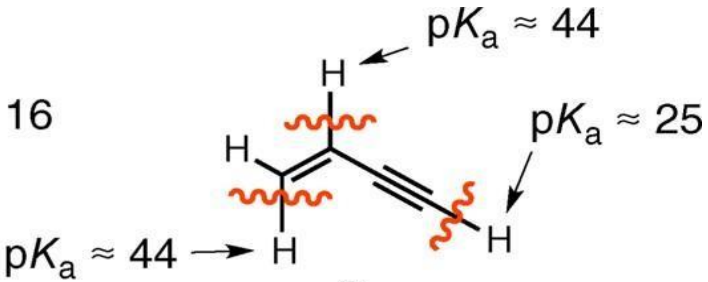
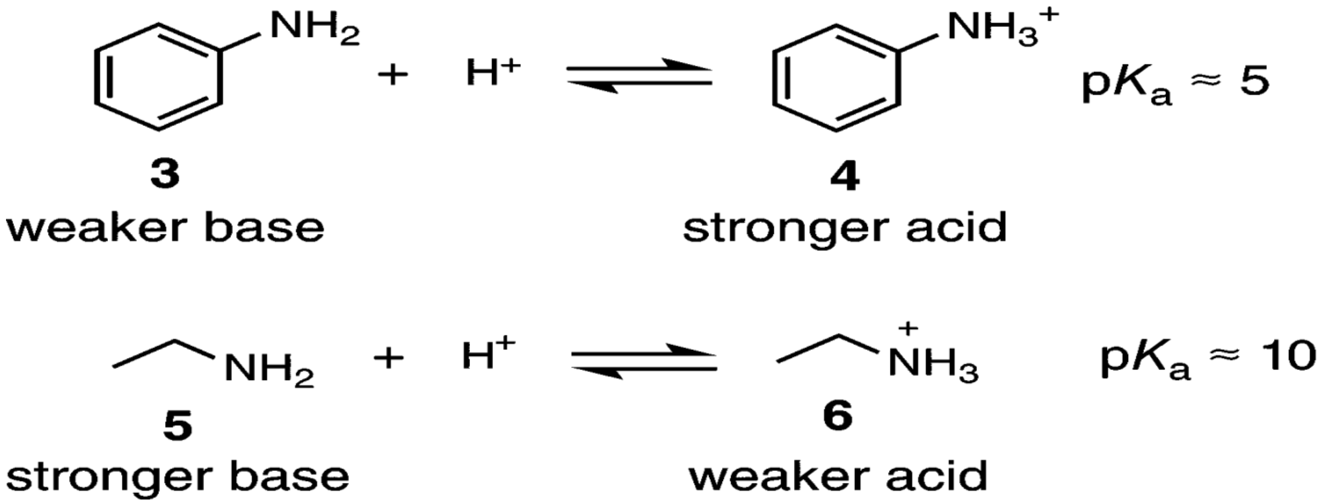


2

## FOR BASIC

The base whose conjugate acid is the weaker acid (has the higher p$K_a$) is the Stronger base.[6] From Bronsted acid-base theory the conjugate acid-base pair, that is the stronger Conjugate acid, the weaker the conjugate base and vice versa

## EXAMPLE:02



## (2) **GIBBS ENERGY CHANGE OF IONISATION**

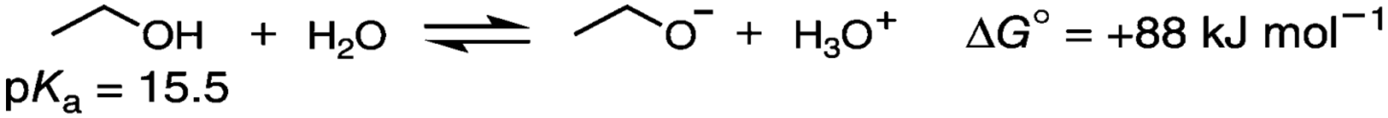
The Sign and magnitude of the $pK_a$ for an acid ionization in $H_2O$. is directly related to the sign and magnitude of the $\Delta G^0$ for ionization.[7,8] Large positive values of $pK_a$ indicate a large positive $\Delta G^0$. small positive values of pKa indicate a small positive $\Delta G^{0.}$ Large negative values of $pK_a$ indicates a large negative $\Delta G^0$. small negative values of pka indicates a small negative $\Delta G^0$.

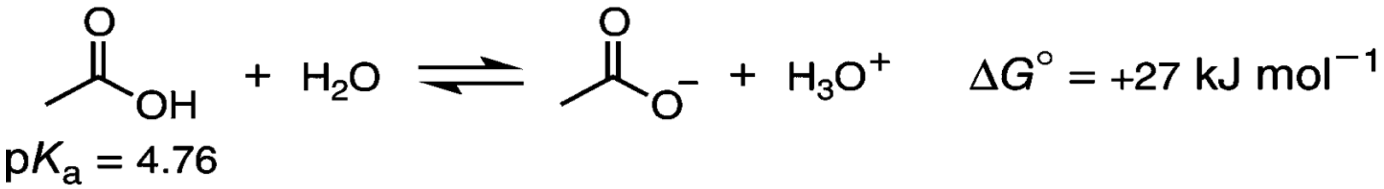
Starting with the relationship $\Delta G^0$ =-2.303RTlog $k_{eq}$

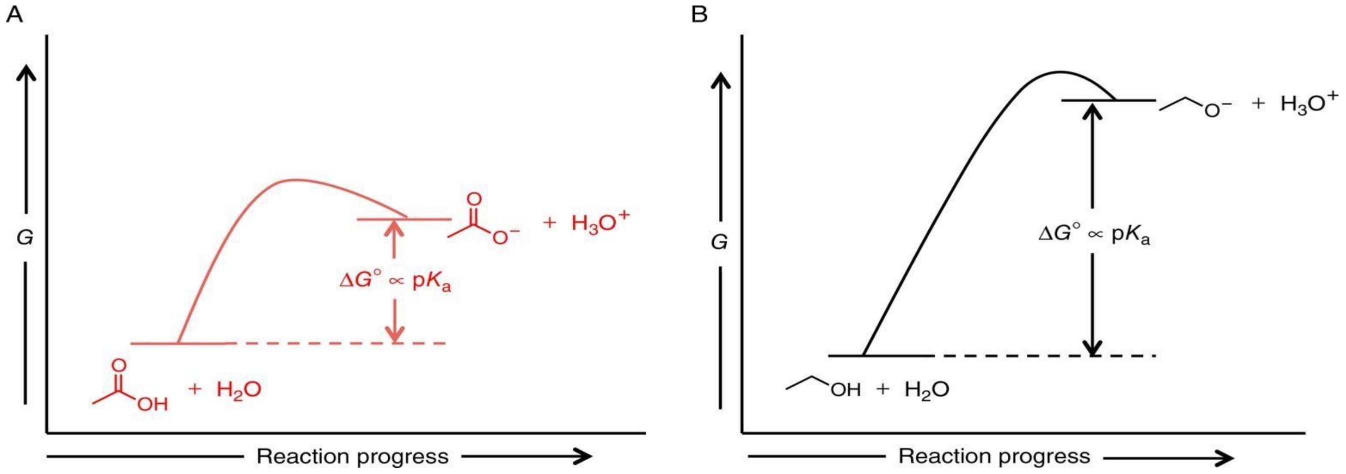
where R = 8.314(J/ mol/ K) and T' is the absolute temperature, for an acid ionization $K_{eq} = K_a$ and because $pK_a$= -log $K_a$, this equation can be restated as $\Delta(G°) = 2.3RT\,(pK_a)$ (1)

As a result, the sign and magnitude of the $pK_a$ for an acid ionization in water is directly related to the sign and magnitude of ΔG° for that ionization. Hence, a large positive $pK_a$ results in a large positive ΔG° and a small positive pKa results in a small positive ΔG° for their respective ionizations

As a specific example comparison of ethanol ($pK_a$= 15.5) and acetic acid ($pK_a$ = 4.76) ionizations in water is used. Applying eq (1), ΔG° values for these ionizations at 25 °C are +88 kJ mol (21 kcal mol$^{-1}$) and +27 kJ mol-$^{1}$ (6.5) kcal mol), respectively





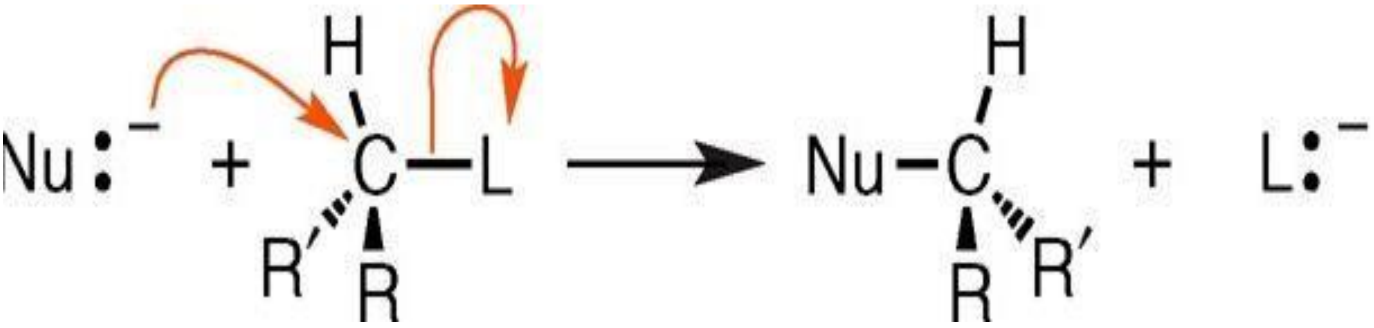


The equilibrium is represented by the help of Gibbs energy diagram (Fig. 1)[14,15]. Here Gibbs energy change is directly proportional to acid ionization constant. The Stronger acid (acetic acid) with a Smaller less $pK_a$, also have smaller less (+) $\Delta G^0$. It is important to note the y axis for alcohols and Carboxylic acids are not to be considered the Same.

## MAGNITUDE:

The magnitude and extent of ΔG° in a $S_N2$ reaction[12] is predicted by $pK_a$. When the $pK_a$ of the Conjugate acid of the nucleophile is much greater than the $PK_a$ of the Conjugate acid of the leaving group, the reaction will be highly exergonic with a large negative $\Delta G^0$. When the $PK_a$ of the Conjugate acid of the nucleophile is only slightly greater than the $pK_a$ of the conjugate acid of the leaving group, the reaction will be only slightly exergonic with a small negative $\Delta G^0$ value.

It is explained using the following reaction. Consider the SN2 reaction



Assuming no other stabilizing or destabilizing effects occurs as the result of the displacement (extended Conjugation in the product, etc) the Gibbs energy Change outcome can be predicted by Comparing the $pK_a$'s of the conjugate acids of the nucleophile (Nu-) and the leaving group (L-) • If the $pK_a$ of the Conjugate acid of the Nu- is much greater than the Pka of the leaving group thereby making the $pK_b$ of the nucleophile much less than the $pk_b$ of the leaving group that is the nucleophile, is a much stronger base than the leaving group, then the reaction will be predicted to proceed nearly to Completion (based on $\Delta G° = -RT$ in $k_{eq}$, which would be a large negative value, reaction proceed from strong base to weak base.

An example, would be the reaction of Chloromethane with hydroxide ion at 60 degrees centigrade reportedly having a $\Delta G^0 = -100$ kJ/ mole (24 kcal/ mol)[11]. This large exergonic value is reflected in and can be predicted from the large difference in the $pk_a$ for water (15.7) and HCl (-7)[9].

$$CH_3Cl + {}^{-}OH \rightleftharpoons CH_3OH + {}^{-}Cl$$

$$\Delta\ G^0 \underline{=} 100\ \text{kJ mol}^{-1}$$

On the other hand, if the $pK_a$ of the nucleophile conjugate acid is only slightly greater than that of the leaving group, the reaction will have a small exergonic $\Delta G°$ and, in fact, be predicted to be reversible. An example of this would be the reaction of bromoethane with iodide ion where there is a small difference in the $pK_a$'s of HBr (−9) and HI (−10).

### (3) **STRENGTH OF A NUCLEOPHILE**

Strength of Nucleophile in a solvent dependent nucleophilic substitution reaction[12] In polar protic solvent, mainly stronger the base (conjugate acid with higher $pk_a$), the stronger nucleophile, but the exceptional case is down the group of periodic table base gets weaker but the nucleophile gets stronger due to increase size of the nucleophilic species becoming poorly solvated, more reactive, simultaneously polarizability increases of this larger atom atoms.

In polar protic solvent, stronger the base, nucleophile also stronger at least for the case of small anionic charged base species.[6]

**TABLE :01**

Nucleophilicity Of Common Nucleophiles As A Function Of $pK_a$ Of Their Conjugate Acid:

| NUCLEOPHILE | NUCLEOPHILIC CONSTANT | $pK_a$ |
|---|---|---|
| $SH^-$ | 5.1 | 7.00 |
| $CN^-$ | 5.1 | 9.4 |
| $I^-$ | 5.04 | -10 |
| $OH^-$ | 4.20 | 15.7 |
| $Cl^-$ | 3.04 | -7 |
| $Br^-$ | 3.89 | -9 |

The prediction trends described above the polar solvents are clearly apparent in this rate data

In polar aprotic solvents, small anions are in solvated and as such made very reactive which again is found to close to closely parellel their basisity

**TABLE:02**

Common Nucleophiles With Their Conjugate Acid p$K_a$ Measured In DMSO And Water:

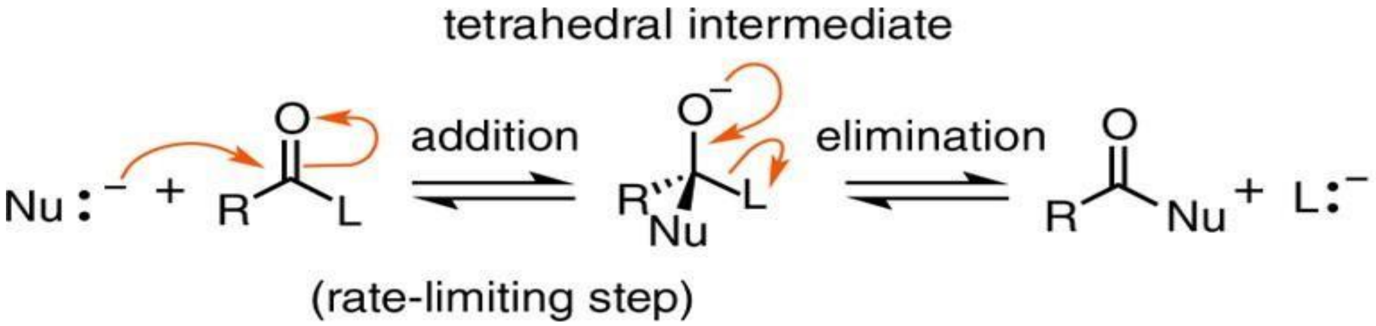
| Nucleophile | p$K_a$ (DMSO) | p$K_a$ (Water) |
|---|---|---|
| $HO^-$ | 31.4 | 15.7 |
| $CH3O-$ | 29.0 | 15.5 |
| $CN^-$ | 12.9 | 9.4 |
| $F-$ | 15.0 | 3.2 |
| $CH3CO2-$ | 12.6 | 4.76 |
| $Cl^-$ | 1.8 | −7 |

In DMSO in order of decreasing nucleophilicity and their corresponding p$k_a$ measured in DMSO and in water.

(4) **REACTIVITY OF CARBOXYLIC ACID DERIVATIVE**

Lower p$K_a$ of the conjugate acid of the leaving group on the Carboxylic acid more, reactive the carboxylic acid derivatives will be in nucleophilic acyl substitution reaction.[14]

In the absence of any steric factors the generally accepted mechanism for a nucleophile acyl substitution proceeds in two steps. The Carboxylic acid derivatives have an acyl carbon bonded to a group i.e.(-L) that can act as a leaving group.[8] Thus, the overall reaction is superficially similar to the kind of nucleophilic substitution that occurs during SN2 rection.



Unlike sn1 and SN2 pathway, which involves the bond breaking to the leaving group of the rate limiting step here the leaving group is still bonded.

Acid derivatives that unhindered react with nucleophiles more readily than sterically hindered group.

However, the nature of the leaving group in the reactivity of these acyl derivatives in two important aspects: by altering the electron density around the acyl carbon and effecting the position of the overall equilibrium of the reaction

Changing the electron density around the acyl carbon will alter the partial positive charge on that carbon, thereby influencing attack by the nucleophile. Leaving groups that withdraw electrons to a greater extent will produce a greater partial positive charge on the acyl carbon, increasing its electrophilicity toward reaction with a nucleophile and hence the rate of reaction. Once the tetrahedral intermediate forms, the group that is lost can either be the nucleophile that added in the first step or the leaving group. The group that is better able to sustain a negative charge will be lost preferentially (weaker base), driving the equilibrium toward products.

The reactivity of the most common carboxylic acid derivatives (acid chloride, anhydride, ester, amide) are found to nicely follow pk$_a$ of the conjugate acid of the leaving group when subjected to attack by the same nucleophile.

## TABLE :03

. Decreasing Order of Reactivity of Carboxylic Acid Derivatives toward Nucleophilic Acyl Substitution versus the p$K_a$ of the Conjugate Acid of the Leaving Group

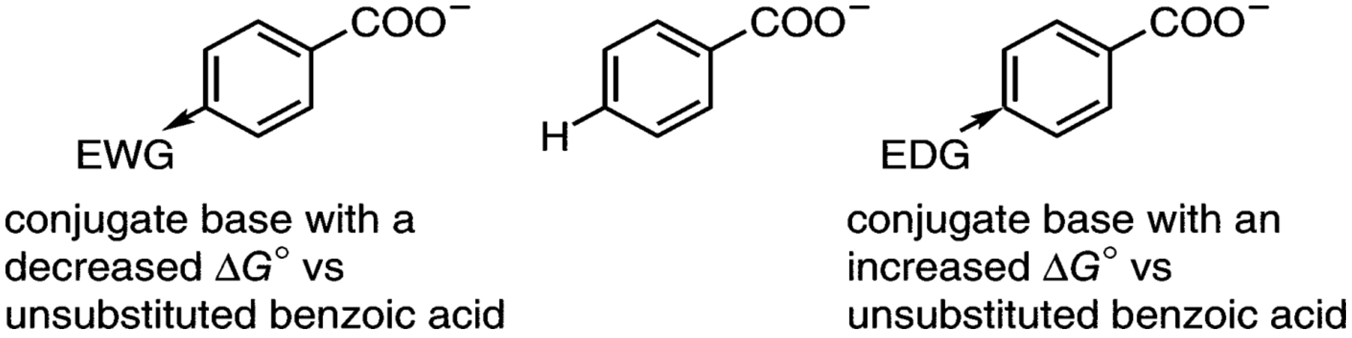
| Carboxylic Acid Derivative | Leaving Group ($L^-$) | Approximate p$K_a$ (LH) |
|---|---|---|
| RCOCl | $Cl^-$ | −7 |
| RCOOCOR | $RCOO^-$ | 5 |
| RCOSAr | $ArS^-$ | 6.5 |
| RCOOAr | $ArO^-$ | 10 |
| RCOSR′ | $R'S^-$ | 10.5 |
| RCOOR′ | $R'O^-$ | 16 |
| $RCONH_2$ | NH2− | 35 |
| $RCONR'_2$ | R′2N− | 36 |

Comparing the p$K_a$ of the conjugate acid of the nucleophile to that of the conjugate acid of the leaving group can also give insight as to which direction the equilibrium for the acyl substitution reaction will lie. If the p$K_a$ of the conjugate acid of the leaving group is lower than that of the nucleophile product formation will be favoured.

## (5) **NATURE OF ACTIVING OR DEACTIVITING GROUP**

The nature of activating or deactivating group is described by the electrophilic aromatic Substitution reaction.[10]

By comparing the p$k_a$ of a benzoic acid para-substituted with that group versus unsubstituted benzoic acid (p$K_a$=4.17) [12] If the p$K_a$ of the para-substituted benzoic acid is smaller, that group
is an electron withdrawing group and most likely a deactivating group.
If the p$k_a$ of the para-substituted benzoic acid is larger, that group is an electron donating group and likely an activating group.
The basis for this particular prediction can be best understood by looking at the stability of the conjugate base of this aromatic acid.[14]



[Conjugate bases from the corresponding para-substituted and unsubstituted benzoic acids]

Electron with drawing groups will electronically stabilize the conjugate base by depleting the aromatic ring of electrons which will delocalize the anionic charge on the carboxylate, leading to a decrease in the standard Gibbs energy change for this deprotonation, resulting in a weaker base or correspondingly stronger acid relative to benzoic acid.

Electron donating groups act to do just the opposite, enriching the electronic nature of the aromatic ring, producing a more localized charge on the carboxylate, and thereby increasing the standard Gibbs energy change for deprotonation resulting in a stronger conjugate base and weaker acid.

**TABLE : 04**

$pK_a$ Values of Unsubstituted and Para-Substituted
Benzoic Acids and Selective Relative Rates for Nitration of the Corresponding R-Substituted Benzenes.

| R | $pK_a$ | $K_{REL}$ |
|---|---|---|
| Deactivating Groups | | |
| $(CH_3)_3N^+-$ | 3.43 | $1.2 \times 10^{-8}$ |
| $O_2N-$ | 3.44 | $6 \times 10^{-8}$ |
| HOOC− | 3.51 | $3.7 \times 10^{-3}$ |
| $CH_3SO_2-$ | 3.52 | $3.5 \times 10^{-3}$ |
| NC− | 3.55 | − |
| Cl− | 3.99 | $3.3 \times 10^{-2}$ |
| Br− | 4.00 | $3.0 \times 10^{-2}$ |
| F− | 4.14 | 0.15 |
| H− | 4.20 | 1 |
| Activating Groups | | |
| $CH_3-$ | 4.34 | 25 |
| $(CH_3)_3C-$ | 4.40 | − |
| $CH_3O-$ | 4.47 | − |
| PhO− | 4.52 | − |
| HO− | 4.58 | 1000 |
| $H_2N-$ | 4.92 | − |
| $(CH_3)_2N-$ | 5.03 | − |

representative examples of this effect along with selected values of relative rates of nitration of the corresponding R substituted benzene for comparison. Para-substituted phenols and para-substituted anilinism ions (p-R-C6H4NH3+)[15] can be used in much the same way.

## CONCLUSION

The Concept of $pK_a$ is a foundational and multifunctional tool in understanding organic Chemistry, particularly in acid-base behaviour, reaction mechanisms, and physical properties of molecules. Through this project, it is Shown that: $pK_a$ allows prediction of acid and base Strength, guiding the direction of acid-base reaction. It is directly related to Gibes free energy Change ($\Delta G^0$) and hence gives insight into thermodynamic favourable. It helps determine the reactivity of nucleophiles and leaving groups, especially in $S_N2$ and acyl substitution reaction. It explains nucleophilic strength trends in both Polar protic and aprotic Solvents. It aids in classifying substituents on aromatic rings as activating or deactivating based on their influence on acidity. Thus, $pK_a$ is not just a number, but a predictive and analytical tool that bridges general chemistry principles with practical organic reactivity and design.

## ACKNOWLEDGEMENT

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# THESIS TITLE

# ADVANCEMENTS IN CHARACTERIZATION AND MODIFICATION OF BIOPLASTICS: A STUDY ON PHB, PHBV, AND PLA

B.Sc. Chemistry (Honours) Semester VI
(Under CBCS) Examination, 2025

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# ABSTRACT

Bioplastics, as a sustainable alternative to petroleum-based plastics, hold tremendous promise in mitigating environmental pollution and promoting circular bioeconomy. This thesis presents a detailed analysis and synthesis based on the research on the characterization and modification of selected bioplastics—specifically, poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(L-lactic acid) (PLLA).. The study encompasses the biosynthesis, thermal behavior, crystallization kinetics, and mechanical properties of PHAs and PLA, along with innovative strategies for improving their processability and performance through reactive melt processing and grafting techniques.

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# INTRODUCTION

The global dependence on fossil-fuel-derived plastics has led to a multitude of environmental challenges, including persistent plastic pollution, greenhouse gas emissions, and the depletion of non-renewable resources. Conventional plastics, such as polyethylene (PE), polypropylene (PP), and polystyrene (PS), are widely used across industries due to their low cost, durability, and processability. However, they are inherently resistant to biodegradation, leading to their accumulation in landfills, oceans, and terrestrial environments. According to data from the United Nations Environment Programme (UNEP), over 300 million tons of plastic waste are generated annually, with less than 10% being effectively recycled.

As awareness of these issues grows, so does the call for sustainable materials—those that originate from renewable resources, have lower carbon footprints, and biodegrade under natural or industrial conditions. In this context, bioplastics—a category of plastics derived from biological materials—have emerged as promising alternatives. These include both bio-based and biodegradable polymers, such as starch blends, polycaprolactone (PCL), polybutylene succinate (PBS), PLA, and PHAs.

## Bioplastics: PLA and PHAs in Focus

Among the various classes of bioplastics, polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) have received extensive attention due to their desirable properties and commercial viability.

### Polylactic Acid (PLA)

PLA is synthesized via fermentation of lactic acid, which is typically obtained from agricultural feedstocks like corn starch, sugarcane, or cassava. It is thermoplastic, biodegradable, and has mechanical properties comparable to polystyrene and PET. PLA is already being used in:

1. Food packaging (e.g., containers, cups, films)
2. Biomedical applications (e.g., sutures, stents, scaffolds)
3. 3D printing filaments

However, PLA suffers from brittleness, low thermal resistance, and poor impact strength, which limits its performance under mechanical and thermal stress.

### Polyhydroxyalkanoates (PHAs)

PHAs are a family of microbial polyesters produced by bacteria as intracellular carbon and energy storage compounds. The most studied member is poly(3-hydroxybutyrate) (PHB), along with its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).

Key advantages of PHAs:

- Biodegradable in both aerobic and anaerobic environments
- Produced from a wide range of renewable feedstocks, including industrial waste
- Tunable mechanical and thermal properties depending on the monomer composition

However, PHAs, especially PHB, also exhibit significant limitations:

- High crystallinity leading to brittleness
- Narrow processing window due to thermal degradation
- Poor melt strength and flexibility compared to conventional plastics

### Challenges Limiting Industrial Adoption

Despite their promising attributes, both PLA and PHAs face critical challenges that hinder their widespread use:

1. Brittleness and Fragility

- PHB and PLA tend to fracture under stress.
- Low elongation-at-break values make them unsuitable for flexible applications.

2. Low Thermal Stability

- Both polymers degrade at temperatures close to their melting points.
- This complicates melt-processing techniques like extrusion and injection molding.

3. Poor Melt Processability

- High melt viscosity and low thermal stability lead to poor flow behavior.

- PHAs, in particular, tend to undergo chain scission and depolymerization when processed thermally.

4. Cost Competitiveness

- Bioplastics remain more expensive than petroleum-derived plastics due to feedstock, processing, and fermentation costs.

5. Variability in Properties

- The mechanical and thermal properties can vary depending on bacterial strain, feedstock, and processing conditions.
- This limits standardization and repeatability in industrial applications.

## Addressing These Challenges:

Recognizing these limitations, Liqing ’s research was directed at understanding and enhancing the fundamental material properties of PHB, PHBV, and PLA. The work was structured around two primary strategies:

### 1. Advanced Characterization

conducted an extensive investigation into the structural, thermal, and mechanical behavior of PHB and PHBV, particularly focusing on:

- Crystallinity
- Melting and glass transition behaviors
- Isothermal and non-isothermal crystallization kinetics
- Thermomechanical stability
- Microstructural sequence distribution (via NMR and ESI-MSn)

These detailed characterizations allowed the identification of critical parameters that influence material behavior under various thermal and mechanical conditions. For instance, PHB was shown to undergo multiple melting transitions due to a melting–recrystallization–remelting mechanism. This insight is crucial for processing optimization.

### 2. Material Modification Techniques

To overcome the physical shortcomings of bioplastics,  implemented chemical and physical modification methods, including:

a) Peroxide-Induced Cross-linking

- Utilized dicumyl peroxide (DCP) to initiate radical cross-linking during melt extrusion.
- Resulted in the formation of long-chain branches in PHB and PLA.
- Enhanced melt strength and viscoelastic properties, reduced crystallinity, and improved thermal resistance.

b) Grafting of PHB onto Cellulose

- Used cellulose (abundant, renewable natural polymer) as a reinforcing material.
- Through in-situ reactive extrusion, PHB was covalently grafted onto cellulose fibers.
- Improved interfacial adhesion, thermal stability, and mechanical strength of the resulting composites.

## Scientific and Industrial Relevance

's work bridges the gap between laboratory research and industrial application of bioplastics by:

- Utilizing low-cost and renewable feedstocks like fermented dairy manure for biosynthesis.
- Demonstrating scalable modification techniques using existing melt-processing equipment.
- Enhancing material versatility by improving toughness, processability, and functionality.

These advancements contribute toward making PHB, PHBV, and PLA more viable for:

- Packaging materials
- Disposable utensils and films
- Agricultural mulches
- Biomedical devices (where biocompatibility and degradation are beneficial)

# BIOPLASTICS OVERVIEW AND IMPORTANCE

### 1. What are Bioplastics?

**Bioplastics** refer to a category of plastics that are either:

- **Bio-based**: derived wholly or partly from renewable biological resources (e.g., corn starch, sugarcane).
- **Biodegradable**: capable of being broken down by microorganisms into natural substances like water, carbon dioxide, and biomass under specific environmental conditions.

Note: Not all bio-based plastics are biodegradable, and not all biodegradable plastics are bio-based.

### 2. Types of Bioplastics

### A. Biodegradable Bioplastics

These degrade in natural environments (soil, compost, marine, etc.) over time.

- **PHAs (Polyhydroxyalkanoates):**
    - Synthesized by various bacterial species during nutrient-deficient growth.
    - Examples:
        - **PHB (Polyhydroxybutyrate)**: A homopolymer, highly crystalline but brittle.
        - **PHBV (Polyhydroxybutyrate-co-valerate)**: A copolymer with improved flexibility over PHB.
    - Applications: Packaging, agriculture, biomedical (e.g., sutures, implants).
- **PLA (Polylactic Acid):**
    - Produced from **fermentation of sugars** (corn, sugarcane) into lactic acid, followed by polymerization.
    - Applications: Disposable packaging, 3D printing, drug delivery systems, tissue engineering.

**3. Importance and Drivers of Adoption**

- **Environmental Regulations**:
    - Governments are banning or taxing traditional petroleum-based plastics.
    - Support for compostable, recyclable, and biodegradable materials is increasing.
- **Consumer Demand**:
    - Growing awareness of plastic pollution and carbon footprints.
    - Push for green, sustainable alternatives.
- **Industrial Interest**:
    - Reduced reliance on fossil fuels.
    - Improved lifecycle assessments and circular economy goals.

**Limitations of Bioplastics**

Despite being eco-friendly, bioplastics like PHAs and PLA have **performance limitations**:

**1. Mechanical Properties**

- **High brittleness** (especially PLA and PHB).
- Low impact strength and elongation at break.
- Often unsuitable for demanding structural applications without modification.

**2. Thermal Properties**

- **Low thermal stability** and heat deflection temperature.
- PLA can deform near 55–60 °C, limiting its use in hot environments.
- Thermal degradation during processing (particularly in PHAs).

**3. Barrier Properties**

- Poor water vapor and gas barrier properties compared to synthetic polymers.
- Limits shelf-life of food when used in packaging.

**Strategies for Overcoming Deficiencies**

To enhance the performance of PHAs and PLA, a **dual approach** is necessary:

### 1. Characterization: Understanding the Material

Before modification, it's essential to analyze the **physical and chemical properties** of the bioplastics:

| Property | Characterization Tool | Purpose |
|---|---|---|
| **Thermal Stability** | TGA (Thermogravimetric Analysis), DSC (Differential Scanning Calorimetry) | To determine degradation and melting temperatures. |
| **Crystallinity** | XRD (X-ray Diffraction), DSC | To assess structural order influencing strength and degradation. |
| **Molecular Structure** | FTIR (Fourier-Transform Infrared Spectroscopy), NMR (Nuclear Magnetic Resonance) | To identify functional groups and chemical composition. |
| **Morphology** | SEM (Scanning Electron Microscopy) | To visualize surface texture and fracture patterns. |
| **Mechanical Testing** | Tensile, impact, flexural tests | To determine strength, elongation, and toughness. |

### 2. Chemical and Physical Modifications: Enhancing Performance

#### A. Blending

- **With other polymers** (e.g., PLA blended with PCL, PBAT, or starch) to improve flexibility or biodegradability.
- Example: PLA/PBAT blends improve toughness for packaging films.

#### B. Copolymerization

- Introducing co-monomers (e.g., valerate in PHBV) to reduce crystallinity and increase ductility.
- Copolymer chains disrupt brittleness and enhance thermal resistance.

#### C. Plasticization

- Adding plasticizers like PEG, citrate esters to reduce intermolecular forces.
- Improves flexibility, but may affect biodegradability and migration resistance.

#### D. Crosslinking

- Chemical or radiation-induced crosslinking can improve mechanical strength and heat resistance.
- Especially useful in biomedical applications where long-term stability is needed.

#### E. Nanocomposite Formation

- Embedding nanomaterials like:
  - **Nanoclay**: improves barrier and thermal properties.
  - **Cellulose nanofibers**: enhances strength and biodegradability.
  - **Graphene oxide**: boosts electrical/thermal conductivity (in niche applications).

**F. Surface Modification**

- Techniques like plasma treatment or grafting to modify surface energy.
- Enhances adhesion, wettability, and printability for applications like packaging or electronics

# BIOSYNTHESIS OF PHAS

**PHAs: Biosynthesis and Classification**

**What are PHAs?**

- **Polyhydroxyalkanoates (PHAs)** are **biodegradable polyesters** naturally produced by many **bacterial strains**.
- They act as **intracellular energy and carbon storage materials**, especially when **nutrients like nitrogen, phosphorus, or oxygen are limited**, but **carbon is available in excess**.
- Under such conditions, bacteria redirect carbon flux to PHA synthesis instead of growth.

**1. Pathways and Microbial Cultures**

**PHA Classification by Chain Length:**

- **SCL-PHAs (Short-Chain-Length PHAs):**
  - Composed of monomers with 3–5 carbon atoms.
  - Examples: **Polyhydroxybutyrate (PHB)**, Poly(3-hydroxyvalerate).
  - **Properties:** High crystallinity, brittle, thermally stable.
- **MCL-PHAs (Medium-Chain-Length PHAs):**
  - Monomers contain 6–14 carbon atoms.
  - Produced by different microbial pathways (e.g., involving *Pseudomonas*).

    - **Properties:** More flexible, lower melting point, elastomeric behavior.

**Mixed Microbial Cultures (MMCs):**

- ’s dissertation investigated the use of **MMCs** rather than pure cultures.
- **Why MMCs?**
    - **Robust and versatile**: Can tolerate complex, variable feedstocks.
    - **Cost-effective**: No need for sterile conditions.
    - **Eco-friendly**: Adaptable to industrial-scale wastewater/waste use.

**Target Product: PHBV**

- PHBV = Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), a copolymer of PHB and 3-hydroxyvalerate (3HV).
- **Advantages over PHB:**
    - More flexible.
    - Lower brittleness.
    - Better processability.
- The **ratio of HB to HV** can be adjusted by controlling the feedstock composition, especially the volatile fatty acid (VFA) content.

**2. Feedstocks and Fermented Dairy Manure**

**Fermented Dairy Manure as Feedstock:**

- **Fermented dairy manure** is a byproduct of agricultural activities and contains:
    - **Volatile Fatty Acids (VFAs)**: Acetic, butyric, propionic, valeric acids, etc.
    - These VFAs serve as direct **precursors for PHA monomer synthesis**.

**Sustainability Aspects:**

- **Low-Cost Raw Material:**
    - Waste-based feedstock avoids use of expensive refined carbon sources like glucose or sucrose.
- **Waste Valorization:**
    - Converts waste into **value-added biodegradable plastics**, reducing pollution.
- **Diverse Monomer Supply:**
    - Different VFAs lead to different monomers being incorporated.
    - This creates **tailorable mechanical and thermal properties** in PHBV (e.g., tensile strength, elasticity, degradation rate).

**Process Overview:**

1. **Fermentation** of manure → Generates VFAs.
2. **MMCs consume VFAs** under nutrient-limited conditions → Produce intracellular PHAs.
3. **PHAs are extracted and purified** → Processed into bioplastic materials. ’s research presents a **sustainable biotechnological route** to produce **PHBV** by:
4. Using **mixed microbial cultures** (low cost, adaptable).
5. Utilizing **fermented dairy manure** (waste-to-resource approach).
6. Producing **customizable bioplastics** with improved properties.

# CHARACTERIZATION OF PHBV SYNTHESIZED FROM FERMENTED DAIRY MANURE

**1 Structural and Thermal Characterization**

**Synthesis Overview**

synthesized **poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)** with a **high hydroxyvalerate (HV) content (~40%)**. The inclusion of a higher proportion of HV disrupts the crystalline regularity of pure PHB, leading to distinct changes in both structure and properties. Various analytical tools were employed to confirm the structural identity and thermal behavior of the copolymer:

**Analytical Techniques Used:**

- **NMR Spectroscopy (Nuclear Magnetic Resonance):**
    - **Purpose:** Determine the monomer sequence and composition.
    - **Findings:**
        - The **1H and 13C NMR spectra** revealed a **random distribution** of 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) units in the copolymer backbone.
        - The **randomness** in copolymer structure is critical because it influences **thermal and mechanical behavior**, such as crystallization and melting.
- **GC-MS (Gas Chromatography–Mass Spectrometry):**
    - **Purpose:** Analyze the chemical composition, specifically the HB/HV ratio.
    - **Findings:**
        - Confirmed the **presence and relative content** of HV (~40%), validating that the desired composition was achieved during synthesis.

- **DSC (Differential Scanning Calorimetry):**
    - **Purpose:** Examine melting and crystallization behavior.
    - **Findings:**
        - Showed a **single melting peak**, which indicates that the copolymer behaves as a **single-phase material** rather than a mixture.
        - The presence of HV units **lowers the melting temperature (Tm)** compared to PHB, reflecting reduced crystallinity.
- **DMA (Dynamic Mechanical Analysis):**
    - **Purpose:** Evaluate viscoelastic and mechanical behavior as a function of temperature.
    - **Findings:**
        - Showed **increased flexibility**, especially at higher temperatures.
        - The reduced stiffness and enhanced chain mobility were attributed to the plasticizing effect of HV segments.

## 2 Crystallinity and Mechanical Properties

### Structural Effects of HV Incorporation:

The inclusion of 3-hydroxyvalerate significantly modifies the **morphology** and **mechanical performance** of the copolymer compared to pure poly(3-hydroxybutyrate) (PHB):

- **Reduced Crystallinity:**
    - PHB is a **highly crystalline** polymer with limited chain mobility, making it brittle.
    - By incorporating HV, the regular packing of chains is disrupted, resulting in:
        - **Lower crystallinity**.
        - **Reduced melting temperature** and less rigid structure.
        - Enhanced **amorphous regions**, which improve flexibility.
- **Mechanical Property Enhancement:**
    - Due to reduced crystallinity and increased amorphous content:
        - **Toughness** improves: The material absorbs more energy before failure.
        - **Ductility** increases: The polymer can undergo greater deformation before breaking.
        - These improvements make PHBV better suited for applications where **mechanical resilience** is critical.
- **Molecular Sequence Confirmation:**

  - **13C-NMR** confirmed the **random sequence distribution** of HB and HV.
  - **ESI-MSn (Electrospray Ionization Tandem Mass Spectrometry):**
    - Provided molecular-level evidence of **sequence randomness** and **copolymer architecture**.
    - This randomness further suppresses crystallinity and aids in achieving **uniform thermal and mechanical performance**.

| **Property** | **PHB** | **PHBV (~40% HV)** |
|---|---|---|
| Crystallinity | High | Lower |
| Flexibility | Low (brittle) | High |
| Ductility | Low | Enhanced |
| Toughness | Low | Improved |
| Melting Temperature | High | Reduced |
| Processability | Difficult | Easier |

# THERMOPHYSICAL ANALYSIS OF PHB

### 1 Crystallization Kinetics of PHB

conducted a comprehensive thermal analysis of **PHB** using:

- **DSC (Differential Scanning Calorimetry)**
- **TMA (Thermomechanical Analysis)**
- **TMDSC (Temperature Modulated DSC)**

These techniques were applied under both **isothermal** (constant temperature) and **non-isothermal** (variable temperature) conditions to study **how PHB crystallizes during cooling** and **how its crystalline structure evolves on reheating**.

**Key Findings:**

**Multiple Melting Peaks:**

- Observed during the **DSC heating scans**.
- These are attributed to **Melting-Recrystallization-Remelting (MRR)** processes:

  - Initially formed **imperfect or less stable crystals** melt at lower temperatures.
  - On continued heating, these partially melted chains reorganize and **recrystallize** into more perfect crystalline forms, which then **remelt** at higher temperatures.
- This complex melting behavior suggests **heterogeneous crystal populations**, common in semicrystalline polymers like PHB.

**Temperature and Cooling Rate Effects:**

- **Higher cooling rates** → less time for polymer chains to organize → formation of **less ordered, imperfect crystals**.
- **Lower crystallization temperatures** → slower chain mobility → **suppressed crystal perfection**.
- **Crystallization rate** is **temperature-dependent**, showing an optimal window where crystallization is fastest. Outside this window (too hot or too cold), crystallization is slow or incomplete.

**Crystallization Kinetics Analysis:**

- Kinetics were studied using **Avrami equations** and **Ozawa analysis**.
- These models help determine:
  - **Nucleation mechanism** (e.g., sporadic vs. instantaneous).
  - **Crystal growth dimensions** (e.g., 2D or 3D growth).
- Results showed a **complex interplay of nucleation and growth behaviors**, impacted by processing conditions.

### 2 Implications for Processing

The complex thermal behavior of PHB, especially its crystallization characteristics, has direct consequences on how it can be processed in industrial settings.

**Key Implications:**

**◆ Melt Behavior Complexity:**

- Due to multiple melting peaks and the MRR phenomenon, **melt consistency** can vary, affecting flow properties during extrusion and molding.
- **Uncontrolled crystallization** during processing (e.g., during cooling in a mold) can lead to **warping, brittleness**, or **non-uniform properties** in the final product.

**◆ Extrusion and Molding Optimization:**

- **Precise control of cooling rates** is necessary to achieve consistent **crystal size and distribution**.
- **Processing window** (melt temperature, mold temperature, and cooling time) needs to be tightly managed to balance **crystallinity and mechanical properties**.

**◆ Annealing Considerations:**

- **Post-processing heat treatments** (annealing) can enhance **crystal perfection** and **mechanical strength**.

| **-Parameter** | **Effect on PHB Behavior** |
|---|---|
| High cooling rate | Lower crystallinity, less perfect crystals |
| Low crystallization temperature | Slower, imperfect crystal formation |
| Multiple melting peaks (DSC) | Indicates MRR and complex crystal morphology |
| Thermal behavior | Influences melt flow, part shrinkage, and final strength |
| Optimized processing | Requires precise temperature and cooling rate control |

- Annealing must be done **above Tg (glass transition temperature)** but below Tm (melting point) to allow molecular reorganization without full melting.

## MODIFICATION OF PHB AND PLA VIA CROSS-LINKING

investigated peroxide-induced cross-linking using dicumyl peroxide (DCP) during reactive melt processing.

**1 Cross-linking Mechanism**

**Role of DCP (Dicumyl Peroxide)**

- DCP is an **organic peroxide** commonly used as a radical initiator in polymer cross-linking.
- When heated, DCP **thermally decomposes** to generate **free radicals**—highly reactive species with unpaired electrons.

**Initiation of Cross-linking**

- These free radicals **abstract hydrogen atoms** from the **polymer backbone** of PHB or PLLA.
- This process generates **macroradicals** (radicals on the polymer chains themselves).

**Formation of Long-Chain Branching (LCB)**

- Macroradicals react with neighboring polymer chains, forming **covalent cross-links**.
- This leads to a **three-dimensional network** or **long-chain branching** within the polymer matrix.
- LCB significantly enhances **melt strength**, making the material easier to process under heat without deformation or sagging.

## 2 Effects on Properties

### Melt Strength

- **Definition**: The resistance of a molten polymer to deformation or flow.
- **Observation**: Cross-linked PHB and PLLA exhibit **improved melt strength** due to the LCB structure.
- **Why it matters**: Better melt strength allows the polymer to maintain shape during extrusion, blow molding, and thermoforming, which is especially important for packaging and fiber production.

### Crystallinity

- **Definition**: The degree to which polymer chains are arranged in an ordered, crystalline structure.
- **Effect of DCP**: Cross-linking **disrupts chain mobility**, reducing the ability of polymer chains to align into ordered crystals.
- **Observation**: As DCP concentration increases, **crystallinity decreases**.
- **Consequence**: Lower crystallinity generally results in softer and more ductile materials but can also impact barrier properties.

## 3. Morphology

- **Observation Tool**: **Hot-stage polarized optical microscopy** is used to observe spherulites—radially growing crystalline structures.
- **Finding**: Cross-linked samples show **smaller spherulite sizes**, indicating:
    - More **nucleation sites**
    - **Slower or disrupted crystal growth**
- **Implication**: Finer morphology can enhance optical clarity and improve mechanical uniformity.

## 4. Thermal Stability

- **Definition**: The resistance of a polymer to degradation at elevated temperatures.
- **Observation**: Cross-linking provides a **slight increase** in the **decomposition temperature** of PHB and PLLA.
- **Reason**: The 3D network structure formed by cross-links restricts thermal motion, delaying the breakdown of the polymer.

**5.Mechanical Properties**

- **Toughness**: The ability of a material to absorb energy and deform without breaking.
  - **Increases** due to the flexible, interconnected network created by cross-linking.
- **Brittleness**: The tendency to fracture without significant deformation.
  - **Decreases** as cross-linking enhances energy dissipation during stress.
- **Overall Improvement**: These changes result in **more durable** and **impact-resistant** bioplastics

. The use of **DCP-induced cross-linking** significantly enhances **melt strength, toughness, and thermal performance**, while reducing crystallinity and brittleness. These changes broaden the applicability of PHB and PLLA, making them suitable for:

- **High-temperature processing**
- **Load-bearing applications**
- **Sustainable alternatives in automotive, packaging, and consumer goods**

## • GRAFTING OF PHB ONTO CELLULOSE

**1 Grafting Methodology**

**Process Overview:**

- **In-situ reactive extrusion is employed — a scalable and industrially relevant technique.**
- **Reactants:**
  - **PHB (the matrix polymer)**
  - **Cellulose fibers (natural reinforcement)**
  - **Dicumyl peroxide (DCP) (a radical initiator)**

**Conditions:**

- **Mixing occurs at ~175°C, which is above PHB's melting point (~170°C) to ensure polymer flow.**
- **DCP decomposes under heat to generate free radicals. These radicals:**
  - **Abstract hydrogen atoms from both PHB and cellulose,**
  - **Initiate covalent bonding (grafting) between them.**

**2 Structural and Thermal Changes**

**1 Spectroscopic Confirmation:**

- **FTIR (Fourier Transform Infrared Spectroscopy):**
    - **Presence of new ester or ether linkages between cellulose and PHB.**
    - **Shift or appearance of bands related to C–O–C stretching, indicating chemical bonding.**
- **NMR (Nuclear Magnetic Resonance):**
    - **Confirms grafting in both amorphous and crystalline regions of cellulose.**
    - **Signals correspond to new chemical environments created by grafting.**
- **ESR (Electron Spin Resonance):**
    - **Used to detect the presence of free radicals during the grafting reaction, verifying the radical mechanism.**

**2. XRD (X-ray Diffraction):**

- **Grafted composites show reduced crystallinity.**
- **Explanation: Grafting disrupts the regular hydrogen bonding network of cellulose and the packing of PHB chains, hindering crystal formation.**

**3. TGA (Thermogravimetric Analysis):**

- **Grafted materials exhibit higher thermal stability than pure PHB or PHB–cellulose blends.**
- **Reason: Improved thermal interface and restricted chain mobility due to grafting delays degradation.**

**4. SEM (Scanning Electron Microscopy):**

- **Shows enhanced interfacial adhesion between cellulose fibers and PHB matrix in grafted composites.**
- **Contrast with non-grafted blends, where fibers may pull out or leave gaps due to weak bonding.**

### 3 Advantages of Grafting

**Grafting PHB onto cellulose significantly enhances the properties of the composite:**

| **Property** | **Effect of Grafting** |
|---|---|
| **Fiber dispersion** | **Prevents agglomeration of cellulose fibers in the PHB matrix** |
| **Interfacial bonding** | **Chemical bonds improve load transfer between fiber and matrix** |
| **Mechanical reinforcement** | **Tensile strength and modulus improve due to better stress distribution** |

| **Property** | **Effect of Grafting** |
|---|---|
| **Thermal resistance** | **Improved thermal degradation profile and potential for higher processing temperatures** |

**Broader Implications**

- **This grafting technique is not limited to cellulose — it can be applied to other natural fibers like:**
  - **Lignin**
  - **Jute**
  - **Kenaf**
  - **Bamboo**
- **The method helps overcome a major challenge in bio-based composites: incompatibility between hydrophilic fibers and hydrophobic biopolymers.**
- **It contributes toward developing high-performance, fully biodegradable biocomposites suitable for:**
  - **Packaging**
  - **Automotive parts**
  - **Consumer goods**

# DISCUSSION AND IMPLICATIONS

’s work provides a significant advancement in understanding and improving bioplastics through:

- **Biosynthetic customization** of PHAs using mixed microbial cultures and waste substrates.
- **Detailed thermophysical characterization** to understand and predict processing behavior.
- **Chemical modification** (cross-linking and grafting) to tailor material properties.

These findings align with global sustainability goals and present a clear pathway for industrial-scale applications in packaging, biomedical, agricultural, and consumer products.

# CONCLUSION

The thesis focuses on three major biodegradable bioplastics: **PHB (Polyhydroxybutyrate)**, **PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate))**, and **PLA (Polylactic Acid)**. While these are promising due to their renewable origin and biodegradability, **they each have limitations** that hinder their broader industrial use — such as poor thermal stability, brittleness, or low impact resistance.

’s dissertation addresses these limitations in three main ways:

### 1. Demonstrating Low-Cost Biosynthesis Routes

- **Significance**: One of the barriers to widespread adoption of bioplastics is the **high production cost**.
- **What  did**:
    - Used **mixed microbial cultures (MMCs)** fed with **low-cost waste materials** (e.g., fermented dairy manure) to synthesize PHAs.
    - This approach **reduces raw material costs**, utilizes **waste valorization**, and improves **environmental sustainability**.

### 2. Elucidating Thermal and Structural Behaviors

- **Why it's important**: Bioplastics’ thermal and crystalline properties affect their **processability and final performance**.
- **’s contribution**:
    - Detailed analysis using **DSC, TMA, TMDSC, FTIR, and NMR**.
    - Identified **multiple melting peaks**, complex **crystallization behaviors**, and **amorphous-crystalline transitions**.
    - These insights guide **thermal processing** and **blending strategies** for enhanced performance.

### 3. Implementing Advanced Modification Strategies

- **Modifications covered**:
    - **Reactive extrusion** with initiators like **DCP (dicumyl peroxide)** to introduce **cross-linking and grafting**.
    - **Grafting PHB onto cellulose fibers** to improve **mechanical strength, barrier properties**, and **biodegradability**.
    - **Cross-linking** helped improve melt strength and viscoelasticity, making the materials better suited for **injection molding, film blowing**, etc.
- **Outcome**: These modifications significantly improve **usability**, especially in packaging and biomedical applications.

**Future Outlook**

To build on these results and bring bioplastics to commercial scale, the thesis suggests several key directions:

**1. Scaling up Reactive Extrusion Techniques**

- **Why**: Reactive extrusion is a continuous, industrially viable method.
- **Challenges**:
    - Optimizing parameters (temperature, shear, initiator concentration).
    - Ensuring **uniform grafting or cross-linking** without degrading the polymer.
- **Goal**: Enable cost-effective **mass production** of functionalized bioplastics with enhanced properties.

**2. Investigating Biodegradation Post-Modification**

- **Concern**: Chemical modifications (e.g., cross-linking, grafting) may alter biodegradability.
- **Research needed**:
    - Long-term **biodegradation studies** in different environments (soil, marine, compost).
    - Understanding the **impact of additives and structural changes** on **microbial activity and degradation rates**.
- **Aim**: Ensure that performance improvements **do not compromise environmental safety**.

**3. Exploring Combinations with Renewable Fillers or Nanomaterials**

- **Opportunity**: Combining bioplastics with **cellulose, chitin, starch, or nanomaterials (like nanoclay, graphene oxide)** can:
    - Enhance **mechanical, thermal, and barrier properties**.
    - Tailor degradation profiles and reduce cost.

- **Example**:
  - Grafting PHB onto cellulose not only improves strength but also introduces **biocompatible reinforcement**.
  - Nanomaterials can enable **smart packaging** or **stimuli-responsive behavior**.

**Impact: Toward Sustainable Commercialization :-**

The dissertation shows that with strategic bioengineering and materials science approaches, the performance limitations of bioplastics can be mitigated. If the suggested future directions are pursued, it could lead to:

- **Wider industrial adoption** (e.g., in automotive, agriculture, electronics).
- Reduced dependence on fossil-based plastics.
- A strong contribution to the **circular bioeconomy and carbon neutrality goals**.

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*(A curated selection from the dissertation; full list can be added as per formatting requirements)*

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# SURFACE REACTION AND THEIR CATALYTIC ACTIVITY

B.Sc. CHEMISTRY (HONOURS) SEMESTER VI EXAMINATION 2025
(UNDER CBCS)

PAPER: DSE – B4 (DISSERTATION)

UNIVERSITY OF CALCUTTA

ST. PAUL'S CATHEDRAL MISSION COLLEGE

CU ROLL NO.: 223114-21-0002
CU REGISTRATION NO.:114-1111-0202-22

# DECLARATION

I hereby declare that this dissertation entitled "SURFACE REACTION AND THEIR CATALYTIC ACTIVITY", submitted as part of Semester-VI-DSE-B4 for the B.Sc. Semester VI Honours Examination, 2025, is a review work carried out by me under the supervision of a faculty member of the Department of Chemistry, St. Paul's Cathedral Mission college. This dissertation has been prepared solely for the purpose of the DSE-B4 examination of Semester 6 (under CBCS) of the University of Calcutta and has not been submitted for any other degree nor used for any other purpose in any university or institute.

Date:

**Signature of the student**
**B. Sc. Chemistry (Semester – VI)**
**Department of Chemistry**
**St. Paul's Cathedral Mission college**

# Index

## 1. Abstract:

This dissertation investigates **heterogeneous catalysis**, focusing on **surface reactions** and **catalytic activity**. It explores **mechanisms**, **material innovations**, **characterization techniques**, and **industrial applications**. Key areas include **reactant adsorption**, **surface diffusion**, and **chemical transformation** at **active sites**.

Material developments covered are **mesoporous silica nanoparticles (MSNs)** for **support functionalization** and **metal dispersion**, and **magnetic nanoparticles (MNPs)** for **catalyst recovery** via **silica coating** and **yolk-shell structures**. **Layered double hydroxides (LDHs)** are also detailed for their **tunable acid-base** and **redox properties** and **memory effect**.

## 2. Introduction:

Surface reactions refer to chemical processes that occur at the interface between two phases, typically solid–gas or solid–liquid. These reactions are highly significant in heterogeneous catalysis, where the active surface of a catalyst facilitates transformation of reactants into products. Surface *reactions* are particularly important in nanomaterials, where the high surface-to-volume ratio enhances catalytic efficiency. On the other hand, catalytic activity, is the power of a catalyst to increase the rate of a chemical reaction by lowering the activation energy, without itself undergoing any permanent chemical change. It depends on factors such as surface area, the nature of the active sites, and the interaction between the catalyst and the reactants.

Both surface reactions and catalytic activity have wide-ranging applications in science and industry. Surface reactions are essential in industrial catalysis, such as in the production of ammonia by the Haber process, or methanol synthesis. They are also vital in environmental systems—for example, catalytic converters in automobiles reduce harmful emissions by surface reactions involving NOx, CO, and hydrocarbons. Moreover, surface reactions are the foundation of sensor technologies and play a crucial role in energy storage and conversion systems like fuel cells and batteries. The largest catalytic activity occurring in nature is photosynthesis, which provides food for the world.

Catalytic activity, similarly, has extensive practical importance. It is exploited in green chemistry to conduct reactions under milder conditions with fewer by-products. In petroleum industries, catalytic activity enables processes like catalytic cracking and reforming to improve fuel quality. It also facilitates selective synthesis in the pharmaceutical and agrochemical sectors. Furthermore, catalytic activity contributes to environmental remediation by accelerating degradation of pollutants and plays a key role in renewable energy systems such as hydrogen generation and $CO_2$ reduction technologies.

## 3. Theoretical Discussion – Mechanisms and Fundamental Principles

### 3.1. The Essence of Catalysis: Lowering the Activation Barrier

Catalysis, at its core, is the art and science of accelerating chemical reactions without being consumed in the process. This remarkable ability stems from the catalyst's capacity to provide an alternative reaction pathway with a significantly lower activation energy (Ea). In contrast to uncatalyzed reactions, where reactants must overcome a high energy barrier to reach the transition state, catalysts interact with reactants to form transient intermediates, facilitating the transformation and regenerating the active sites. This fundamental principle, rooted in transition state theory, is mathematically expressed by the Arrhenius equation ($k=A\cdot e-Ea/RT$), where a decrease in Ea leads to an exponential increase in the rate constant (k). For heterogeneous catalysis, this interaction occurs at the interface between a solid catalyst and fluid reactants, making the catalyst surface the epicenter of chemical transformation. The vast majority of industrial chemical processes, approximately 90%, rely on this principle, underscoring its profound economic and environmental impact. The intrinsic advantage of heterogeneous catalysts lies in their ease of separation from fluid products, allowing for continuous operation and efficient recycling, which are critical for large-scale industrial applications.

### 3.2. The Heterogeneous Catalyst Surface: A Complex Molecular Arena

The solid-fluid interface in heterogeneous catalysis is a dynamic and intricate environment where a sequence of elementary steps orchestrates the overall reaction. These steps are meticulously choreographed and collectively dictate the catalyst's activity, selectivity, stability, and lifetime. Understanding and controlling these surface-mediated processes is paramount for rational catalyst design and optimization. The journey of a reactant molecule from the fluid phase to a transformed product molecule involves:

- **Mass Transport to the Surface:** Reactant molecules from the bulk fluid phase must diffuse to the external surface of the catalyst particle. This step can be rate-limiting in cases of highly active catalysts or poor mixing.
- **Pore Diffusion (for porous catalysts):** For catalysts with internal pore structures (e.g., zeolites, mesoporous materials), reactants must diffuse through these pores to reach active sites embedded within the particle. This is a critical factor for catalyst effectiveness.
- **Adsorption:** Reactant molecules chemically or physically bind to the active sites on the catalyst surface. This is a pivotal step, as the strength and nature of adsorption directly influence the subsequent reaction. Physisorption involves weak van der Waals forces, while chemisorption involves stronger chemical bonding, often accompanied by electron transfer. The configuration and orientation of adsorbed species are crucial for facilitating subsequent reactions.

  **Surface Diffusion:** Once adsorbed, molecules may migrate across the catalyst surface, seeking out optimal active sites or encountering other adsorbed species for reaction. The mobility of adsorbed species plays a role in reaction kinetics and selectivity.

- **Surface Reaction:** The adsorbed reactants undergo chemical transformation at the active sites, forming new chemical bonds and breaking old ones. This is the catalytic step where the activation energy is lowered. Reactions can occur between two adsorbed species (Langmuir-Hinshelwood mechanism), between an adsorbed species and a gas-phase molecule (Eley-Rideal mechanism), or through other more complex pathways.
- **Desorption:** The newly formed product molecules detach from the catalyst surface, freeing up the active sites for further catalytic cycles. The desorption step must be efficient enough not to poison the catalyst surface by product accumulation.
- **Pore Diffusion and Mass Transport from the Surface:** Products then diffuse out of the catalyst pores and into the bulk fluid phase.

Each of these elementary steps is influenced by a myriad of factors, including:

- **Surface Composition:** The elemental makeup of the catalyst surface determines the types of active sites available.
- **Morphology:** The shape, size, and crystal facets exposed on the catalyst surface can significantly impact reactivity and selectivity.
- **Electronic Structure:** The electronic properties of the active sites, including oxidation states and coordination environments, dictate their ability to activate reactants and stabilize transition states.
- **Local Reaction Environment:** Pressure, temperature, and the presence of other species (e.g., poisons, promoters) can dynamically alter the catalyst surface and its performance.

This inherent complexity necessitates an interdisciplinary approach, integrating principles from chemistry, physics, materials science, and engineering to fully comprehend and optimize surface catalysis.

## 3.3. Mechanisms of Surface Reactions: Unraveling the Molecular Dance

Understanding the precise molecular pathways and intermediates involved in surface reactions is fundamental to rational catalyst design. While the overarching principle is the lowering of activation energy, the specific mechanism can vary significantly depending on the catalyst and the reaction.

### 3.3.1. Adsorption: The Gateway to Catalysis

Adsorption is the initial and often rate-determining step in heterogeneous catalysis. It can be categorized into:

- **Physisorption:** A weak, non-specific interaction primarily driven by van der Waals forces. It is reversible and typically occurs at low temperatures, with adsorption enthalpies comparable to liquefaction enthalpies (<40 kJ/mol). Physisorption generally does not lead to significant changes in the electronic structure of the adsorbate or the surface.
- **Chemisorption:** A stronger, specific interaction involving the formation of chemical bonds (covalent or ionic) between the adsorbate and the surface atoms. This process is

often accompanied by electron transfer and significant changes in the electronic structure of both the adsorbate and the catalyst. Chemisorption enthalpies are typically much higher (40-800 kJ/mol), and it is the prerequisite for most catalytic reactions. Chemisorption can be dissociative (e.g., $H_2 \rightarrow 2H(ads)$) or non-dissociative (e.g., $CO \rightarrow CO\ (ads)$). The binding strength of reactants to active sites is crucial: too weak, and activation is inefficient; too strong, and active sites become blocked (poisoning). The Sabatier principle highlights this "Goldilocks" effect, suggesting an optimal binding strength for maximum catalytic activity.

### 3.3.2. Reaction Mechanisms at the Surface

Once adsorbed, reactants can undergo various transformations. Two prevalent mechanisms describe these surface reactions:

- **Langmuir-Hinshelwood (LH) Mechanism:** In this mechanism, both reactants must first adsorb onto the catalyst surface before they can react. The surface reaction then occurs between two adsorbed species.
  - $A(g) + S \rightleftharpoons \text{Aads}$
  - $B(g) + S \rightleftharpoons \text{Bads}$
  - $\text{Aads} + \text{Bads} \rightarrow \text{Cads}$
  - $\text{Cads} \rightleftharpoons C(g) + S$ This mechanism is common for many gas-phase reactions over solid catalysts, where the surface coverage of reactants plays a critical role in the reaction rate.
- **Eley-Rideal (ER) Mechanism:** Here, one reactant adsorbs onto the catalyst surface, while the other reactant reacts directly from the gas phase (or liquid phase) with the adsorbed species.
  - $A(g) + S \rightleftharpoons \text{Aads}$
  - $B(g) + \text{Aads} \rightarrow \text{Cads}$
  - $\text{Cads} \rightleftharpoons C(g) + S$ While less common than the LH mechanism for many industrially relevant reactions, the ER mechanism can be observed in specific systems, particularly when one reactant has a very low sticking coefficient or a high gas-phase concentration.

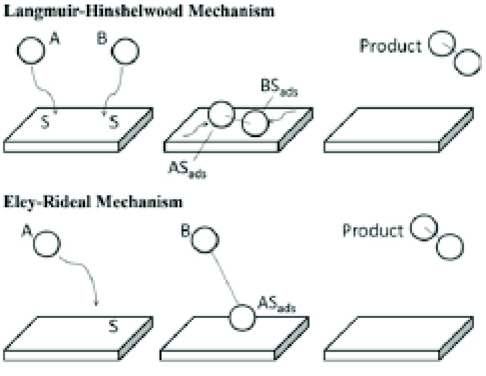

Diagram: **Langmuir- Hinshelwood mechanism and Eley-Rideal mechanism**

For single substance on a solid surface:

**$-dp/dt=z_1(ap/1+ap)$** [Langmuir Isotherm]

At low pressure or low adsorption capacity (a is small) $ap<<1$ Or,

$-dp/dt=z_1ap=kp$

Or, $kt=\ln(p^0/p)$, the adsorption process will follow 1st order kinetics. Example, dissociation of HI on platinum, $N_2O$/gold or $PH_3$/Glass. Again, pressure is high or adsorption surface is high, 'θ' is the almost unity or $ap>>1$

Then $-dp/dt=z_1$, the adsorption rate(reaction) is constant or independent of pressure. The relation will follow 'zero order' kinetics. Examples are HI/gold(Au), $NH_3$/tungsten(W).

More complex mechanisms involve surface intermediates, rearrangements, and multiple sequential steps. For instance, in selective oxidation reactions, the Mars-van Krevelen mechanism describes the lattice oxygen participation, where the catalyst provides oxygen for the oxidation, gets reduced, and is then reoxidized by gaseous oxygen.

### 3.4. The Role of Active Sites: The Catalyst's True Identity

Catalytic activity is not uniformly distributed across the entire catalyst surface. Instead, it originates from specific locations known as "active sites." These sites are typically characterized by unique coordination environments, electronic states, or structural defects that enable them to activate reactants and facilitate the reaction. Examples of active sites include:

- **Metal Atoms/Clusters:** In supported metal catalysts, individual metal atoms or small metal clusters serve as active sites. Their coordination number, oxidation state, and interaction with the support material can profoundly influence their catalytic performance.
- **Acidic/Basic Sites:** In acid-base catalysis, Brønsted acid sites (proton donors) and Lewis acid sites (electron pair acceptors) or their basic counterparts (Brønsted base sites – proton acceptors, Lewis base sites – electron pair donors) play crucial roles in proton transfer or electron donation/acceptance, respectively. Examples include zeolites, supported metal oxides, and layered double hydroxides.
- **Defects and Edges:** Surface defects, such as vacancies, kinks, and steps, can exhibit different coordination environments and electronic properties compared to terrace sites, often leading to enhanced reactivity.
- **Metal-Support Interface:** The interface between a supported metal nanoparticle and its oxide support can be a highly active region, exhibiting synergistic effects that surpass the activity of either component in isolation (e.g., strong metal-support interactions in $CO_2$ methanation over $Ni/CeO_2$).
- **Confined Environments:** The unique pore structures of materials like zeolites and mesoporous silicas can create confined environments that promote specific reaction pathways, influence product selectivity (shape selectivity), or stabilize reactive intermediates.

### 3.5. Fundamental Principles in Environmental Catalysis (NOx Reduction)

The selective catalytic reduction (SCR) of nitrogen oxides (NOx) with ammonia ($NH_3$) is a prime example of a complex catalytic system where fundamental understanding of surface reactions has led to significant real-world impact. The overall reaction converts harmful NOx (NO, $NO_2$) into benign $N_2$ and $H_2O$.

**3.5.1. Vanadium-based Catalysts ($V_2O_5/TiO_2$):** For mid-temperature applications (300-400°C), $V_2O_5$ supported on anatase $TiO_2$ is the industry standard, often promoted with $WO_3$ or $MoO_3$. The mechanism is complex but largely understood to involve the following key steps:

- **Ammonia Adsorption:** $NH_3$ adsorbs on Brønsted acid sites (V-OH groups) and/or Lewis acid sites (V=O, Ti-O groups) on the catalyst surface.
    - NH3(g)+H+S⇌NH4+S (Brønsted acid site)
    - NH3(g)+S⇌NH3S (Lewis acid site)
- **NOx Adsorption/Activation:** NOx molecules can also adsorb, though typically more weakly.
- **Surface Reaction:** The core SCR reaction occurs between adsorbed ammonia (or its activated forms) and gaseous or weakly adsorbed NO. The mechanism often involves:
    - **"Standard SCR" (NO + $NH_3$):** 4NO+4NH3+O2→4N2+6H2O
    - **"Fast SCR" (NO + $NO_2$ + $NH_3$):** NO+NO2+2NH3→2N2+3H2O (often faster and more active)
    - The vanadium sites provide redox functionality, facilitating electron transfer and oxygen participation. Vanadium cycles between different oxidation states (e.g., V5+ and V4+).
- **Promoter Role:** $WO_3$ or $MoO_3$ promoters enhance surface acidity (increasing $NH_3$ adsorption capacity) and improve thermal stability by inhibiting the sintering of $V_2O_5$.
- **Support Role:** Anatase $TiO_2$ provides a high surface area, preventing sintering of the active components, and influences the electronic properties of the vanadium species.

**3.5.2. Zeolite-based Catalysts (Cu-SSZ-13, Cu-SAPO-34):** For low-temperature SCR (150-300°C), particularly in mobile applications, copper-exchanged small-pore zeolites have emerged as superior catalysts. Their remarkable performance stems from a combination of unique features:

- **Confined Environments:** The small pores (e.g., CHA structure in SSZ-13) create nanoconfined environments that favor the desired SCR reaction while sterically hindering undesirable side reactions (e.g., $NH_3$ oxidation at higher temperatures).
- **Active Sites:** Isolated $Cu^{2+}$ ions within the zeolite framework serve as highly active redox sites. These copper ions can undergo reversible changes in coordination environment and oxidation state during the catalytic cycle.
- **Brønsted Acidity:** The aluminosilicate framework provides Brønsted acid sites essential for the activation and adsorption of ammonia.
- **Dynamic Nature of Cu Sites:** In situ and operando studies have revealed that the active copper sites are dynamic, transitioning between isolated monomeric $Cu^{2+}$ species and small oligomeric clusters depending on temperature and reaction conditions. The monomeric $Cu^{2+}$ species are particularly active for the SCR reaction. This dynamic behavior highlights the importance of understanding the catalyst under realistic operating conditions.

### 3.6. Fundamental Principles in $CO_2$ Utilization (Methanation)

$CO_2$ hydrogenation to methane (the Sabatier reaction) is a promising pathway for $CO_2$ utilization, offering both a method for converting a greenhouse gas into a useful fuel and a means for energy storage. The reaction is exothermic: $CO2+4H2\rightarrow CH4+2H2O$, $\Delta H\circ=-165$ kJ/mol. The surface chemistry involved is complex, with multiple proposed mechanistic pathways:

#### A. CO Pathway:

- $CO_2$ is first reduced to CO on the catalyst surface: $CO2(g)+H2(g)\rightarrow CO(g)+H2O(g)$
- The resulting CO then undergoes further hydrogenation to methane: $CO(g)+3H2(g)\rightarrow CH4(g)+H2O(g)$ Noble metals like Ru and Rh often favor this pathway, where CO dissociation on the metal surface is a critical step.

#### B. Formate Pathway:

- 1.$CO_2$ hydrogenates directly to formate intermediates (HCOOads) on the catalyst surface.
- 2.These formate species are then further hydrogenated and dehydrated to form methane. Some Ni and Co catalysts may proceed more predominantly via formate intermediates. The role of surface oxygen species and C-O bond activation is crucial here.

### 3.7. Photosynthesis (natural process):

- Photosynthesis acts as a natural model for $CO_2$ utilisation, where sunlight-driven surface reactions convert $CO_2$ into organic compounds — inspiring the design of catalysts for artificial $CO_2$ methanation.
- Both photosynthesis and methanation involve surface-mediated, multi-step redox reactions, highlighting the importance of catalytic active sites and energy input to drive $CO_2$ conversion efficiently.

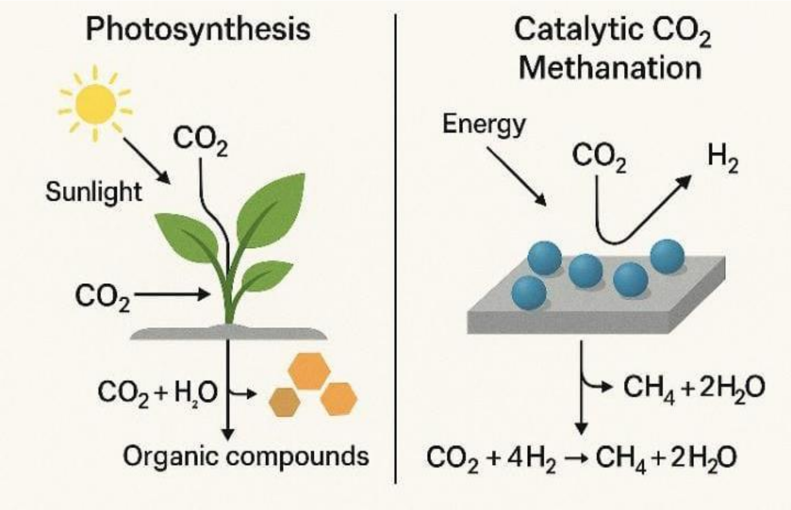

Diagram: **Photosynthesis and $CO_2$ utilization (Methanation)**

## 4. Experimental Section – Materials, Characterization, and Applications

### 4.1. Catalytic Materials: Innovations in Synthesis and Design

The past few decades have witnessed a revolution in catalytic materials, largely driven by advances in nanoscience and nanotechnology. The ability to control matter at the nanoscale has enabled the design of catalysts with precisely tailored surface properties and architectures, leading to dramatic improvements in performance across various applications.

#### 4.1.1. Mesoporous Silica Nanoparticles (MSNs) as Versatile Supports

MSNs, characterized by their uniform pore sizes (typically 2-50 nm), exceptionally high surface areas (often exceeding 1000 $m^2/g$), and remarkable thermal and chemical stability, have emerged as ideal supports for catalytic metal nanoparticles. Their synthesis typically involves surfactant-templated methods (e.g., Stöber method for spherical particles or cooperative self-assembly).

- **Synthesis and Functionalization:** MSNs are synthesized by the hydrolysis and condensation of silica precursors (e.g., tetraethyl orthosilicate, TEOS) in the presence of structure-directing agents (surfactants). The removal of these surfactants leaves behind a highly ordered mesoporous structure.
    - **Metal Dispersion:** The high surface area and uniform pore channels of MSNs allow for excellent dispersion of active metal nanoparticles (e.g., Pt, Pd, Ru, Ni). The confinement within the pores can prevent aggregation and sintering of these metal particles even under harsh reaction conditions, leading to enhanced stability and activity.
    - **Surface Tuning:** The silica surface can be further functionalized with various organic groups or metal complexes through post-synthesis grafting or co-condensation methods. For instance, amine-functionalized MSNs serve as effective base catalysts due to the presence of basic amine groups. MSNs doped with transition metals like Ti or Zr during synthesis or post-synthesis exhibit excellent redox activity, useful in oxidation reactions or acid catalysis.
    - **Nanoscale Reactors:** Perhaps most impressively, MSNs can be engineered with multiple distinct functional groups or catalytic sites in different regions of their pore structures. This enables the creation of nanoscale reactors where different catalytic transformations can occur in sequence or in cascade, mimicking enzymatic systems and facilitating complex multi-step syntheses. This level of control over surface chemistry and architecture represents a major leap forward in designing highly efficient and selective catalysts.

#### 4.1.2. Magnetic Nanoparticles (MNPs) for Recoverable Catalysis

MNPs, particularly those based on iron oxides like magnetite ($Fe_3O_4$) or maghemite ($\gamma$-$Fe_2O_3$), have transformed catalytic practice by combining intrinsic catalytic activity with the practical advantage of magnetic recoverability.

- **Synthesis and Magnetic Properties:** MNPs are typically synthesized via co-precipitation, thermal decomposition, or hydrothermal methods. Their superparamagnetic behavior (exhibiting magnetism only in the presence of an external magnetic field, with no residual magnetization upon removal) allows them to be easily separated from reaction mixtures using external magnetic fields. This addresses a longstanding challenge in liquid-phase catalysis – efficient catalyst recovery and reuse, which is particularly valuable for expensive catalytic systems (e.g., noble metal catalysts, enzymes, organocatalysts) where recovery and recycling are economically critical, such as in pharmaceutical synthesis or fine chemical production.
- **Silica-Coated Magnetic Nanoparticles (SMNPs):** The development of silica-coated magnetic nanoparticles (SMNPs) has expanded these applications further. The silica shell not only protects the magnetic core from oxidation or dissolution (enhancing chemical robustness) but also provides a versatile, inert surface for further functionalization and immobilization of sensitive catalytic species like enzymes or organocatalysts. This allows for the integration of homogeneous catalysis advantages (high selectivity) with heterogeneous benefits (easy separation).
- **Advanced Architectures:** Recent innovations include the creation of yolk-shell structures, where catalytic nanoparticles are enclosed within porous silica shells, combining the benefits of nanoconfinement (protection, controlled access) with magnetic separation. These advanced architectures demonstrate how sophisticated materials design can simultaneously address multiple challenges in catalysis, from enhancing activity and selectivity to ensuring efficient separation and recyclability.

### 4.2. Advanced Characterization Techniques: Unveiling the Catalyst at Work, determination:

- **Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS):**
    - **Principle:** DRIFTS is a powerful spectroscopic technique that allows for the identification of surface-bound intermediates, adsorbed species, and changes in surface functional groups under actual reaction conditions (temperature, pressure, gas flow). Infrared light is shone onto the catalyst sample, and the diffusely scattered light is collected and analyzed.
    - **Applications:** It provides vibrational fingerprints of molecules adsorbed on the catalyst surface, helping to elucidate reaction mechanisms, identify active sites (e.g., Brønsted vs. Lewis acid sites by probing adsorbed probe molecules like pyridine or ammonia), and observe the formation and consumption of reaction intermediates. It's particularly useful for gas-solid reactions.
- **X-ray Absorption Spectroscopy (XAS):**
    - **Principle:** XAS techniques, including Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES), are synchrotron-based techniques that provide atomic-level information about the local coordination environment, oxidation state, and electronic structure of specific elements within the catalyst.
    - **EXAFS:** Provides information on the type, number, and distance of neighboring atoms around the absorbing atom, allowing for the determination of coordination numbers and bond lengths, even for disordered or amorphous materials.
    - **XANES:** Provides information about the oxidation state and electronic structure of the absorbing atom, reflecting changes in bond character and orbital occupancy.

  - **Applications:** XAS is instrumental for probing the nature of active metal centers (e.g., Cu species in zeolites, Ni particles in $CO_2$ methanation catalysts), monitoring their structural evolution (e.g., sintering, reduction, oxidation) during catalytic reactions, and identifying active sites. Its element specificity and ability to work in operando conditions make it a cornerstone of modern catalysis research.
- **Temperature-Programmed Methods (TPD, TPR, TPO):**
  - **Principle:** These are widely used thermogravimetric techniques that involve heating a catalyst sample in a controlled gas atmosphere while monitoring gas uptake, release, or consumption.
  - **Temperature-Programmed Desorption (TPD):** A pre-adsorbed species is desorbed by increasing temperature, and the desorbed species are detected (e.g., by mass spectrometry). It provides information on the number, strength, and heterogeneity of adsorption sites. (e.g., $NH_3$-TPD for acid sites, $CO_2$-TPD for basic sites).
  - **Temperature-Programmed Reduction (TPR):** A reducible catalyst (e.g., metal oxide) is heated in a reducing atmosphere (e.g., $H_2/Ar$), and $H_2$ consumption is monitored. It provides information on the reducibility of metal oxides, the dispersion of active metal species, and metal-support interactions.
  - **Temperature-Programmed Oxidation (TPO):** A coked or reduced catalyst is heated in an oxidizing atmosphere (e.g., $O_2/He$), and $CO_2/H_2O$ evolution is monitored. It provides information on the amount and nature of coke deposited or the extent of metal re-oxidation.
- **Electron Paramagnetic Resonance (EPR) Spectroscopy:**
  - **Principle:** EPR detects species with unpaired electrons (e.g., certain transition metal ions like $Cu^{2+}$, $V^{4+}$, or radicals). It provides information on the electronic environment, coordination geometry, and interaction of paramagnetic species with their surroundings.
  - **Applications:** Crucial for elucidating the nature of active metal centers in heterogeneous catalysts, particularly for understanding the coordination environment and oxidation states of active transition metal ions (e.g., $Cu^{2+}$ in zeolites for SCR, $V^{4+}$ in $V_2O_5/TiO_2$ catalysts).
- **Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy:**
  - **Principle:** Solid-state NMR probes the local atomic environment of specific nuclei (e.g., $^{27}Al$, $^{29}Si$, $^{31}P$, $^{13}C$, $^{1}H$) within solid materials. It provides information on connectivity, local structure, and dynamics.
  - **Applications:** Useful for characterizing the framework structure of zeolites, identifying different types of acid sites (e.g., Brønsted vs. Lewis), tracking the transformation of organic species within catalyst pores, and studying surface functional groups.
- **Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM):**
  - **Principle:** Electron microscopy techniques provide high-resolution images of catalyst morphology, particle size distribution, crystal structure, and elemental composition.
  - **TEM:** Offers atomic-resolution imaging (HRTEM) to visualize crystal lattices, defects, and the interface between metal nanoparticles and supports. Coupled with Energy-Dispersive X-ray Spectroscopy (EDX) or Electron Energy Loss Spectroscopy (EELS), it provides elemental mapping.

  - **SEM:** Provides surface morphology and topography information, useful for examining particle size, shape, and overall catalyst architecture.
  - **Applications:** Essential for characterizing the nanostructure of catalysts, assessing metal dispersion, observing sintering, and identifying the location of active components within complex materials.

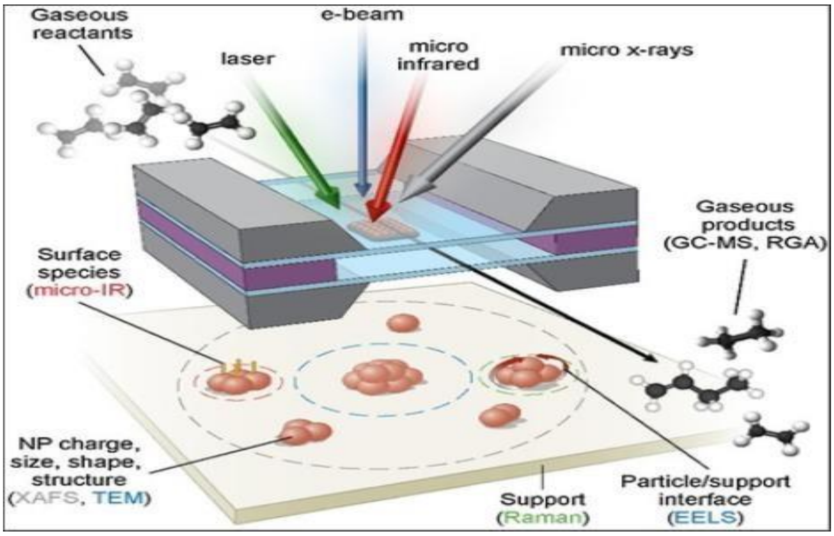

Diagram**: Advanced characterization techniques**

### 4.3. Industrial Applications and Societal Impact

The advancements in surface reactions and catalytic materials have profound economic and environmental implications, enabling sustainable chemical production and addressing critical global challenges.

### 4.3.1. Petroleum Refining and Bulk Chemicals:

- **Fluid Catalytic Cracking (FCC):** Catalytic cracking of heavy crude oil fractions into lighter, more valuable transportation fuels (gasoline, diesel) using zeolite-based catalysts.
- **Hydroprocessing (Hydrotreating, Hydrocracking):** Removal of sulfur, nitrogen, and other impurities from petroleum fractions, and conversion of heavy oils into lighter products, typically using sulfided Ni-Mo or Co-Mo on alumina catalysts.

### 4.3.2. Sustainable Chemistry and Circular Economy:

- **Biomass Conversion:** Catalytic conversion of lignocellulosic biomass into biofuels, biochemicals, and value-added products. This involves processes like hydrogenation, dehydration, and reforming.

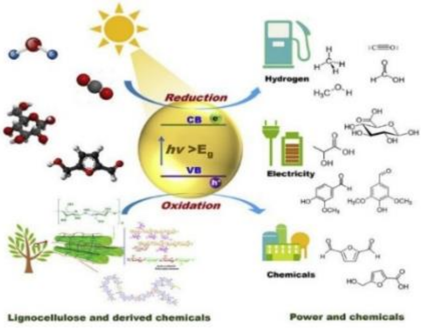

Diagram**: Biomass conversion**

- **$CO_2$ Utilization:** As discussed, the hydrogenation of $CO_2$ to methane, methanol, or other chemicals. This helps to close the carbon loop and provide renewable feedstocks.

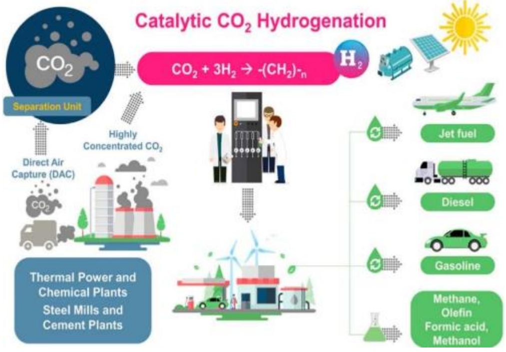

Diagram: **$CO_2$ utilization**

- **Plastic Recycling:** Catalytic depolymerization or pyrolysis of plastic waste into monomers or valuable hydrocarbon fractions, enabling a more circular economy for plastics.

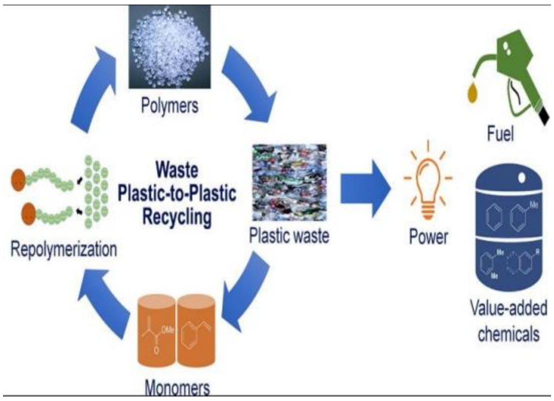

Diagram: **Plastic recycling**

- **Hydrogen Production:** Catalytic steam reforming of natural gas or biomass, or catalytic water splitting (photocatalytic or electrocatalytic) for sustainable hydrogen generation.

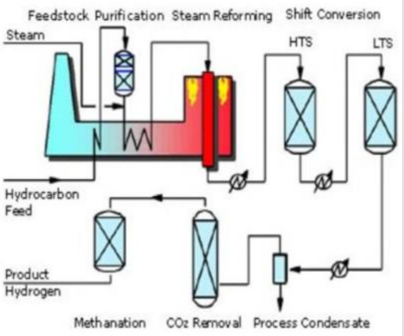

Diagram: **Hydrogen Production**

- **Electrocatalysis and Photocatalysis:**

  - **Electrocatalysis:** Using electricity to drive chemical reactions at electrode surfaces. Applications include fuel cells (oxygen reduction reaction, ORR; hydrogen oxidation reaction, HOR), water electrolysis (oxygen evolution reaction, OER; hydrogen evolution reaction, HER), and $CO_2$ electroreduction.
  - **Photocatalysis:** Using light energy to drive chemical reactions, typically over semiconductor materials. Applications include water splitting to produce hydrogen, $CO_2$ photoreduction, and environmental purification (degradation of pollutants). These emerging fields hold immense promise for energy-efficient and sustainable chemical processes.

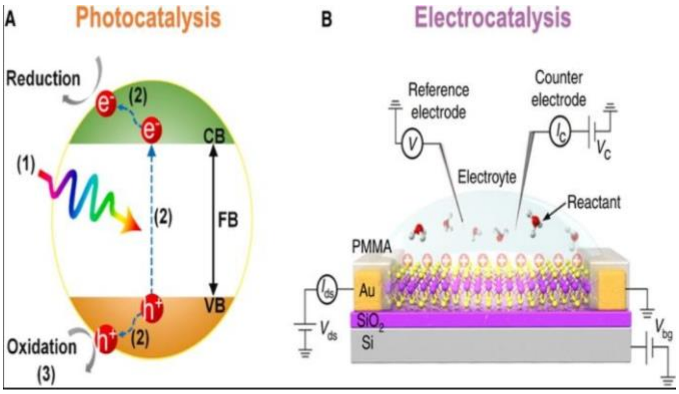

Diagram: **Photocatalysis and Electrocatalysis**

## 4.1. Current Challenges and Future Directions

Despite significant progress, the field of surface catalysis faces several key challenges that also represent opportunities for future research:

- **Catalyst Durability and Deactivation:** Developing more robust catalytic materials that can withstand harsh reaction conditions (high temperatures, corrosive environments) and resist deactivation mechanisms (sintering, coking, poisoning) remains a major challenge. Innovative stabilization strategies, such as protective overlayers, strong metal-support interactions, or confinement within porous matrices, are active research areas.
- **Catalyst Scalability and Manufacturing:** Translating laboratory-scale successes to industrial production requires addressing challenges in catalyst synthesis scale-up, cost-effectiveness, and process integration.

- **Rational Design of Complex Multifunctional Catalysts:** Designing catalysts for complex multi-step reactions or cascade reactions requires precise control over multiple active sites and their cooperative interactions. This is a grand challenge, aiming to mimic the efficiency of enzymatic systems.

- **Understanding Catalyst Dynamics "In Operando":** Further development of advanced in situ and operando characterization techniques, combined with sophisticated computational modeling, is crucial for unraveling the dynamic structural and electronic changes that occur in catalysts under realistic working conditions. This will provide unprecedented insights into catalyst activation, deactivation, and the true nature of active sites.

- **Catalysis for Renewable Energy and Sustainability:** The growing urgency for sustainable chemical production drives interest in catalysts that can operate under mild conditions, utilize renewable feedstocks (biomass, $CO_2$), and harness renewable energy inputs (photocatalysis, electrocatalysis).+
- **Data-Driven Catalyst Discovery:** The integration of machine learning, artificial intelligence, and high-throughput experimentation will accelerate catalyst discovery and optimization by efficiently navigating the vast parameter space of possible compositions and structures. This paradigm shift will revolutionize the traditional empirical approach.
- **Bridging the Gaps (Pressure, Materials, Knowledge):** Continuously striving to bridge the gaps between idealized theoretical models, laboratory experiments, and real-world industrial operating conditions is paramount. This requires interdisciplinary collaboration and a holistic approach from fundamental science to process engineering.

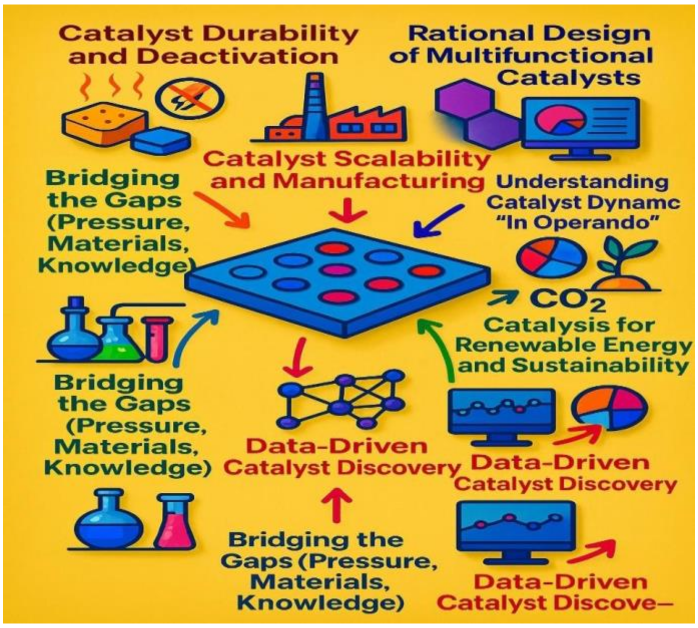

Diagram**: Current challenges and future directions**

## 5. Conclusion:

The study of surface reactions and catalytic activity is a dynamic and essential field at the nexus of chemistry, materials science, and chemical engineering. The remarkable progress achieved in recent years, from the synthesis of sophisticated nanostructured catalysts to the elucidation of complex reaction mechanisms through advanced characterization and computational techniques, has dramatically expanded our ability to control and optimize chemical processes. These advancements have facilitated more efficient, selective, and sustainable chemical transformations with wide-ranging applications in energy, environmental protection, and chemical manufacturing. As we move forward, the continued integration of experimental and theoretical approaches, coupled with emerging technologies like machine learning and automated synthesis, promises to further accelerate catalyst discovery and development. By deepening our understanding of surface phenomena and learning to engineer catalytic materials with ever-greater precision, we move closer to realizing the full potential of catalysis to address some of society's most pressing challenges, from climate change and resource scarcity to clean energy and sustainable production. The journey from fundamental surface science to practical catalytic technologies is complex and often challenging, but the rewards – in terms of both scientific insight and real-world impact – solidify its position as one of the most exciting and important endeavors in modern science and engineering.

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