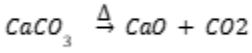
UNIT-III:PHOTO CHEMISTRY

Thermal Process (Thermochemical Process)

A **thermal process** is a chemical reaction that is initiated and carried out by the absorption of **heat energy**, where the reacting molecules remain in their **ground state**. The rate of such processes mainly depends on **temperature** and follows the **Arrhenius equation**.

Example: Thermal decomposition of calcium carbonate,

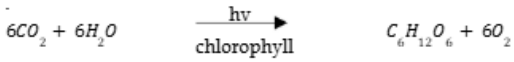


$$CaCO_3 \xrightarrow{\Delta} CaO + CO2$$

Photochemical Process

A **photochemical process** is a chemical reaction that is initiated by the **absorption of light energy (photons)**, where the molecules are excited to higher electronic states before undergoing reaction. The rate of these reactions depends on the **intensity and wavelength of light** rather than temperature.

Example: Photosynthesis



$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2$$

Differences between Thermal and Photochemical Processes

Aspect	Thermal Process	Photochemical Process
Source of Energy	Reaction is initiated by heat energy.	Reaction is initiated by absorption of ligl (photons).
Activation Energy	High activation energy is required start the reaction.	Lower activation energy is needed, sinc photons directly excite molecules.
Temperature Dependence	Rate of reaction increases wi increase in temperature (Arrheniu law).	Rate of reaction depends mainly on ligl intensity and wavelength, not strongly c temperature.
Excited State	Molecules react in their **ground stat**	Molecules react in their **excited state** aft absorbing photons.
Governing Law	Follows **Arrhenius equation**: $K = A\,e^{\frac{-E_a}{RT}}$	Follows **Grothus–Draper law** an **Einstein's law of photochemic equivalence**.
Quantum Yield	Usually close to 1 (one molecu reacts per activation event).	May be much greater or smaller than 1 (du to chain reactions or side processes).
Example Reactions	Combustion, thermal decompositic of $CaCO_3 \rightarrow CaO + CO_2$.	Photosynthesis, chlorination of alkanes sunlight, $H_2 + Cl_2 \rightarrow 2HCl$ (light induced).

Laws of photochemistry

Grothus–Draper's Law (Law of Photochemical Activation)

Definition:

Only the light **absorbed by a system** is effective in producing a photochemical change. The light that is **reflected or transmitted** cannot bring about any chemical reaction.

Explanation:

When light of a suitable wavelength falls on a substance, only the absorbed photons raise molecules to an **excited state**.

This excited state molecule then undergoes chemical changes.

If the radiation is not absorbed, no photochemical reaction takes place.

Example:

Photosynthesis in green plants occurs only in the **blue and red regions** of visible light because

Stark–Einstein Law of Photochemical Equivalence

Definition:

Each molecule of a substance, on absorbing **one quantum of light (one photon)**, is activated to undergo a primary chemical reaction.

Explanation:

According to quantum theory, light consists of discrete packets of energy called **photons**.

The energy of each photon is given by:

$E = h\nu = h\frac{c}{\lambda}$

where h = Planck's constant, v = frequency,λ = wavelength.

The law states that **one photon activates only one molecule** in the primary step.

This means, for every mole of reactant molecules undergoing photochemical change, **one mole of photons (called one Einstein of energy)** must be absorbed.

Example:

The photochemical decomposition of chlorine:

$Cl2 + h\nu \rightarrow 2Cl\cdot$

One photon excites one molecule of Cl2 to produce two chlorine free radicals.

Quantum Yield (Φ)

Definition:

The **quantum yield** (or quantum efficiency) of a photochemical reaction is defined as:

$\Phi = \frac{Number\ of\ photons\ absorbed}{Number\ of\ molecules\ reacting}$

It represents how many molecules undergo chemical change **per photon absorbed**.

If $\Phi \gg 1$: Many molecules react per absorbed photon (chain reactions).

If Φ = 1: One photon produces reaction in one molecule.

If Φ << 1: Reaction is inefficient; some absorbed energy is lost as fluorescence, phosphorescence, or heat.

Photochemical Reaction Mechanism

(A) Hydrogen–Chlorine Reaction

Reaction:

$H2 + Cl2 \xrightarrow{h\nu} 2HCl$

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Steps (Chain Mechanism):

Initiation:

$Cl2 \xrightarrow{h\nu}$ 2Cl· (Cl radical)

Propagation:

$Cl\cdot + H2 \rightarrow HCl + H\cdot$

$H\cdot + Cl2 \rightarrow HCl + Cl\cdot$

(Radicals regenerate and continue the chain).

Termination:

$Cl\cdot + Cl\cdot \rightarrow Cl2$

$H\cdot + H\cdot \rightarrow H2$

$H\cdot + Cl\cdot \rightarrow HCl$

Quantum Yield:

Very **high (10^4 – 10^6)** because each absorbed photon initiates a **chain reaction** producing many molecules of HCl.

(B) Hydrogen–Bromine Reaction

Reaction:

$H2 + Br2 \xrightarrow{h\nu} 2HBr$

Steps (Chain Mechanism):

Initiation:

$Br2 + h\nu \rightarrow 2Br\cdot$

Propagation:

$Br\cdot + H2 \rightarrow HBr + H\cdot$

$H\cdot + Br2 \rightarrow HBr + Br\cdot$

Termination:

$Br\cdot + Br\cdot \rightarrow Br2$

$H\cdot + H\cdot \rightarrow H2$

Quantum Yield:

Very **low ($\Phi \approx 1$)** because:

Side reactions occur (e.g., formation of excited Br_2^*).

Bromine radicals are less reactive than chlorine radicals.

Competing recombination reduces efficiency.

1. Fluorescence

Definition:

Fluorescence is the process in which an excited molecule emits radiation (light) while returning from the **first singlet excited state (S_1)** to the **ground state (S_0)**.

Key Features:

Very **fast process** (~10^{-9} to 10^{-7} seconds).

Stops almost immediately when the incident light is removed.

Involves **singlet → singlet transition** (allowed transition, hence rapid).

Common in aromatic compounds (e.g., quinine, fluorescein, chlorophyll).

Example: Fluorescein in aqueous solution emits bright green fluorescence.

2. Phosphorescence

Definition:

Phosphorescence is the delayed emission of light by a substance after absorption of radiation, due to transition from the **triplet excited state (T_1)** to the **singlet ground state (S_0)**.

Key Features:

Slow process (time scale: 10^{-3} seconds to minutes or even hours).

Continues even after the source of light is removed ("afterglow").

Involves **triplet → singlet transition** (spin-forbidden, hence slow).

Strongly observed in compounds with heavy atoms, aromatic ketones, and inorganic phosphors.

Example: ZnS:Cu (zinc sulfide doped with copper) glows in the dark after UV excitation.

3. Photosensitized Reactions

Definition:

A **photosensitized reaction** occurs when a molecule (called the *sensitizer*) absorbs light and transfers its

energy to another molecule which itself does not absorb at that wavelength.

Mechanism:

1. Sensitizer (S) absorbs photon:

   $S + h\nu \rightarrow S*$

2. Excited sensitizer transfers energy to substrate (A):

   $S* + A \rightarrow S + A*$

3. Excited substrate undergoes chemical change.

Examples:

Photosynthesis: Chlorophyll acts as a sensitizer, absorbing visible light and transferring energy to CO_2 and H_2O for glucose formation.

Photosensitized oxidation: O_2 is excited by a sensitizer to form singlet oxygen, which reacts with organic substrates.

Photopolymerization: Sensitizers initiate free-radical reactions in polymers.

Comparison Table

Property	Fluorescence	Phosphorescence	Photosensitized Reacti
Nature	Emission of light	Delayed emission of light	Energy transfer process
State involved	$S_1 \rightarrow S_0$ (singlet)	$T_1 \rightarrow S_0$ (triplet to singlet)	Excited sensitizer transfers energy to substrate
Time scale	10^{-9} – 10^{-7} s (fast)	10^{-3} s to minutes/hours (slow)	Depends on reaction pathway
Persistence after light removal	No	Yes (afterglow)	Yes, reaction continues
Example	Fluorescein, chlorophyll	ZnS:Cu, aromatic ketones	Photosynthesis, singlet oxygen reactions

Energy Transfer Processes – Jablonski Diagram

The **Jablonski diagram** is a pictorial representation of the electronic states of a molecule and the transitions between them.

Processes of Energy Transfer

1.Absorption: A molecule in ground state (S_0) absorbs a photon and gets excited to a higher singlet state (S_1 or S_2).

$S0 + h\nu \rightarrow S1$

2.Fluorescence (Radiative decay):

Excited molecule in singlet state (S_1) returns to ground state (S_0) by emitting light.

$S_1 \rightarrow S_0 + h\nu_f$

(fast process, 10^{-9} – 10^{-7} s)

3.Inter system Crossing (ISC):

Non-radiative transition from singlet (S_1) to triplet state (T_1).

4.Phosphorescence:

Molecule in triplet state (T_1) returns to singlet ground state (S_0) by emitting light.

$T_1 \rightarrow S_0 + h\nu_p$ (slow, spin-forbidden, afterglow)

Photosensitization (Energy Transfer):

Excited molecule (Sensitizer, S*) transfers its energy to another molecule (A).

$S* + A \rightarrow S + A*$

Example: Chlorophyll (S) absorbs visible light, excites O_2 to singlet oxygen (A*).