Photochemistry
Introduction

ENERGY

- Heat
- Electricity
- Electromagnetic irradiation (light)
How the eye perceives light
Vision: Triggered by a photochemical reaction

Is red in the dark?

The answer must be NO - Since what we see as colour must be light which is reflected off the object. In darkness this cannot happen.
Photochemistry

Chemical reactions accompanied with light.

Photochemistry is the study of the interaction of electromagnetic radiation with matter resulting into a physical change or into a chemical reaction.

1. Action of light $\rightarrow$ chemical change
   (light induced reactions)

2. Chemical reaction $\rightarrow$ light emission
   (chemiluminescence)
## Definitions and terms

**Light:** electromagnetic vibrations spreading in quanta (photons)

**Photon:** the smallest amount of light carries energy
Electromagnetic Radiation

Electromagnetic radiation consists of waves of electric and magnetic fields traveling in space at right angles to one another (Figure 1).
Distance and Size scales of the Electromagnetic Spectrum

![Diagram showing the electromagnetic spectrum with distance and size scales.](image-url)
The image shows a diagram of the electromagnetic spectrum, with wavelengths ranging from gamma rays to radio waves. The table below lists the corresponding wavelengths (λ) in meters, frequencies (ν) in Hz, energies (ε) in eV, and temperatures (T) in Kelvin for each region of the spectrum.

<table>
<thead>
<tr>
<th></th>
<th>gamma-rays</th>
<th>X-rays</th>
<th>UV</th>
<th>IR</th>
<th>microwaves</th>
<th>radio-waves</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ (m)</td>
<td>10^{-16}</td>
<td>10^{-14}</td>
<td>10^{-12}</td>
<td>10^{-10}</td>
<td>10^{-8}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>ν (Hz)</td>
<td>10^{24}</td>
<td>10^{22}</td>
<td>10^{20}</td>
<td>10^{18}</td>
<td>10^{16}</td>
<td>10^{12}</td>
</tr>
<tr>
<td>ε (eV)</td>
<td>10^{10}</td>
<td>10^{8}</td>
<td>10^{6}</td>
<td>10^{4}</td>
<td>10^{2}</td>
<td>10^{0}</td>
</tr>
<tr>
<td>T (K)</td>
<td>10^{12}</td>
<td>10^{10}</td>
<td>10^{8}</td>
<td>10^{6}</td>
<td>10^{4}</td>
<td>10^{2}</td>
</tr>
</tbody>
</table>
### Photochemical Vs Thermal reactions

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Photochemical reactions</th>
<th>Thermo-chemical reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>These involve the absorption of light.</strong></td>
<td>These involve either absorption or evolution of heat.</td>
</tr>
<tr>
<td>2.</td>
<td><strong>Take place in presence of light.</strong></td>
<td>Take place in dark or in presence of light.</td>
</tr>
<tr>
<td>3.</td>
<td><strong>They are independent of temperature.</strong></td>
<td>They are dependent of temperature.</td>
</tr>
<tr>
<td>4.</td>
<td><strong>Rate of reactions is dependent on the intensity of the light absorbed.</strong></td>
<td>Rate of reactions is not affected by the intensity of light.</td>
</tr>
<tr>
<td>5.</td>
<td><strong>The free energy change is negative or positive.</strong></td>
<td>The free energy change is always negative.</td>
</tr>
</tbody>
</table>
Grotthuss-Draper law:

*Only the light absorbed in a molecule can produce photochemical Change in the molecule*

Stark – Einstein law:

*If a species absorbs radiation, then one particle is excited for each quantum of radiation absorbed*
He I $\alpha$
$\nu = 21.2 \text{ eV}$

He I $\beta$
$\nu = 23.1 \text{ eV}$
Scheme of photochemical reaction

\[ A \xrightarrow{h\nu} A^* \rightarrow I \rightarrow B + C \]

Intermediates  Stable products
In terms of Quantum efficiency:

Quantum Efficiency \( \phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta's of light absorbed at same time}} \)

Experimentally,

\[ \phi = \frac{\text{rate of chemical reaction}}{\text{quanta absorbed per second}} \]

Stark - Einstein:

*If a species absorbs radiation, then one particle is excited for each quantum of radiation absorbed*
Energy of photons (A. Einstein)

\[ E = h \nu = h \frac{c}{\lambda} \]

- \( h = \) Planck’s constant (6.6 \( \cdot \) 10\(^{-34}\) Js)
- \( C = \) speed of light (3 \( \cdot \) 10\(^8\) ms\(^{-1}\))
- \( \lambda = \) wavelength
- \( \nu = \) frequency
Einstein’s Equivalency Principle

One particle of a chemical substance can absorb only one photon from a light beam: $\Delta E = h\nu$

For one mole: $\Delta E = Nh\nu = \text{One Einstein}$

$N = \text{Avogadro’s number } (6.02 \cdot 10^{23})$
Photons $\equiv$ quanta

One molecule absorbs $\equiv$ one photon

One mole of a substance containing $6.023 \times 10^{23}$ (Avogadro number) $\equiv$ 6.023 x $10^{23}$ quanta of light (or) one Einstein

Molecules absorbs
\[ E = h \nu \]
\[ \nu \lambda = c \]

\[ E = \frac{hc}{\lambda} \]

\[ E = \left( 6.6 \times 10^{-34} \text{Js} \right) \left( 3 \times 10^8 \text{m/s} \right) = \]
\[ \frac{2 \times 10^{-16}}{\lambda [\text{nm}]} \text{J} \]

\[ \frac{1}{1.6 \times 10^{-19}} \times \frac{N}{1000} \]

\[ \frac{1234}{\lambda [\text{nm}]} \text{eV} \]

\[ \frac{119627}{\lambda [\text{nm}]} \text{kJ/mol} \]
Numerical value of Einstein

In CGS Units

\[ E = \frac{2.86}{\lambda} \text{ cal / mole} \]

or

\[ 2.86 \times 10^5 / \lambda (\text{Å}) \text{ K cal / mole} \]

In SI units

\[ E = \frac{0.1197}{\lambda} \text{ J mol}^{-1} \]

or

\[ 11.97 \times 10^{-5} / \lambda (\text{m}) \text{ KJ mol}^{-1} \]
This law states that **decrease in the intensity of** monochromatic light with the **thickness** of the absorbing medium is proportional to the **intensity of incident light**.

\[- \frac{dI}{dx} \propto I \quad \text{or} \quad - \frac{dI}{dx} = kI\]

which on integration changes to

\[
\ln \frac{I}{I_0} = -kx
\]

(or) \( I = I_0 e^{-kx} \)

Where \( I_0 \) = intensity of incident light.
\( I \) = intensity of transmitted light.
\( K \) = absorption coefficient.
Beer-Lambert’s Law

It states that decrease in the intensity of monochromatic light with the thickness of the solution is not only proportional to the intensity of the incident light but also to the concentration ‘C’ of the solution.

Mathematically,

\[ -\frac{dI}{dx} = IC \]

\( (or) -\frac{dI}{dx} = \varepsilon IC \)

which on integration changes to, \( I = I_0 e^{-\varepsilon Cx} \)

Where, \( \varepsilon = \text{Molar absorption coefficient} \)
On combining both laws, we get

\[
\log \frac{I_0}{I} = \varepsilon Cx
\]

\[
A = \log \frac{I_0}{I} = \varepsilon Cx
\]

**Mathematical statement of Beer-Lambert’s law**

In the above equation,

\(\varepsilon = \) Molar absorption coefficient = \(k/2.303\)

\(A = \log \frac{I_0}{I}\) is the absorbance (or) Optical density (OD)
A solution shows a transmittance of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration if the molar absorption coefficient is 12,000 dm$^3$/mol.cm?

%$T = 20\% \Rightarrow T = 0.20, \quad x = 2.5\text{cm}, \quad \varepsilon = 12,000 \text{ dm}^3/\text{mol.cm}$

We know that, \[ A = \varepsilon C x \]

\[
C = \frac{A}{\varepsilon x} = -\frac{\log T}{\varepsilon x}
\]

\[
C = \frac{-\log 0.20}{12000 \times 2.5} = \frac{0.699}{12000 \times 2.5}
\]

\[ = 2.33 \times 10^{-5} \text{ mol/dm}^3 \]
Limitations of Beer-Lambert’s law

The law is not valid

i) When non-monochromatic radiation is used,

ii) If temperature changes during measurements,

iii) The law is applicable only to dilute solutions,

iv) Deviation may occur, if the solution contains impurities or dissociation or association
Classification of photochemical reaction based on quantum yield

Three categories

• The reaction in which $\phi$ is a small integer like 1, 2...

Ex: a) Dissociation of HI & HBr, b) Combination of SO$_2$ + Cl$_2$ and c) Ozonisation of O$_2$

• The reaction in which $\phi < 1$

Ex: a) Dissociation of NH$_3$, CH$_3$COCH$_3$ & NO$_2$ and b) Transformation of maleic acid into fumaric acid.

• The reaction in which $\phi$ is extremely high

Ex: a) Combination of CO with Cl$_2$ and b) Combination of H$_2$ with Cl$_2$
The overall photochemical reaction consists of

i) Primary reaction

ii) Secondary reaction

In the primary reaction, the quantum of light is absorbed by a molecule ‘A’ formations an excited molecule ‘A*’

\[ A + h\nu \rightarrow A^* \]

In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.

\[ A^* \rightarrow B \]
Reasons for high quantum yield

✓ Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions

✓ Formation of intermediate products will act as a catalyst

✓ If the reactions are exothermic, the heat evolved may activate other molecules

✓ The active molecules may collide with other molecules and activate them
primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I.

\[ \text{HI} + \text{hv} \rightarrow \text{H}^* + \text{I}^* \]

secondary reaction

\[ \text{H}^* + \text{HI} \rightarrow \text{H}_2 + \text{I}^* \]

\[ \text{I}^* + \text{I}^* \rightarrow \text{I}_2 \]

Overall reaction: \[ 2\text{HI} + \text{hv} \rightarrow \text{H}_2 + \text{I}_2 \]

The overall reaction shows that the two HI are decomposed for one photon (hv).

Thus, the quantum yield (\(\phi\)) = \(2/1=2\)
Primary reaction: \( \text{Cl}_2 + \text{hv} \rightarrow 2 \text{Cl}^* \)

Secondary reaction:

\[ \text{Cl}^* + \text{H}_2 \rightarrow \text{HCl} + \text{H}^* \]

\[ \text{H}^* + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^* \]

The Cl atom consumed in step 2 is regenerated in step 3.......

this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

\[ \text{H}^* + \text{Cl}^* \rightarrow \text{HCl} \]

\[ \text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2 \]

Thus the quantum yield varies from \(10^4\) to \(10^6\).
Reasons for low quantum yield

✓ Excited molecules may get deactivated before they form products

✓ Excited molecules may lose their energy by collisions with non-excited molecules

✓ Molecules may not receive sufficient energy to enable them to react

✓ Recombination of dissociated fragments will give low quantum yield.
Dimerization of anthracene to dianthracene

\[ 2\text{C}_{14}\text{H}_{10} + \text{hv} \rightarrow \text{C}_{28}\text{H}_{20} \]

The quantum yield = 2, but actually it is found to be = 0.5;

the reason is the above reaction is reversible

\[ \text{C}_{28}\text{H}_{20} \rightarrow 2\text{C}_{14}\text{H}_{10} \]
A chemical actinometer is a device, used to measure the amount of radiation absorbed and rate of photochemical reaction.

**Uranyl oxalate actinometer** is a commonly used

It consists of 0.05 M oxalic acid and 0.01 M Uranyl sulphate in water.

When it is exposed to radiation, Oxalic acid undergoes decomposition to give CO$_2$, CO and H$_2$O.

\[
\text{UO}_2^{2+} + \text{hv} \rightarrow (\text{UO}_2^{2+})^* \\
(\text{UO}_2^{2+})^* + \text{COOH} \rightarrow \text{UO}_2^{2+} + \text{CO}_2 + \text{CO} + \text{H}_2\text{O}
\]
The residual concentration of oxalic acid can be found out by titrating with standard KMnO₄. The amount of oxalic acid consumed is a measure of the intensity of radiation

*Calculation of the amount of radiation absorbed:*

The empty cell (or) the cell filled with solvent is exposed to radiation and reading is noted  
\[= \text{Total incident energy}\]

The cell is filled with the reactants and again the reading is noted  
\[= \text{Residual energy}\]

\[\therefore \text{Total energy absorbed by the reacting mixture} = \text{Total incident energy} - \text{Residual energy}\]
**ENERGY TRANSFER**

*Photosensitization*

The foreign substance absorbs the radiation and transfers energy to the reactants is called a **photosensitizer**

This process is called **photosensitization**.

Ex:
Atomic photosensitizers: Mercury, Cadmium, Zinc and

Molecular photosensitizers: Benzophenone, Sulphur dioxide.

*Quenching*

When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance.
**MECHANISM**

\[
D + h\nu \rightarrow ^1D
\]

\[
^1D \rightarrow ^3D
\]

\[
^3D + A \rightarrow D + ^3A
\]

\[
^3A \rightarrow \text{Products (photosensitization)} \quad \text{(photosensitizer is D)}
\]

If,

\[
^3D \rightarrow \text{Products (quenching)} \quad \text{(quencher is A)}
\]

\[
S_0 \text{ or } D \quad \rightarrow \quad T_1 \text{ or } ^3A
\]

\[
S_0 \text{ or } A \quad \rightarrow \quad S_1 \text{ or } ^1A
\]

\[
S_1 \text{ or } ^1D \quad \rightarrow \quad \text{ISC}
\]

\[
T_1 \text{ or } ^3D \quad \rightarrow \quad \text{Collision}
\]

\[
h\nu' \quad \rightarrow \quad S_0 \text{ or } D
\]

\[
S_1 \text{ or } ^1A \quad \rightarrow \quad S_0 \text{ or } A
\]
**Dissociation of hydrogen molecule**

UV light does not dissociate $H_2$ molecule, because the molecule is unable to absorb the radiation.

But, if a small amount of **mercury** vapour is added, dissociation of hydrogen takes place. Here **Hg** acts as **photo sensitizer**

\[
Hg + hv \rightarrow Hg^* \\
Hg^* + H_2 \rightarrow H_2^* + Hg \\
H_2^* \rightarrow 2H
\]
**Vision**: Early theories of light were theories of vision

**Photosynthesis**: Life requires the capture, storage and release of the sun’s energy

- Wald (Nobel in Medicine)
- Calvin (Nobel in Chemistry)
- Marcus (Nobel in Chemistry)

_Mechanism of Vision_

_Mechanism of Photosynthesis_
Water + Carbon dioxide = Food (carbohydrates) + Oxygen

Photosynthesis

- Light
- Chlorophyll: traps light energy to make food.
- Water: absorbed from the roots
- Carbon dioxide: enters through the stomata of the leaves
- Oxygen: given off into air
- Starch: stored food in other parts of the plant, turns iodine dark blue
Photosynthesis:  \[ \text{Chll} + \text{hv} \rightarrow \text{*Chll} \text{ (electrically excited)} \]

\[ 6 \text{H}_2\text{O} + 6 \text{CO}_2 + \text{*Chll} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 + \text{Chl} , \text{ } \Delta G = -\text{Ve} \]
Mechanism of Energy transfer

**Antiparallel spin**

\[ S = S_1 + S_2 = \left( + \frac{1}{2} \right) + \left( - \frac{1}{2} \right) = 0 \]

Spin multiplicity = \(2S+1 = 2\times 0 + 1 = 1\)

**Singlet Excited state**

\( S_1, S_2, S_3, \text{ etc.}, \)

**Parallel spin**

\[ S = S_1 + S_2 = \left( + \frac{1}{2} \right) + \left( + \frac{1}{2} \right) = 1 \]

Spin multiplicity = \(2S+1 = 2\times 1 + 1 = 3\)

**Excited Triplet state**

\( T_1, T_2, T_3, \text{ etc.}, \)
JABLONSKI - DIAGRAM

**Singlet State:**
- \( S_0 \)
- \( S_1 \)

**Excited State:**
- \( T_1 \)
- \( S_1 \)

- **Fluorescence:** \( h\nu \)
- **Phosphorescence:** \( h\nu'' \)
- **Radiationless Deactivation Heat:**

**Transitions:**
- **ISC (Internal Conversion):** \( S_1 \rightarrow S_0 \)
- **IC (Internal Conversion):** \( S_1 \rightarrow T_1 \)

**Note:** The diagram illustrates the Jablonski energy levels, showing the transitions between singlet and triplet states under various energy inputs and outputs.
Fluorescence $S_1 \rightarrow S_0$ very fast
so lifetime of $S_1$ short $\sim 10^{-9}$ sec.

So fluorescence occurs within first $10^{-9}$ sec. that $S_1$ formed

$T_1 \rightarrow S_0$ is slower, $T_1$ lifetime $\sim 10^{-3}$ sec.

So phosphorescence lasts much longer than fluorescence
FLUORESCENCE
Fluorescence of Various sea stones
Phosphorescence
Jablonski Diagram

Allowed singlet states

Forbidden triplet states due to spin conversion

Absorption

Fluorescence

Phosphorescence
Excitation of electrons

Singlet ground state $S_0$
(Singlet excited state $S_1$
(pair of electrons with opposite spins but each in different orbital))

Triplet excited state $T_1$
(pair of electrons with parallel spins in different orbitals)

The excited species can return to the ground state by losing all of its excess energy by any one of the paths shown in Jablonski diagram.
<table>
<thead>
<tr>
<th>Process</th>
<th>Transition</th>
<th>Timescale (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Absorption (Excitation)</td>
<td>$S_0 \rightarrow S_n$</td>
<td>ca. $10^{-15}$ (instantaneous)</td>
</tr>
<tr>
<td>Internal Conversion</td>
<td>$S_n \rightarrow S_1$</td>
<td>$10^{-14}$ to $10^{-11}$</td>
</tr>
<tr>
<td>Vibrational Relaxation</td>
<td>$S_n^* \rightarrow S_n$</td>
<td>$10^{-12}$ to $10^{-10}$</td>
</tr>
<tr>
<td>Intersystem Crossing</td>
<td>$S_1 \rightarrow T_1$</td>
<td>$10^{-11}$ to $10^{-6}$</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>$S_1 \rightarrow S_0$</td>
<td>$10^{-9}$ to $10^{-6}$</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>$T_1 \rightarrow S_0$</td>
<td>$10^{-3}$ to 100</td>
</tr>
<tr>
<td>Non-Radiative Decay</td>
<td>$S_1 \rightarrow S_0$, $T_1 \rightarrow S_0$</td>
<td>$10^{-7}$ to $10^{-5}$, $10^{-3}$ to 100</td>
</tr>
</tbody>
</table>
Explanation of Jablonski Diagram

The first step is the transition from higher excited singlet states to the lowest excited singlet state $S_1$. This is called internal conversion (IC). It is a non-radiative process and occurs in less than $10^{-11}$ second.

Now from $S_1$ the molecule return to ground state by any of the following paths.

- **Path I:**

  The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative.
- **Path II**

Molecule releases energy in the form of light or uv radiation. This is called **Fluorescence**

- **Path III**

Some energy may be lost in transfer from $S_1$ to $T_1$ in the form of heat. It is called **intersystem crossing (ISC)**. This path is non-radiative.

- **Path IV**

After ISC, the molecule may lose energy in the form of light in going from the excited triplet state to the ground state. This is called **phosphorescence**.
Fluorescence

Certain substances when exposed to light or certain other radiations absorb the energy and then immediately start re-emitting the energy. Such substances are called fluorescent substances and the phenomenon is called fluorescence.

e.g. Organic dyes such as eosin, fluorescein etc. vapour of sodium, mercury and iodine.

Phosphorescence

There are certain substances which continue to glow for some time even after the external light is cut off. Thus, phosphorescence is a slow fluorescence. E.g. ZnS, Sulfides and sulfates of Ca, Ba and Sr.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Fluorescence</th>
<th>Phosphorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>These involve singlet to singlet transition. $S_1 \rightarrow S_0$</td>
<td>These involve triplet to singlet transition. $T_1 \rightarrow S_0$</td>
</tr>
<tr>
<td>2.</td>
<td>This transition is allowed transition</td>
<td>This transition is forbidden transition</td>
</tr>
<tr>
<td>3.</td>
<td>This transition is fast occurs in $10^{-8}$ sec</td>
<td>This transition is slow</td>
</tr>
<tr>
<td>4.</td>
<td>Efficiency is low</td>
<td>Efficiency is more</td>
</tr>
<tr>
<td>5.</td>
<td>It is less selective and sensitive</td>
<td>It is more selective and sensitive</td>
</tr>
<tr>
<td>6.</td>
<td>It is not observed in the solution</td>
<td>It is observed in the solution</td>
</tr>
<tr>
<td>7.</td>
<td>It stops as soon as the incident radiation is cut off</td>
<td>It continuous for some time even after the incident radiation is cut off</td>
</tr>
</tbody>
</table>
Luminescence

The glow produced in the body by methods other than action of heat i.e. the production of **cold light** is called Luminescence

Chemiluminescence

The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence

e.g. The light emitted by glow-worms