Basic Photochemistry

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Basic Photochemistry

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Foreword

This book is a simple and easy approach for the understandings of basic concepts in the field of photochemistry. I strongly believe that this book is very beneficial for undergraduate and postgraduate students. What is especially important about this effort is that the materials have been very carefully studied and screened by the authors to ensure quality, and then organized to cover a broad range of topics from the field of photochemistry. You will be amazed how easily you can get to grips with this tricky subject. This book will give you clear guidelines to the areas where you should focus. Figures and diagrams presented in this book are very interesting and easy to understand the basic ideas about UV-light, process of photolysis, kinetics of light reaction, rate of reaction, and applications of photochemistry in environmental sciences. Authors of this book are very well known scholars in their respective field with rich experience in writing and publication.

Prof. Dr. Muhammad Ashraf
Chairman, Pakistan Science Foundation, Ministry of Science and Technology, Islamabad

Awards: University Best Teacher Award-HEC, Pride of Performance, Hilal-i-Imtiaz, Sitara-i-Imtiaz
Arif Malik
Dr. Arif Malik is an professor in “The Institute of Molecular Biology and Biotechnology (IMBB) at the University of Lahore, Lahore-Pakistan. Dr. Arif Malik is a eminent research scholar and has published and co-authored more than 100 research articles in highly reputed international journals of biological sciences. He has also presented and published his research in numerous national and international conferences. Dr. Malik has very strong record of supervising postgraduate students and has produced numerous PhD scholars for the country. Dr. Malik holds a PhD degree in biology of stress tolerance from the University of Agriculture Faisalabad, Pakistan. He is an approved supervisor by the Higher Education Commission (HEC) of Pakistan for postgraduate studies.

Saima Jadoon
Dr. Saima Jadoon is currently working as Assistant professor in the Institute of Molecular Biology and biotechnology (IMBB) at “The University of Lahore, Lahore Pakistan. Prior to that she worked as lecturer and assistant professor in the department of natural resources engineering and management (NREM) at the University of Kurdistan Hewler-Iraq. Throughout her academic career, Dr. Jadoon has been very active on research ground and has published and co-authored several research papers in peer reviewed international journals of science with high impact factors. Dr. Jadoon also has rich experience of supervising students in their research project both at undergraduate and postgraduate levels. Her experience of working with chemical industry and multinational companies further strengthens her resume as a very strong professional in the field of bio and photo chemistry. Dr. Saima Jadoon holds a PhD degree in biochemistry from the University of Lahore, master degrees in analytical chemistry, and education and Bachelor degrees in chemistry and education from the University of Baluchistan, Quetta Pakistan.
CHAPTER I
INTRODUCTION:

The photochemistry is the branch of chemistry concerned with physical processes and chemical reactions produced by light (electromagnetic radiations) chiefly by ultraviolet and visible radiation (1800-8000Å). The influence of light on a chemical reaction is also called photo catalysis when light shines into certain mixture of chemicals it starts off a chemical reaction. It is an initiator in some cases; the reactions once started, continue in the absence of light, in others the light must be a continual source of energy to keep the reaction going. There are many reactions that are affected by electromagnetic radiations. During the last three decades, there also has been a growing interest in the effects on matter of short wavelength electromagnetic radiation in the x – ray (0.1 – 10Å) and γ – ray (10⁻⁴ – 1Å) region far beyond the range of visible light. This field is generally called radiation chemistry, which deals specifically with the effects of ionization radiations (for example alpha and beta particles).

When molecular dissociation occurs in a radiation chemical reaction, the process is called a radiolysis. Since photochemical processes are associated with electronic excitation, for practical purposes, the most interest is centered on the ultraviolet and visible regions of the spectrum. Photochemical reactions are valuable in organic and inorganic chemistry because they proceed differently than thermal reactions. In ordinary chemical reaction the energy of activation is supplied by a chance collection in a molecule or pair of molecules of a large amount of thermal energy. The reactions caused by heat and in absence of light are called thermal or dark reactions. Photochemical reactions occur only when photons of radiant energy (hv) are absorbed by the reactant. Absorption of this energy provides the necessary energy needed to cross the activation barrier and form products. A wide variety of reactions can be initiated photo-chemically. Photochemical reactions are important in nature, particularly, terrestrial life is dependent upon the carbohydrate – forming reactions involving solar radiation (Photosynthesis). Photochemical reactions are not only very useful but also can be a serious nuisance, as in the photo degradation of many materials, for example, polyvinyl chloride. A large – scale application of photochemistry is photo resist technology, used in the production of microelectronic components. Vision is initiated by a photochemical reaction of rhodopsin. Photochemical reactions occur only when photons of radiant energy (hv) are absorbed by the reactant.
Absorption of this energy provides the necessary energy needed to cross the activation barrier and form products. A wide variety of reactions can be initiated photochemically.

Typical photochemical reactions include dissociations such as

$$2 \text{HBr} \xrightarrow{h\nu} \text{H}_2 + \text{Br}_2$$

$$h\nu = \text{Energy (E) of photon or quantum}$$

$$h = 6.62 \times 10^{-34} \text{ J s.}$$

$$\nu = \text{frequency of radiation} = \frac{E}{h}$$

(Where h is called the Planck’s constant after the name of the German Physicist Max Planck who in 1900 related the energy of a photon to its frequency. He was awarded Nobel Prize for physics in 1918).

dimerization such as

\[
\begin{align*}
2 \text{C}_{14} \text{H}_{10} & \xrightarrow{h\nu} \text{C}_{28} \text{H}_{20} \\
\text{anthracene} & \xrightarrow{} \text{dianthracene}
\end{align*}
\]

Rearrangements such as

\[
\begin{align*}
\text{HOOC. CH: CH. COOH} & \xrightarrow{h\nu} \text{HOOC. CH: CH. COOH} \\
\text{Fumaric acid} & \xrightarrow{} \text{Maleic acid} \\
\text{(trans-butenedioic acid)} & \xrightarrow{} \text{(cis-butenedioic acid)}
\end{align*}
\]

Addition reactions such as

\[
\begin{align*}
\text{C}_2 \text{H}_2 & \xrightarrow{h\nu} \frac{1}{n}(\text{C}_2 \text{H}_2)_n
\end{align*}
\]

Chain reactions such as

\[
\begin{align*}
n \text{H}_2 + n \text{Cl}_2 & \xrightarrow{h\nu} 2n \text{HCl}
\end{align*}
\]

For a gas there is often a fairly sharp transition from a spectral region where there is no absorption and no chemical reaction to one in which a considerable amount of chemical reaction occurs. The frequency or wavelength at this transition is known as the photochemical threshold. Reaction occurs on the higher – frequency, or shorter – wavelength, side of the threshold. The sun is an extremely powerful source of ultraviolet – visible radiation, consequently, a typical photochemical process, such as photosynthesis goes on around us all the time. The utilization of sunlight (visible light) by plants to convert carbon dioxide and water into carbohydrates. Chlorophyll acts as the energy converter (the energy accumulated from the sun’s light absorbing blue and red light) in this reaction, which is perhaps the most important on earth. Sugars are probably formed first and then starch and cellulose. It may be represented as:
\[ xCO_2 + yH_2O + \text{chlorophyll}^{\text{Sunlight}} \rightarrow C_{x+y},O_y + xO_2 + \text{chlorophyll} \]

e.g. \[ 6CO_2 + 6H_2O + \text{chlorophyll}^{\text{Sunlight}} \rightarrow C_6H_{12}O_6 + 6O_2 + \text{chlorophyll}. \]

Or

\[ 6nCO_2 + 5nH_2O^{\text{Sunlight}} \rightarrow \left(C_{6}H_{10}O_{5}\right)_n + 6nO_2 + \text{chlorophyll} \]

Starch

It should be noted that photosynthesis is in fact the opposite of combustion i.e. when a carbohydrate burns; it combines with oxygen to form \( CO_2 \). The oxygen is liberated from water. Photosynthesis is the source of all atmospheric oxygen. Since virtually all other forms of life are directly or indirectly dependent on plants for food, photosynthesis is the basis for all life on earth. In addition to above there are many others photochemical processes including photography. Without photochemical processes the world would be simply a warm, sterile, rock. Inorganic complexes are also photo reactive. Thus, metal carbonyls that resist thermal substitution undergo decarboxylation upon irradiation with UV light. UV irradiation of a tetrahydrofuran (THF) solution of molybdenum hexacarbonyl gives the THF complex, which is synthetically useful:

\[ \text{Mo} (\text{CO})_6 + \text{THF}^{h\nu} \rightarrow \text{Mo} (\text{CO})_5 (\text{THF}) + \text{CO} \]

In a related reaction, photolysis of iron pentacarbonyl affords diiron nonacarbonyl.

\[ 2 \text{Fe} (\text{CO})_5^{h\nu} \rightarrow \text{Fe}_2 (\text{CO})_9 + \text{CO} \]

The important phenomenon of vision is the outcome of a photochemical reaction that occurs very fast \((\sim 10^{-12} s)\). The pigment in the eye called rhodopsin absorbs light in the near UV and visible region. On absorption of light, a sequence of reactions takes place. The actual chemical in rhodopsin that gets excited is retinal. Excited retinal undergoes isomerization and the energy is stored as chemical energy. Shortly after that, retinal is regenerated and the energy released is used to send a signal to the brain. This gives us the sensation of vision. The formation of ozone and its dissociation in the atmosphere maintains the oxygen-ozone balance in the ozone layer. Both the reactions occur in the presence of sunlight. The reactions involved are given below:

\[ O_2 \rightarrow^{h\nu} O + O \]

\[ O + O_2 \rightarrow O_3 \]

\[ O_3 \rightarrow^{h\nu} O_2 + O + \text{heat} \]

In an industrial application, about 100,000 tons of benzyl chloride is prepared annually by the gas phase, photochemical reaction of toluene with chlorine. The light is absorbed by chlorine
molecule, the low energy of this transition being indicated by the yellowish color of the gas. The photon induces homolysis of the Cl-Cl bond, and the resulting chlorine radical converts toluene to the benzyl radical:

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl} \\
\text{C}_6\text{H}_5\text{CH}_3 + \text{Cl} & \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{HCl} \\
\text{C}_6\text{H}_5\text{CH}_2 + \text{Cl} & \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl}
\end{align*}
\]

The study of photochemistry includes phenomena that are mainly spectroscopic, such as fluorescence and phosphorescence, luminescent chemical reactions, such as flames and the gleam of the firefly; and photo stimulated reactions, such as photographic, photosynthetic and photolytic reactions of various kinds. Those reactions which are caused by energizing molecular collisions by heat and in the absence of light are described as thermal or dark reactions.

1.1. ELECTROMAGNETIC RADIATION:

Electromagnetic radiation which is a form of energy can be considered in terms of electric and magnetic fields which oscillate sinusoidally in mutually perpendicular planes at right angles to the direction of propagation of the radiation. This situation is shown in Fig. 1.1 where, for clarity, plane polarized radiation is depicted.

![Plane Polarized electromagnetic radiation](image)

Fig. 1.1: Plane Polarized electromagnetic radiation.
Electromagnetic radiation is described in terms of the wavelength, \( \lambda \), the frequency, \( \nu \), the wave number, \( \kappa \), or the energy, \( E \), of a quantum of radiation. The relationships between these terms and also the units used for these terms are summarized below in Table 1.1.

### Table 1.1: The relationship, units and symbols used for electromagnetic radiation.

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Units</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda = \frac{c}{\nu} \lambda )</td>
<td>nanometer (10^{-9} m)</td>
<td>nm</td>
</tr>
<tr>
<td>( \nu, \text{hertz} ) (Cycles / Sec)</td>
<td></td>
<td>Hz</td>
</tr>
<tr>
<td>( \kappa = 10^7 \frac{\nu}{\lambda} )</td>
<td>reciprocal centimeter</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td>( E = h \nu )</td>
<td>E, kilojoules per mole</td>
<td>k J mol(^{-1})</td>
</tr>
<tr>
<td>( = h \frac{c}{\lambda} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \equiv \frac{hc}{\nu} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( c \) is the speed of light = 3 x 10\(^8\) m s\(^{-1}\)

\( h \) is Planck’s constant = 6.626 \times 10^{-34} J s

The \( \lambda \) changes throughout the electromagnetic spectrum (Fig. 1.2) and in the range of the UV – VIS region, which is of main interest for photochemistry, the \( \lambda \) varies from ~ 200 nm to 750 nm. The Fig. 1.2 shows that this constitutes a very small range within the electromagnetic spectrum. Longer wavelength for example far infrared, tend to cause the vibrational excitation of molecules which results in heating. Shorter wavelength X-ray causes ionization.
Fig. 1.2: The electromagnetic spectrum highlighting the visible region, which along with the ultraviolet region, is capable of producing photochemical changes in molecules.

As the energy of a photon is given by $E = h \nu = \frac{hc}{\lambda}$ therefore, It is found that 1 einstein (1 mole of photons) of visible light of $\lambda = 6000 \text{ Å}$ has energy equal to 45 k cal mol$^{-1}$, for a wavelength of 2000 Å, the energy of 1 Einstein is 135 k cal mol$^{-1}$. The absorption of radiation in the visible or UV region is sufficient to break a chemical bond or produce high energy reactive complex. Thus, the visible or UV radiations are quite sufficient to split a chemical bond, as bond energies are of the order 50 – 100 k cal mol$^{-1}$. Thus absorption of radiation in visible (35 – 75 k cal mol$^{-1}$) and UV (75 to 286 k cal mol$^{-1}$) range under suitable conditions may lead to a photochemical reaction. For example, oxygen gas is dissociated into oxygen atoms by far UV light (200 – 300 nm) as given below:

$$O_2(g) \stackrel{h\nu}{\longrightarrow} 2 \text{ O}$$

Some values for the energy of radiation in the ultraviolet and visible regions are given in Table 1.2.
Table 1.2: Energy of ultraviolet – visible radiation.

<table>
<thead>
<tr>
<th>Region</th>
<th>Wave Length $\lambda$ (nm)</th>
<th>Wave Number $\bar{\nu}$ (cm$^{-1}$)</th>
<th>Energy $x 10^5$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet</td>
<td>200 – 400</td>
<td>50000 – 25000</td>
<td>5.95 – 2.98</td>
</tr>
<tr>
<td>Violet</td>
<td>400 – 450</td>
<td>25000 – 22222</td>
<td>2.98 – 2.65</td>
</tr>
<tr>
<td>Blue</td>
<td>450 – 500</td>
<td>22222 – 20000</td>
<td>2.65 – 2.39</td>
</tr>
<tr>
<td>Green</td>
<td>500 – 570</td>
<td>20000 – 17544</td>
<td>2.39 – 2.09</td>
</tr>
<tr>
<td>Yellow</td>
<td>570 – 590</td>
<td>17544 – 16949</td>
<td>2.09 – 2.03</td>
</tr>
<tr>
<td>Orange</td>
<td>590 – 620</td>
<td>16949 – 16129</td>
<td>2.03 – 1.93</td>
</tr>
<tr>
<td>Red</td>
<td>620 – 750</td>
<td>16129 – 13333</td>
<td>1.93 – 1.59</td>
</tr>
</tbody>
</table>

Example 1.1:

The longest wavelength band observed in the spectrum of benzophenone had a peak maximum at 342 nm.

(i). What will be the energy required to produce one excited state molecule?

(ii). What will be energy of an Einstein?

Solution:

(i). $E = \frac{hc}{\lambda}$

$= \frac{6.606 \times 10^{-34} (Js) \times 2.998 \times 10^8 (ms^{-1})}{342 \times 10^{-9} (m)}$

$= 19.865 \times 10^{-17} J$

$= 0.058 \times 10^{-17} J$

$= 5.80 \times 10^{-19} J$
(ii). The energy required to excite one mole of compound is called an Einstein, therefore, the value of an Einstein for the example under consideration is:

\[ 6.023 \times 10^{23} \times 5.80 \times 10^{-19} \text{ J mol}^{-1} \]
\[ = 34.9334 \times 10^{4} \text{ J mol}^{-1} \]
\[ = 3.50 \times 10^{5} \text{ J mol}^{-1} \]

**Note:**
The energy of an Einstein of radiation of wavelength \( \lambda \) can be calculated by substituting the numerical value of \( \lambda \), when in units of nm, into the expression

\[ \frac{1.196 \times 10^{8}}{\lambda} \text{ J mol}^{-1} \]

If \( \lambda = 400 \text{ nm} \) then the energy of an Einstein will be

\[ \frac{1.196 \times 10^{-1}}{400} \text{ J mol}^{-1} \]
\[ = 2.99 \times 10^{5} \text{ J mol}^{-1} \]

**The Laws of Absorption:**

When a parallel beam of monochromatic radiation passes through a parallel sided layer of a homogeneous absorbing substance, the Beer – Lambert Law stated in 1852 is obeyed in a simple system. Fig. 1.3 shows the absorption of monochromatic radiation.

![Cuvette Diagram](image)

**Fig. 1.3:** Absorption of monochromatic radiation (\( I_o \) and \( I_t \) are sometimes symbolized by \( p_o \) and \( p_t \), since the intensity has units of energy per unit time or power). The intensity of the emergent beam, (\( I_t \)) in this situation is given by:

\[ I_t = I_o 10^{-de} \]  (1.1)
Where $I_0$ is the intensity of the incident light on the layer of absorbing medium of thickness $l$ (cm) and molar concentration, $c$ (moles L$^{-1}$). The intensity of radiation can be defined as the number of photons that pass across a unit area in unit time. In Eq (1.1) the quantity $\epsilon$ is normally expressed in litres per mole per centimeter (L mol$^{-1}$ cm$^{-1}$) is called the molar absorption coefficient. Alternative units are square centimeters per mole (cm$^2$ mol$^{-1}$). This change of units demonstrates that $\epsilon$ may be regarded as a molar cross-section for absorption and, the greater the cross-sectional area of the molecules for absorption, the greater its ability to block the passage of the incident radiation. It is characteristic of the substance and depends on the wavelength, temperature and solvent but not upon the concentration. $\epsilon$ is directly useful where comparisons are to be made of the absorption of several substances of known molecular weight. The value of $\epsilon$ is greatest where the absorption is most intense.

Eq (1.1) is an expression of the Beer – Lambert law, often called simply Beer’s law.

Equation (1.1) can be written in the following form

$$\log_{10} \frac{I_0}{I_t} = \epsilon l c$$

(1.2)

$\log_{10} \frac{I_0}{I_t}$ is known as the optical density or absorbance (A).

The fraction of radiant energy transmitted decays exponentially with path length, we can write it in exponential form:

$$T = \frac{I_t}{I_o} = 10^{-kl}$$

(1.3)

where $k(k = \frac{\epsilon c}{2.303})$ is the extinction coefficient of the substance, which is generally defined as the reciprocal of the thickness ($l$) required to reduce the light to $\frac{1}{10}$ of its intensity. Consequently, $\ln T$ falls off linearly, and $\frac{I_t}{I_o}$ exponentially, with the distance $l$ the light travels through the absorbing medium. In Eq (1.3).

$$A = - \log T = \log \frac{I_0}{I_t} \epsilon l c$$

(1.4)

Eq. (1.4) indicates that the absorbance is directly proportional to the concentration ($c$) and the path length ($l$). (The SI units for $\epsilon$, $l$ and $c$ in Eq. 1.4 are m$^2$ mol$^{-1}$, mm and mol dm$^{-3}$ respectively). It is this absorbed portion of light which causes photochemical reactions.

The percentage transmittance is given by
\% \text{T} = \frac{I_t}{I_o} \times 100 \tag{1.5}

Eq (1.4) can be rearranged.
\[ A = \log 100 - \log \% \text{T} \tag{1.6} \]
or
\[ A = 2.00 - \log \% \text{T} \tag{1.7} \]

From Eq. (1.4) the following relation can be obtained
\[ T = 10^{-A} \tag{1.8} \]

If the absorbance increases by unity, the transmittance drops by a factor of ten.

**Example 1.2:** Calculate the transmittance, absorbance and absorption coefficient of a solution. This absorbs 80\% of a certain wavelength of light beam passed through a 1cm cell containing 0.35 M solution;

Ans. It is given that
\[ I_{\text{abs}} = 0.80 \ I_o; \ b = 1 \text{cm}; \ c = 0.25 \text{ M} \]
\[ I_t = I_o - I_{\text{abs}} = I_o - 0.80 \ I_o = (1 - 0.80) \ I_o \]
\[ = 0.20 \ I_o \]

Transmittance \[ T = \frac{I_t}{I_o} = 0.20 \]

Absorbance \[ A = -\log \frac{I_t}{I_o} = \log \frac{I_o}{I_t} = \log \frac{1}{0.2} = \frac{1}{2} \]

Applying Beer – Lambert law, we have
\[ \log = \frac{I_t}{I_o} = -\varepsilon lc \]
\[ \log = 0.2 = - \varepsilon \times 1 \times 0.35 \]
\[ = - \varepsilon \times 0.35 \]
\[ \varepsilon = \text{L mol}^{-1} \text{ cm}^{-1} \]

A summary of notation and synonymous used in Beer – Lambert law is given in Table 1.3.
Table 1.3: Beer – Lambert law nomenclature

<table>
<thead>
<tr>
<th>Accepted Symbols</th>
<th>Meaning</th>
<th>Accepted Name</th>
<th>Synonyms</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>$\frac{I_t}{I_o}$ Transmittance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>$\log \frac{I_o}{I_t}$ Absorbance</td>
<td></td>
<td>O.D. Optical density</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$\frac{A}{l c}$ Absorptivity</td>
<td></td>
<td>k Extinction</td>
</tr>
<tr>
<td></td>
<td>$(c = g L^{-1})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>$\frac{A}{l c}$ Molar absorptivity</td>
<td>$\alpha_m$</td>
<td>Molar extinction</td>
</tr>
<tr>
<td></td>
<td>$(c = \text{mol} L^{-1})$</td>
<td></td>
<td>coefficient</td>
</tr>
<tr>
<td>l</td>
<td>path length cell path $\ell$ or d</td>
<td>Millimicron</td>
<td>in cm nanometer</td>
</tr>
<tr>
<td>nm</td>
<td>wavelength</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is possible to make quantitative calculations when a solution containing more than one kind of absorbing substance having no interaction species and have overlapping spectra. Thus, for a multi component system, then if $C$ is in grams per liter, we may write.

$$A = A_1 + A_2 + \ldots + A_n$$

Total

$$= \varepsilon_1 b c_1 + \varepsilon_2 b c_2 + \ldots + \varepsilon_n b c_n \quad (1.9)$$

where the subscripts refer to absorbing components 1, 2, $\ldots$, $n$.

Fluorescence may invalidate measurements of the transmitted – beam
intensity. If there is more than one absorbing species present the law becomes:

$$I_t = I_o \ 10^{\sum \varepsilon l c}$$

(1.10)

Where the summation $\varepsilon$ b c is for all the absorbing species. A specific situation that is of practical importance is found when some form of molecular association occurs, for example:

$$A + A \rightarrow A_2$$

$\Sigma$ values can be affected by intermolecular perturbations which can occur in solutions and may change with concentration for this reason also. T is $\varepsilon$ called directly useful where comparisons are to be made of the absorption of several substances of known molecular weight transmittance and is dimensionless. The absorbance (A) is given by the following Equation:

**Example 1.3:** An aqueous solution of a purine triphosphate, at a concentration of 57.8 mg dm$^{-3}$ of its trisodium dehydrate (molar mass 586 g mol$^{-1}$) gave an absorbance of 1.014 with a light path of 1 cm. Calculate the molar absorption coefficient. What would be the absorbance of a 10 $\mu$m solution, and what would be the percentage of light transmittance?

Solution: From Eq. (1.2)

$$A = 1.014 = \varepsilon \ c \ \ell$$

$$c = \frac{57.8 \times 10^{-3} \ \text{(g dm}^{-3}\text{)}}{586 \ \text{(g mol}^{-1}\text{)}} = 9.86 \times 10^{-5} \ \text{M}$$

Thus,

$$\varepsilon \sum = \frac{A}{c \ \ell} = \frac{1.014}{9.86 \times 10^{-5} \ \text{(mol dm}^{-3}\text{)} \times 1 \ \text{(cm)}}$$

$$= \frac{1.04}{9.86 \times 10^{-5} \ \text{(mol dm}^{-3}\text{)} \times 1 \ \text{(cm)}}$$

$$= 0.1028 \times 10^5 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1}$$

$$= 1.028 \times 10^4 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1}$$

For a 10 $\mu$m solution

$$A = \varepsilon \ c \ \ell = 1.028 \times 10^4 \ \text{(dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1}\text{)} \times 10 \times 10^{-6} \ \text{(mol dm}^{-3}\text{)} \times 1 \ \text{(cm)}$$
The percentage light transmittance \( T \% \) is given by

Eq. (1.7) \( A = 2.00 - \log \% T \)

or \( \log \% T = 2.00 - A \)

\[ = 2 - 0.1028 \]

\[ = 1.8972 \]

\( T \% = 78.9 \% \)

DIFFERENCE BETWEEN THERMAL AND PHOTOCHEMICAL REACTIONS

The total energy of a molecule is the sum of electronic, vibrational, rotational and translational energies. The first three energies are quantized (Fig 1.4);

\[ E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{transitional}} \]

They can change only by discrete jumps \( (\Delta E = h\nu) \). Translational energy is not quantized and changes in a continuous manner. There are two different means by which energy can be supplied to molecules. First, changing the temperature produces a continuous increase in
energy; second, a quantum of energy may be absorbed by the molecule from a beam of quanta (a light beam). These two modes of energy input give rise to thermal chemistry and photochemistry. The difference between thermal and photochemical reactions is noteworthy. The temperature coefficient in thermal reactions is generally very large as compared with those of photochemical reactions. In photochemical reactions, only the intensity of light radiation counts and does not depend upon temperature and hence these reactions have a low temperature coefficient. A thermal reaction is invariably accompanied by a decrease in free energy of the system but a number of photochemical reactions are known to involve an increase in free energy. Photosynthesis is an important example of free energy increase during reaction.

Thermal excitation and photochemical excitation provide two complementary methods of introducing energy into molecules. Thermal excitation introduces energy randomly into translational, rotational, and vibrational modes, producing an energy distribution in the system such that most molecules have about the same amount of energy. Absorption of electromagnetic radiation in the visible or ultraviolet region of the spectrum excites an individual molecule instantaneously to an excited electronic state. This process involves promotion of an electron from a bonding molecular orbital to an antibonding molecular orbital. A large amount of energy is thus placed in a single molecule. It is not surprising that the chemical consequences of the two methods of introducing energy are often profoundly different. In thermal or dark reactions the molecules absorb heat energy from outside and are energized and molecular collisions become effective. These bring about the reaction. In photochemical reactions, the reactant molecules absorb UV-VIS light (2000 to 8000 Å) and get excited. These excited molecules undergo the reaction.

Normally a reaction occurs when a molecule gains the necessary activation energy to undergo change. A simple example can be the combustion of gasoline into CO₂ and H₂O. This is a chemical reaction where one or more molecules / chemical species are converted into others. For this reaction to take place activation energy is provided in the form of heat or a spark. Whereas in case of photochemical reactions light provides the energy. The absorption of a photon of light by a reactant molecule may also permit a reaction to occur not just by bringing the molecule to the necessary activation energy, but also by changing the symmetry of the molecule’s electronic configuration, enabling an otherwise inaccessible reaction path. Photochemical reactions involve electronic reorganization initiated by electromagnetic radiation. These reactions
are several orders of magnitude faster than thermal reactions, reactions as fast as $10^{-9}$ seconds and associated processes as fast as $10^{-15}$ seconds are often observed. Another example, if ethane is heated, molecular motions increase. Molecules collide with one another more frequently and with greater energy. As a consequence of these collisions the vibrational motions of the carbon – carbon and the carbon – hydrogen bonds become more and more energetic. The carbon – carbon bond in ethane is a strong one (83 k cal mol$^{-1}$) and temperatures in excess of 600 °C are required in order to break it.

$$\text{CH}_3 – \text{CH}_3 \xrightarrow{\Delta} 2 \text{CH}_3$$

As the amount of energy required to dissociate a bond, depending on the structure of the molecule and the nature of the atoms involved in the bond. For example, typical bond dissociation energy is 101 k cal mol$^{-1}$ for the C – H bond in methane. The rate laws which photochemical reactions follow are generally more complex than those for thermal reactions. The intensity of light and the size and shape of the vessel may affect the rate of the reaction. A photochemical reaction may be accompanied by a thermal reaction, identical with the photochemical reaction, or opposite to it, or entirely different in character. For example, the thermal dissociation of HI at 450 °C is bimolecular (2 HI $\xrightarrow{}$ H$_2$ + I$_2$), but the photochemical reaction is unimolecular (HI $\xrightarrow{}$ H+I) because sufficient energy to produce free atom is available. The Table 1.4 summarizes the points of distinction between thermal and photochemical reactions.
Table 1.4: Distinction between thermochemical and photochemical reactions.

<table>
<thead>
<tr>
<th>Thermochemical Reactions</th>
<th>Photochemical Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i). These reactions involve absorption or liberation of heat energy.</td>
<td>(i). These reactions involve absorption of UV - VIS light.</td>
</tr>
<tr>
<td>(ii). They can take place in light and even in the dark.</td>
<td>(ii). The presence of light is the primary requisite for the reaction to take place.</td>
</tr>
<tr>
<td>(iii). The free energy change ($\Delta G$) of a thermochemical reaction is always negative.</td>
<td>(iii). The free energy change ($\Delta G$) of a photochemical reaction may be positive or negative.</td>
</tr>
<tr>
<td>(iv). Temperature has significant effect on the rate of a thermochemical reaction.</td>
<td>(iv). The intensity of light has a marked effect on the rate of a photochemical reaction. Temperature has a very little effect on the rate of photochemical reactions.</td>
</tr>
<tr>
<td>(v). Thermochemical activation is not selective in nature.</td>
<td>(v). Photochemical reactions are highly selective.</td>
</tr>
<tr>
<td>(vi). Thermal excitation introduces energy randomly into translational, rotational and vibrational modes, producing an energy distribution in the system such that most molecules have about the same amount of energy.</td>
<td>(vi). Absorption of electromagnetic radiation in the uv – vis region of the spectrum excites an individual molecule instantaneously to an excited electronic state.</td>
</tr>
<tr>
<td>(vii). The reacting molecules need activation energy to cross the energy barrier separating reactants and products.</td>
<td>(vii). The reacting molecules need light of correct frequency for excitation of an electron from bonding molecular orbital to an anti bonding molecular orbital for reaction to occur.</td>
</tr>
</tbody>
</table>
Exercise

A. Provide short answers to the following questions.

1. What is photochemistry?
2. What are the consequences of light absorption?
3. What is visible light spectrum?
4. What are similarities and differences between thermochemical and photochemical reactions?
5. Differentiate between thermal excitation and photochemical excitation.
6. Explain the phenomenon of vision in higher animals.
7. What is photosynthesis?

B. Fill in the blanks with suitable words.
   a. When molecular dissociation occurs in a radiation chemical reaction, the process is called __________________________
   b. The important phenomenon of vision is the outcome of a __________________________
   c. __________________________ is the energy required to excite one mole of compound.
   d. __________________________ acts as the energy converter (the energy accumulated from the sun’s light absorbing blue and red light).
   e. A large scale application of photochemistry is __________________________
   f. __________________________ is a form of energy can be considered in terms of electric and magnetic fields.

C. Define the following terms:

- Quantum Yield
- Lambert Beer Law
- Translational energy
- Absorption
- Absorption Coefficient
- Absorption Spectrum
- +
- Action Spectrum
- Beer Lambert Law
CHAPTER 2

Photochemical Excitation

The absorption of ultraviolet or visible radiation by a molecule results in the molecule changing from the ground state to an excited state. The electronic structure of the excited molecule changes and it reacts differently with other molecules. The absorption of a photon by a molecule can lead to changes in the rotational and vibrational energy as well as electronic excitation. In the case of atoms only electronic excitation is possible. The three types of quantized energy can, to a reasonable approximation, be considered independently since the frequencies of rotational, vibrational and electronic motion are about $10^{10}, 10^{12}$ and $10^{15}$ sec$^{-1}$. Typical energy separations are 0.4 and $4 - 400$ J mol$^{-1}$ for rotational and vibrational levels respectively. Electronic energy levels can go up to $1000$ k J mol$^{-1}$; above this ionization occurs.

The physical effect of the absorption of radiation by a molecule is to cause the promotion of an electron from an orbital of lower energy to one of higher energy. The molecule with an electron in a higher energy orbital is then said to be in an excited state. Photochemistry is concerned with the physical and chemical reactions of excited state molecules. To gain an understanding of photochemical processes it is necessary to consider the types of molecular orbital involved in the initial electronic transition.

Photochemical Energy:

Besides temperature, a second mean of exciting molecules involves absorption of electromagnetic radiation. As mentioned in chapter 1, the amount of energy that such radiation contains depends upon its wavelength according to the relationship:

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

The energy of light in k cal mol$^{-1}$ is given by the expression

$$E (k \text{ cal mol}^{-1}) = \frac{2.86 \times 10^5}{\lambda (\text{Å})}.$$  

An energy of 1 k cal mol$^{-1}$ corresponds to radiation of wavelength 286, 000 Å or

$$\frac{10^6 \text{ Å cm}^{-1}}{286,000 \text{ Å}} = 353 \text{ cm}^{-1}.$$
in the infrared portion of the spectrum. 10 k cal mol\(^{-1}\) corresponds to 3530 cm\(^{-1}\), also in the infrared region of the spectrum. When electromagnetic radiation of these frequencies is absorbed, molecules are excited to higher vibrational states. Radiation of shorter wavelength (higher frequency) contains more energy. Visible light has a wavelength of 4000 Å (violet) to 8000 Å (red). Light of these wavelengths contains 71 – 36 k cal mol\(^{-1}\). Ultraviolet light is even shorter wavelength (2000 – 4000 Å) for the near ultraviolet, 100 – 2000 Å for the far ultraviolet). Light of 2000 Å corresponds to energy of 143 k cal mol\(^{-1}\). Light in the ultraviolet – visible region has energy sufficient to excite molecules to higher electronic states. As the absorption of light by an atom involves the excitation of an electron to a higher – energy orbital, therefore, a hydrogen atom with a single 1 S electron can absorb light and excite the electron to the 2S orbital. The absorption of electromagnetic radiation thus produces a transition from the ground electronic state (1S\(^1\)) to first excited state (2S\(^1\)). When we discuss molecules, we need to consider molecular orbitals rather than atomic orbitals. As the temperature is raised, molecules can acquire additional vibrational and rotational as well as translational energy. Vibrational energy and rotational energy are quantized i.e; they can change only by discrete jumps. This can be illustrated most simply for a diatomic molecule by means of a Morse curve shown in Fig. 2.1. If we imagine two atoms coming join to form a chemical bond, and the energy of the system will decrease. If the internuclear distance decreases below the Equilibrium position, nuclear – nuclear repulsions increases rapidly, and the energy rises. The molecule thus finds itself in a “potential well” corresponding to a chemical bond. Within this potential well the molecule can occupy any of a number of discrete vibrational energy levels.
Fig. 2.1: Potential energy curves for a diatomic molecule.

Fig. 2.1 indicates that the lowest energy level is not at the bottom of the well, and molecules will continue to vibrate even at absolute zero. When energy is supplied to the molecule, higher vibrational states \( (\nu_1, \nu_2, \text{ etc}) \) may become populated. Only the exact amount of energy needed to go from \( \nu_0 \) to \( \nu_1, \nu_2, \nu_3 \) or some higher level may be absorbed. In typical organic molecules \( \nu_1 \) lies from 2 to 10 k cal mol\(^{-1}\) above \( \nu_0 \). Molecules at room temperature have an average thermal energy content of about 0.6 k cal mol\(^{-1}\). At higher temperatures, enough vibrational energy may be absorbed to bring about rupture of a bond. The minimum energy required to do this is known as the bond dissociation energy and is shown in Fig. 2.1. The amount of energy required to dissociate a bond varies widely, depending on the structure of the molecule and the nature of the atoms involved in the bond. Typical bond dissociation energies are 101 k cal mol\(^{-1}\) for the C – H bond in methane and 83 k cal mol\(^{-1}\) for the C – C bond in ethane. In Fig.2.2 the lower curve corresponds to the ground electronic state, and the upper curve to an excited electronic state. Light of the correct frequency (\( \Delta E = h \nu \)) can be absorbed by the molecule. The transition involves excitation of an electron from a bonding molecular orbital to an antibonding molecular orbital. Absorption of light provides the means of introducing a large amount of energy (36 – 143
k cal mol\(^{-1}\)) into a molecule. Clearly, the introduction of so much energy will have profound effects on the molecule. Hence, photochemistry can also be defined that it is the study of the chemistry of electronically excited molecules produced by the absorption of electromagnetic radiation in the range of wavelength of 1800 – 8000 Å.

Further, consider now the Morse curves for the ground state (\(E_0\)) and first excited state (\(E_1\)) shown in Fig. 2.2. At room temperature we, have insufficient energy to populate excited vibrational levels, and most transitions will start from \(v_0\) of the ground state. The Franck – Condon principle tells us that absorption of a quantum of light will occur rapidly, even with respect to molecular vibrations. No changes in nuclear positions occur during the excitation process, i.e; we have vertical excitation as shown in Fig. 2.3. Changes in molecular structure (bond angles and bond lengths) will occur as the electronically excited molecule comes to thermal Equilibrium with its surroundings. Transition from \(v_0\) of the ground state may terminate in any of several vibrational levels of the excited state. This is the reason for band spectra rather than sharp lines in ultraviolet spectra. The energy of the electronic transition is measured from \(v_0\) of the ground state to \(v_0\) of the excited state, \(E_1(v_0) - E_0(v_0) = \Delta E = h\nu\). In an electronically excited state of a molecule the distribution of the electrons surrounding the nuclei change as well.
as the force between the atomic nuclei of a molecule. As a result molecules in electronically excited states often have very different chemical and physical properties than their electronic ground states. For example α-hydroxy naphthalene becomes a strong acid in its excited state. The ground state to of α-hydroxy naphthalene has a pka of 9.2 but this is reduced to 0.4 in the excited singlet state. Molecule such as this are known as photoacids.

Fig. 2.3: Potential energy curves for the two states of a diatomic molecule. Transitions between two states according to the Franck–Condon Principle are illustrated.
Orbital Types

An understanding of electronic excitation in molecular orbital terms is possible only if we consider bonding and anti bonding orbitals. Molecular orbitals are formed by the linear combination of the atomic orbitals of the atoms forming the molecular structure. The atomic and molecular orbitals represent electronic wave functions which relate to the probability of finding an electron in the region surrounding the nuclei and they can be represented diagrammatically by enclosing the space around the nuclei in which there is a relatively high electron probability. Wave functions are mathematical expressions and can have either positive or negative values in the different regions of space around the nuclei (Figs. 2.4 and 2.5). The combination of atomic orbitals leads to the formation of both bonding and antibonding molecular orbitals, the bonding orbitals having a high electron probability between the nuclei and the antibonding orbitals having a plane of zero electron probability between the nuclei. Bonding orbitals are of lower energy than the combining atomic orbitals while the antibonding orbitals are of higher energy.

Figs. 2.4 and 2.5
Sigma (σ) Orbitals

Sigma orbitals may be formed by combination of two one-electron atomic orbitals lying along the axis joining the atoms. The molecular orbitals resulting from the combination of 1S and 2P atomic orbitals are shown in Fig. 2.4. Bonding and antibonding sigma orbitals are designated by the symbols σ and σ* respectively.
**Fig 2.4.** Bonding (σ) and anti-bonding (σ*) molecular orbitals.

The difference in energy between the bonding and antibonding orbitals is normally such that the promotion of an electron from a σ orbital to a σ* orbital requires the absorption of radiation in the wavelength range 100 – 200 nm (vacuum ultraviolet) for example, the lowest energy σ → σ* (sigma to sigma star) transition gives rise to an absorption band at 154 nm.

**Pi (π) orbitals.**
Pi orbitals may be formed by the sidewise overlap of atomic 2P orbitals. The overlap of two such orbitals will give a bonding π orbital and an antibonding π* (Pi star) orbital having an approximate form as shown in Fig. 2.5.
Fig. 2.5 Bonding \( \pi \) and anti-bonding \( \pi^* \) molecular orbitals.

The difference in energy between \( \pi \) and \( \pi^* \) orbitals is less than that between \( \sigma \) and \( \sigma^* \) orbitals with the result that \( \pi \rightarrow \pi^* \) (pi to pi-star) transitions give rise to absorption bands at longer wavelengths than \( \sigma \rightarrow \sigma^* \) transitions. Imagine an ethane molecule with the \( \sigma \) framework already formed but with one electron localized on each carbon in a \( 2p \) atomic orbital. Now let these two electrons interact to form a bond. Just as with a diatomic molecule, two molecular orbitals are formed, a bonding molecular orbital and an antibonding molecular orbital (Fig. 2.6). The Fig. 2.6: Representation of \( \pi \) bonding and \( \pi^* \) antibonding molecular orbitals in ethane. Schematically the situation is shown in Fig. 2.7.
**Fig. 2.7:** Two 2P atomic orbitals of carbon mix, giving rise to a lower energy, bonding molecular orbital ($\pi$) and a higher energy, antibonding molecular orbital $\pi^*$. Each atomic orbital initially contained one electron. In the molecular orbitals both electrons will occupy the lower energy, bonding $\pi$ molecular orbital. Absorption of a quantum of light excites an electron from the bonding orbital to the antibonding orbital. This is known as a $\pi \rightarrow \pi^*$ transition. For ethane this transition occurs at 1800 Å (Fig. 2.8).

![Diagram of molecular orbitals](image)

**Fig. 2.8:** $\pi$ to $\pi^*$ transition for ethene excitation of electrons.

**Fig. 2.9:** Schematic representation of atomic, $\pi$, and $\pi^*$ molecular orbitals.

There will be a number of $\pi$ and $\pi^*$ orbitals for a molecule possessing a delocalized $\pi$ electron system. For example, there are six molecular orbitals in benzene formed by overlap of the six
atomic orbitals; three of these are $\pi$ orbitals and three are $\pi^*$ orbitals. The ultraviolet absorption spectrum of benzene (Fig. 2.10) exhibits three bands and each of these represents a transition of an electron from one of the $\pi$ orbitals to one of the $\pi^*$ orbitals.

Fig. 2.10: Absorption spectrum of benzene.

Non–Bonding Orbitals

The $n \rightarrow \sigma^*$ transition occurs in saturated molecules containing heteroatoms such as oxygen, nitrogen, sulphur and halogens, and involve the excitation of an electron from the non-bonding P orbital of the heteroatom to an antibonding sigma orbital of the molecule. These transitions involve less energy than $\sigma \rightarrow \sigma^*$ transitions and, consequently, result in the absorption at the longer wavelength end of the vacuum UV region and the shorter – wavelength end of the ordinary UV region, i.e; between 1500 and 2500 Å, of the electromagnetic spectrum. Methyl alcohol has an $n \rightarrow \sigma^*$ absorption band at 1830 Å, and trimethylamine at 2270 Å. Many of the $n \rightarrow \sigma^*$ transitions are observable with ordinary UV / VIS spectrophotometer. For instance, in carbonyl compounds there are two electrons in the nonbonding 2P orbitals (n orbital) on the oxygen atom (Fig. 2.11). The absorption of radiation can lead to the promotion of one of these
electrons into either a $\sigma^*$ or a $\pi^*$ orbital. Further, $n \rightarrow \pi^*$ transitions occur in molecules that contain double or triple bonds involving heteroatoms, e.g:

$$C = \hat{O}; \quad -C \equiv N; \ etc.$$

In these transitions an electron in a nonbonding atomic orbital associated with the heteroatom is excited to an antibonding $\pi^*$ orbital associated with the double or triple bond in the molecule. These transitions require less energy than the $\pi \rightarrow \pi^*$ transitions, and therefore, absorb at longer wavelengths, within the range of the ordinary UV/VIS spectrophotometers. For example, saturated aldehydes and ketones show absorption at 2750 – 2950 Å.

**Fig. 2.11:** Representation of the $n$, $\pi$ and $\pi^*$ orbitals with the carbonyl group. The $n$ orbital (2P) points along the x axis while the $\pi$ and $\pi^*$ orbitals lie in the yz plane. Let us consider a carbonyl group constructed from an SP$^2$-hybridized carbon and an SP – hybridized oxygen. We shall assume the sigma – bond framework to be present, and we shall direct our attention to the nonbonding orbitals and the $\pi$ - molecular orbitals. Before formation of the $\pi$ - molecule orbitals we have 2P$_z$ atomic orbitals on carbon and oxygen (Fig. 2.11). These orbitals are mixed to form a bonding ($\pi$) molecular orbital and an antibonding ($\pi^*$) molecular orbital similar to those of ethene. The remaining orbitals of the oxygen atom (2P$_x$ and SP) are doubly occupied and are nonbonding orbitals (n). The 2P$_x$ orbitals is relatively high – energy orbital and very important in photochemistry whereas the SP orbital is a low-energy orbital that is not important in photochemistry. In simple energy level diagrams the n (SP) orbital is ignored. Schematically, it can be represented as shown in Fig.2.12.
Fig. 2.12(a): Schematic representation of atomic, molecular and non-bonding orbitals.

Fig. 2.12(b): Relative energies of atomic, molecular, antibonding molecular and nonbonding orbitals.

\[
\begin{align*}
\pi^* & \quad \downarrow & \quad \pi^* \\
\pi^* & \\
n & \quad \downarrow & \quad \pi \rightarrow \pi^* & \quad \uparrow & \quad n \\
\pi & \quad \downarrow & \quad \uparrow & \quad \pi \\
(\pi, \pi^*) & \quad \downarrow & \quad (n, \pi^*) & \quad \uparrow & \quad S_2 & \quad S_0 & \quad S_1
\end{align*}
\]
The n → \( \pi^* \) transition is the lowest energy transition for most ketones and is thus the \( S_0 \) → \( S_1 \) transition. The \( \pi \rightarrow \pi^* \) transition corresponds to the \( S_0 \rightarrow S_2 \) transition. The lower energy n → \( \pi^* \) transition occurs at longer wavelength than the \( \pi \rightarrow \pi^* \) transition (Fig. 2.14). These transitions are labeled in the ultraviolet spectrum of benzophenone \((C_6H_5)_2C=O\) shown in Fig. 2.15.

The n → \( \pi^* \) transition is symmetry forbidden and thus is less intense than the symmetry allowed \( \pi \rightarrow \pi^* \) transition (Fig. 2.15). Most ketones shown → \( \pi^* \) absorption maxima above 2850 Å. Pyrex glass transmits light above 2900 Å. It is thus quite easy to limit excitation of many ketones to the n → \( \pi^* \) transition. The \( \pi \rightarrow \pi^* \) transitions are allowed transitions and are usually characterized by high molar absorptivity (\( \varepsilon > 10,000 \)). The n → \( \pi^* \) transitions are forbidden transitions and are usually characterized by low molar absorptivity (\( \varepsilon < 100 \)). Intensity, is a measure of the concentration of the excited molecules (Fig. 2.14).
**Fig. 2.15:** Representation of (a) $\pi \rightarrow \pi^*$ and (b) $n \rightarrow \pi^*$ electronic transition for a carbonyl group.

**Transition Energies:**

The absorption of UV / VIS radiations by molecules is associated with the excitation of valence electrons from the ground state to the higher energy states. In fact, the electronic transitions generally occur from the highest occupied molecular orbital (bonding or nonbonding) to the lowest unoccupied molecular orbital (Antibonding). The energy required for an electronic transition is the difference between the energy of the orbital from which the electron originates and the orbital into which it is promoted. The relative energies of the different types of molecular orbitals are shown schematically in Fig. 2.16. The energy changes shown in the figure are not to the scale, but just relative.
Fig. 2.16: Relative energies of molecular orbitals and possible various electronic transitions between orbitals.

\( \sigma \rightarrow \sigma^* \) and \( n \rightarrow \sigma^* \) transitions are of relatively high energy and usually require the absorption of radiation of shorter wavelength than either \( n \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \) transition. The wavelength of the radiation required for \( \sigma \rightarrow \sigma^* \) and \( n \rightarrow \sigma^* \) transition is often shorter than 200 nm and hence inconvenient from a practical point of view. The \( \sigma \rightarrow \sigma^* \) transitions occur in saturated hydrocarbons, such as \( \text{CH}_3 - \text{CH}_3 \), which contain only strong bound sigma electrons. The \( n \rightarrow \sigma^* \) transition occur in saturated molecules containing heteroatoms such as oxygen, nitrogen, sulphur and halogens, and involve the excitation of an electron from the bonding \( p \) orbital of the heteroatom to an antibonding sigma orbital of the molecule. The majority of photochemical reactions studied have resulted from an initial \( n \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \) transitions in the molecular system. \( n \rightarrow \pi^* \) transitions require less energy than the \( \pi \rightarrow \pi^* \) transition, and therefore absorb at longer wavelengths, usually well within the range of the UV / VIS, region (2750 – 2950 Å). The unsaturated organic compounds can absorb light between 7000 Å (red) and 2000 Å (far ultraviolet) regions of the spectrum. At shorter wavelengths, less than 2000 Å, even saturated molecules absorb strongly and photo – ionization may occur if the energy of the photon exceeds the ionization potential. While \( \pi \rightarrow \pi^* \) transitions generally absorb at 1600 – 1900 Å e.g; ethylene absorbs at 1710 Å. However, a conjugated system of unsaturated bonds absorbs at a
much longer wavelength, e.g; butadiene absorbs at 2170 Å. The $n \rightarrow \pi^*$ transitions occur in molecules that contain double or triple bonds involving heteroatoms, e.g; $> \equiv \text{O}$, $- \equiv \text{N}$, etc.

**Electronic States:**

The multiplicity of an electronically excited state is defined by the expression $2S + 1$ where $S$ is the algebraic sum of the spin quantum numbers of the electrons in the system. The spin quantum numbers can be either $+ \frac{1}{2}$, or $- \frac{1}{2}$. As a consequence of the Pauli exclusion principle electrons in the same orbital must have their spins paired, i.e; one will have the spin quantum number $+ \frac{1}{2}$ (represented by $\uparrow$) and the other $- \frac{1}{2}$ (represented by $\downarrow$). In molecules where all the electrons are paired in orbitals the sum, $S$, of the spin quantum numbers must equal zero and hence the multiplicity will be one. The molecule is then said to be in a singlet state; this state being designated by the symbol $S$. The ground states of the majority of organic molecules are singlet states.

If on promotion of an electron into a higher energy orbital the promoted electron retains its spin configuration the sum of the spin quantum numbers will still be equal to zero but the molecule will now be in an excited singlet state. If the spin configuration of the promoted electron is changed on excitation the spin of the promoted electron will not be paired with the spin of the electron in the vacated orbital. The spin quantum numbers of the unpaired electrons will be either $+ \frac{1}{2} + \frac{1}{2}$ ($\uparrow \uparrow$) or $- \frac{1}{2} - \frac{1}{2}$ ($\downarrow \downarrow$). In such a case the algebraic sum of the spin quantum numbers will be one and the multiplicity of the state, $2S + 1$, will be three. Thus a molecule with two unpaired electrons is described as being in triplet state. Triplet states are designated by the symbol $T$.

The singlet and triplet designations derive from the fact that singlet states do not split in a magnetic field, whereas triplet states split into three different energy levels. Free radicals that have one unpaired electron give rise to two energy levels in a magnetic field and are thus known as doublet states. Electronic transitions between states of the same multiplicity i.e; singlet – singlet and triplet – triplet transitions, are spin – allowed and transitions between states of different multiplicity, i.e; singlet – triplet or triplet – singlet transition, are spin – forbidden.
Transitions between excited singlet and triplet states (intersystem crossing) occur in many molecules.

Molecules have minimum electronic energy when in the ground state, and when this is a singlet state it is given the symbol \( S_0 \). Promotion of an electron from the highest occupied molecular orbital (HOMO) in the ground state to the lowest vacant molecular orbital (LUMO) will require the minimum energy uptake consistent with a change in electronic configuration. The resultant state, which can be either singlet or triplet, will be the first excited state and is given the symbol \( S_1 \) or \( T_1 \). Singlet states are invariably of higher energy than the corresponding triplet states because of greater electron repulsion in the singlet state.

Excited states of greater energy than the \( S_1 \) and \( T_1 \) states may be formed by either exciting an electron from the HOMO to an orbital of higher energy than the LUMO or from an orbital of lower energy than the HOMO to the LUMO or one of higher energy. The higher energy singlet and triplet excited states are labeled \( S_2, S_3, \ldots, T_2, T_3, \ldots \), in increasing order of energy.

The carbonyl group reacts photochemically in a large number of systems and consideration of the different types of singlet and triplet electronic states associated with this group illustrates concepts applicable to many other photochemically reactive species. In carbonyl compounds the filled orbitals of highest energy are often those associated with the carbonyl group and many instances the relative energies of the \( \sigma, \pi \) and \( n \) orbitals of the carbonyl group are as shown in Fig. 2.17. This figure shows only the three filled orbitals of highest energy (\( \sigma, \pi \) and \( n \)) but obviously there will be other filled orbitals of lower energy in the molecular system. The latter orbitals are not shown because they are not normally involved in electronic transitions. The electrons in these lower energy orbitals are termed inner electrons.

The transition of lowest energy in the carbonyl compounds, which have an energy diagram as in Fig. 2.14, will be \( n \rightarrow \pi^* \). Thus molecules in the first excited states (\( S_1 \) and \( T_1 \)) will
have n and $\pi^*$ orbitals which contain a single electron. This situation can be indicated by using the full symbols $S_1 (n, \pi^*)$ and $T_1 (n, \pi^*)$ to represent the first excited states. An alternative designation is $^1(n, \pi^*)$ and $^3(n, \pi^*)$. The electronic configuration for molecules in these states and in the ground states $S_0$ can be written as below:

<table>
<thead>
<tr>
<th>State</th>
<th>Electronic Configuration</th>
<th>Electron Spins</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>[Inner electrons] $\sigma^2\pi^2 n^2$</td>
<td>$\uparrow\downarrow$ or $\downarrow\uparrow$</td>
</tr>
<tr>
<td>$S_1 (n, \pi^*)$</td>
<td>[Inner electrons] $\sigma^2\pi^2 n^1 (\pi^*)^1$</td>
<td>$\uparrow \downarrow$ or $\downarrow \uparrow$</td>
</tr>
<tr>
<td>$T_1 (n, \pi^*)$</td>
<td>[Inner electrons] $\sigma^2\pi^2 n^1 (\pi^*)^1$</td>
<td>$\uparrow \uparrow$ or $\downarrow \downarrow$</td>
</tr>
</tbody>
</table>

One possible arrangement for the relative energies of the ground and the first three sets (S and T) of excited states of an aromatic carbonyl compound is given in Fig. 2.17. The type of transition leading to each of the excited states can be deduced from the symbols $(n, \pi^*)$, $(n, \sigma^*)$ and $(\pi, \pi^*)$ alongside the states in the Figure.
Fig. 2.17: Typical energy level diagram for ground and excited states of a carbonyl compound.
Exercise

A. Write short notes on the followings:
   1. Photochemical excitation
   2. Photochemical energy
   3. Transition energies
   4. Electronic states.
   5. Energy level diagrams

B. Write detailed answer to the following questions:
   1. Discuss various types of orbitals, what is their function? Explain with suitable examples.
   2. Discuss potential energy curves for the two states of a diatomic molecule.
There are two basic laws which govern all photochemical transformations.

1. Grotthus – Draper Law

**GROTTHUS DRAPER LAW**

(First Law of Photochemistry)

The Grotthus – Draper Law, which is also called the first law of photochemistry, was stated by “T” van Grotthus in 1818. This law which was revived by J. W. Draper in 1839, was named as the Grotthus Draper Law. It states that: only light which is absorbed by a substance or substances can be effective in producing chemical change. The light which simply passes through the reaction medium does not initiate the reaction. It does not necessarily follow that absorbed light will always cause reaction. The particular radiations which are absorbed by the reactants only produce the chemical change. When the conditions are not favorable for the molecules to react, the absorbed light energy remains unused and may be given out as heat energy or as light of a different wavelength. The light does not need to be absorbed directly by the reacting substances. It is possible, for example, in photosensitization that light can be absorbed by an inert substance, which subsequently transfers the absorbed energy (as thermal energy) to the reactants. The various possible consequences of light absorption are summarized in the table below:
System + Light Energy

Photo Process

(Photochemical or Photo physical)

Increase in the
Electronic
thermal energy
excitation
of the system
(Predominant) (Negligible in case
of visible light)

Excited electron
Electron
ejected
transferred to high
and an ion left
behind
energy level
(photoelectric
effect)

Reverts to its normal state

Instantaneously
After some time
producing

After
The processes dependent upon transfer of ‘energy’ or ‘change’ from a photo excited molecule to a ground state are not covered by Grotthus – Draper Law. This basic law of photochemistry has been confirmed to be valid by photochemical studies since the time of Draper. The law is purely qualitative in nature. It gives no idea of the relation between the light absorbed and the molecules undergoing a chemical change. For application of the Grotthus Draper Law to processes where absorption of light does lead to chemical change it is necessary to know the amount of light absorbed. If we let $I_0$, be the intensity of light that enters a medium and $I_t$, the intensity of the transmitted light, then the intensity of the light absorbed, $I_a$, must be

$$I_a = I_0 - I_t$$

(3.1)

Now, for substances other than solution or gases the intensity of the transmitted light is given by Lambert’s law, namely,

$$I_t = I_0 e^{-k\ell}$$

(3.2)

where $\ell$ is the thickness of the absorbing substance. $k$ is called the absorption coefficient and is characteristic of the absorbing medium. The value of $k$ varies with the wavelength of light used and the temperature. A large value of $k$ indicates that the material is very absorbing.

Again for solutions or gases $I_t$ is given by Beer’s law

$$I_t = I_0 e^{-\alpha c \ell}$$

(3.3)

In Eq (2.3) $c$ is the concentration of the absorbing medium and $\alpha$ is called the molar absorption coefficient. $\alpha$ is a proportionality constant determined by the nature of the absorbing medium and the wavelength of light used. From these relations the light absorbed by media other than solutions or gases follows then as:

$$I_a = I_0 - I_0 e^{-k\ell}$$

[From Eqs. (3.1) and (3.2)]

or

$$I_a = I_0 (1 - e^{-k\ell})$$

(3.4)

while that absorbed by solutions or gases is
\[ I_a = I_o - I_o e^{-\alpha l} \] [From Eqs. (3.1) and (3.3)]

or

\[ = I_o \left( 1 - e^{-\alpha l} \right) \] (3.5)

**STARK – EINSTEIN LAW OF PHOTOCHEMICAL EQUIVALENCE**

**(SECOND LAW OF PHOTOCHEMISTRY)**

The Stark-Einstein law of photochemical Equivalence is in a sense simply a quantum-mechanical statement of the Grotthus – Draper Law. It states that each molecule which takes part in the photochemical reaction absorbs one quantum of the light which induces the primary photochemical process. i.e; one molecule absorbs the entire quantum; the energy of the light beam is not spread continuously over a number of molecules. In other words, a photochemical reaction is a one – quantum process. It can form a product, it can catalyze a chain reaction, or it can get de-excited.

The above law which was framed and substantiated as a result of the research done by J. Stark in 1908 and A. Einstein (both Germans) in 1912 applied the concept of the quantum of energy to photochemical reaction of molecules is now known as the Einstein-Stark Law of photochemical Equivalence and is often referred to as the ‘second law of photochemistry’. This law made the photochemistry a quantitative science and became the guiding principle in the theoretical interpretation of photochemical reactions.

The Einstein-Stark law of photochemical Equivalence can be written in equation form as:

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

\[ A^* \rightarrow B \]

\[ A + h\nu \rightarrow B \] over all reaction

Where ‘A’ absorbs a photon of radiation and gets activated. The activated molecule ‘A*’ then decomposes to yield B. This law has been of great value in photochemical studies, since it
enables the rates of formation of radicals to be calculated from the results of optical measurements.

For example, a photon of light dissociates acetone into two radicals, as given below:

\[
\text{CH}_3\text{COCH}_3 \xrightarrow{h\nu} \text{CO} + 2\text{CH}_3
\]

The rate of formation of methyl radicals is in this case twice the rate of absorption of photon.

Example 3.1: When a substance A was exposed to light, 0.004 mole of it reacted in 40 minutes and 8 seconds. In the same time A absorbed \(4.0 \times 10^6\) photons of light per second. Calculate the quantum yield of the reaction.

**Solution:**

Number of molecules of A reacting = moles \(\times\) Avogadro Number \((N_A)\)

\[= 0.004 \times N_A = 0.004 \times 6.02 \times 10^{23}\]

Number of photons absorbed per second = \(4.0 \times 10^6\)

Number of photons absorbed in 40 minutes and 8 seconds

\[= 4.0 \times 10^6 \times 2408\]

Quantum yield \(\Phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}\)

\[= \frac{0.004 \times 6.02 \times 10^{23}}{4.0 \times 10^6 \times 2408}\]

\[= \frac{0.02408 \times 10^{23-6}}{9632}\]

\[= 2.5 \times 10^{23-12}\]

\[= 2.5 \times 10^{11}\]

Example 3.2: When propionaldehyde is irradiated with light of \(\lambda = 3000\) Å, it is decomposed to form CO.

\[
\text{CH}_3\text{CH}_2\text{CHO} + h\nu \rightarrow \text{C}_2\text{H}_6 + \text{CO}
\]

The quantum yield for the reaction is 0.55. The light energy absorbed 20000 erg mol\(^{-1}\) in a given time. Find the amount of CO formed in moles in the same time.

**Solution:**

As from the following equation one Einstein is
\[ (E_e) = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1} \]

When \( \lambda = 3000 \text{ Å} \), one Einstein = \( \frac{1.196 \times 10^{16}}{3000} \text{ erg mol}^{-1} \)

or 20000 erg mol\(^{-1}\) of energy = \( \frac{20000 \times 3000}{1.196 \times 10^{16}} \)

\[ = \frac{6 \times 10^{10^{-16}}}{1196} = 5.016 \times 10^{-3} \times 10^{-6} \]

\[ = 5.016 \times 10^{-9} \]

But \( \Phi = \frac{\text{No. of moles of CO formed}}{\text{No. of Einstein absorbed}} \)

Hence the number of moles of CO formed = \( 0.55 \times 5.016 \times 10^{-9} \)

\[ = 2.759 \times 10^{-9} \]

**Violation of Photochemical Equivalence Law:**

In photochemical experiments, it is often found that the number of molecules that are chemically transformed differs markedly from the number of photons absorbed. In such cases it is sometimes said that law of photochemical equivalence is not obeyed, although the violation is only an apparent one. There are two main reasons for the apparent failure of the law. In the first place, radicals that are produced initially may recombine before they can undergo reaction, this very commonly occurs in solution. The rate of reaction is then less than predicted by the law of photochemical equivalence. In other systems the radicals produced may initiated chain reactions, in which case the rate of reaction may be much larger than expected. Deviations from the law of photochemical equivalence obviously provide valuable information about reaction mechanism.

The energy acquired by a single atom or molecule in absorbing the one quantum depends on the frequency of the irradiating light and is given by Planck relation

\[ E = h \nu = h \frac{c}{\lambda} \quad (3.6) \]

Where \( h \) is Planck’s constant (6.626 x \( 10^{-27} \) erg – sec or 6.626 x \( 10^{-34} \) J – sec) \( c \) is the velocity of the radiation in vacuum (3 x \( 10^{10} \) cm sec\(^{-1}\)); \( \nu \) and \( \lambda \) are the frequency and wavelength of the
radiant energy respectively. It \( \nu \) is expressed in cycles sec\(^{-1} \) and \( \lambda \) in cm, the energy is given in ergs. Since the energy required in reactions is measured per mole, it is customary to employ a mole (= Avogadro’s number) of quanta. The energy of an Avogadro’s number (\( N_A = 6.026 \times 10^{23} \)) of photons is called an Einstein. Thus an Einstein of energy \( E_e \) is given by

\[
E_e = N\hbar \nu = N\hbar \frac{c}{\lambda}
\]

Substituting numerical values of \( N, h \) and \( c \) in Eq.2.7,

\[
E_e = \frac{6.02 \times 10^{23} \times 6.626 \times 10^{-27} \times 3 \times 10^{10}}{\lambda}
\]

\[
= \frac{1.196 \times 10^8}{\lambda}
\]

Energy per mole

(3.8)

Eq (3.8) indicates that energy is inversely proportional to wavelength. Here we have value of \( \lambda \) in cm but if \( \lambda \) be expressed in Å (1Å = 10\(^{-8} \) cm), then Eq. (2.8) becomes,

\[
E_e = \frac{1.196 \times 10^8}{\lambda (\text{Å}) \times 10^{-8}}
\]

or

\[
E_e = \frac{1.196 \times 10^{16}}{\lambda} \text{ ergs mole}^{-1}
\]

It is more convenient to state the energy in calories, since 1 cal = 4.184 \times 10^7 ergs

\[
E_e = \frac{1.196 \times 10^{16}}{\lambda} \times 4.184 \times 10^7 \text{ cal mole}^{-1}
\]

\[
E_e = \frac{2.859 \times 10^8}{\lambda} \text{ cal mole}^{-1}
\]

(3.9)

\[
= \frac{2.859 \times 10^5}{\lambda} \text{ k cal mole}^{-1}
\]

(3.10)
It is clear from this Equation (3.10) that the numerical value of Einstein varies inversely as the wavelength of radiation. Thus it is found that one einstein for UV radiation of $\lambda = 2000 \text{ Å}$ may be calculated as

$$E = \frac{2.859 \times 10^5}{2000} = 1.429 \times 10^2 \text{ k cal mole}^{-1}$$

Similarly the value of $E_c$ for orange light with $\lambda = 0.6 \mu \text{ m}$

$$E_c = \frac{6.02 \times 10^{23} \times 6.626 \times 10^{-27} \times 3 \times 10^{10}}{0.6 \times 10^{-4} \times 10^7 \times 10^3} = 199 KJ$$

This energy is enough to break certain weak covalent bonds, but for C — C bonds and others with energies higher than 300 k J, radiation in the ultraviolet region is required. The photochemical equivalence law applies only to the absorption of primary photochemical process. When as a result of the primary absorption only one molecule decomposes, and the products enter no further reaction, the number of molecules reacting will be equal to the number of energy quanta absorbed and the ratio would be (1:1). If a chain reaction takes place then the quantum efficiency can be high. The efficiency of a photochemical reaction is measured in terms of the photon yield, or quantum yield, or quantum efficiency and given the symbol $\Phi$ (phi). It is the ratio of the number of molecules undergoing reaction in a given time to the number of photons absorbed:

$$\Phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta of light absorbed in the same time}}$$

$$\Phi = \frac{\text{No. of moles reacting in a given time}}{\text{No. of Einsteins of light absorbed in the same time}}$$

Each molecule can absorb a quantum of energy and produce an excited molecule. If each of these excited molecules yields a molecule of product, the quantum yield is unity. In practices, the excited molecule can undergo, besides a chemical change, other processes that do not involve the breakage of a bond. This means that the quantum yield can often be less than unity. In other reactions if the primary process of light absorption produces free radicals, a chain reaction can be initiated in which a large number of product molecules are formed for each light quantum absorbed. In this case the apparent quantum yield will be very much greater than unity. It is
essential to note that the Stark-Einstein law applies only to the primary process in which one
quantum of light absorbed produces one excited molecule.

Consider the photochemical reaction between hydrogen and chlorine. The mechanism for this
reaction is as follows:

1. $\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$  \hspace{0.5cm} \text{photo – initiation}
2. $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$  \hspace{0.5cm} \text{Chain}
3. $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$  \hspace{0.5cm} \text{Propagation}
4. $\text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2$  \hspace{0.5cm} \text{(wall) Termination}

The quantum yield for the primary process, viz; photo – initiation, cannot be greater than
two since at maximum only 2 Cl atoms can be produced per quantum absorbed. On the other
hand, the quantum yield for the consumption of Cl$_2$ and H$_2$ is extremely large ($\Phi > 10^6$) because of
the chain reaction occurring in the second and third steps. Thus in this reaction, as in many other
reactions, there are a number of processes occurring each of which has a different quantum yield.
This law may be restated. In the primary photochemical process, each molecule is activated by
the absorption of one photon.

**Example 3.3:**

When acetone was photolysed at 56°C with 313 nm radiations for 23000 s, 5.23 x $10^{19}$ molecules were decomposed. If $8.52 \times 10^3$ J of radiation were absorbed per second, calculate
the quantum yield.

The energy of one quantum $= \frac{hc}{\lambda}$
$$= \frac{6.626 \times 10^{-34} \text{J.sec.} \times 2.99 \times 10^8 \text{ms}^{-1}}{313 \times 10^{-9} \text{m}}$$
$$= 6.345 \times 10^{-19} \text{J}$$

Therefore, No. of quanta absorbed per second
$$= \frac{8.52 \times 10^{-3}}{6.345 \times 10^{-19}}$$

and during the reaction
$$= \frac{8.52 \times 10^{-3} \times 2.3 \times 10^4}{6.345 \times 10^{-19}}$$
\[ \Phi = \frac{\text{No. of molecules decomposed}}{\text{No. of quanta absorbed}} \]

\[ = \frac{5.23 \times 10^{19} \times 6.345 \times 10^{-19}}{8.52 \times 10^{-3} \times 2.3 \times 10^{1}} \]

\[ = 0.17 \]

**Electron Volt (eV):**

An energy unit which is used a great deal in photochemistry and nuclear chemistry is the electron volt (eV), which is the energy acquired by an electron in falling through a potential difference of 1 volt. Since the charge of the electron is $1.602 \times 10^{-19}$ coulomb this energy is $1.602 \times 10^{-19}$ volt coulomb or joule. The energy of Avogadro’s number of electrons each accelerated by a potential of a volt is 1 electron volt

\[ = \left(1.602 \times 10^{-19} \text{ joule electron}^{-1}\right) \left(6.023 \times 10^{23} \text{ electron mole}^{-1}\right) \]

\[ = 23,060 \text{ cal mole}^{-1} \]

\[ = 23.060 \text{ k cal mol}^{-1} \]

This is a useful conversion factor.

**Example 3.4** (a). Calculate the frequency of UV light having a wavelength of 3000 Å.

\[ \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{10} \text{ cm s}^{-1}}{3000 \times 10^{-8} \text{ cm}} = 1 \times 10^{15} \text{ s}^{-1} \]

(b). Calculate the wavelength in centimeters and the wave number \( \nu \) of light which has a wavelength of 3000 Å.\[ 3000 \text{ Å} = 3000 \times 10^{-8} \text{ cm} = 3.00 \times 10^{-5} \text{ cm} \]

\[ \nu = \frac{1}{\lambda} = \frac{1}{3.00 \times 10^{-5} \text{ cm}} = 33,333 \text{ cm}^{-1} \]

(c). Calculate the energy in ergs per quantum and calories per “mole” or per einstein in radiation of this frequency:

\[ h \nu = (6.62 \times 10^{-27} \text{ erg sec}) \left(10^{15} \text{ sec}^{-1}\right) = 6.60 \times 10^{-12} \text{ erg} \]

\[ N h \nu = (6.02 \times 10^{23} \text{ molecules mole}^{-1}) \left(6.62 \times 10^{-12} \text{ erg molecule}^{-1}\right) \]

\[ = 3.98 \times 10^{12} \text{ ergs mole}^{-1} \]
\[ Nhv = \frac{3.98 \times 10^7 \text{ergs mole}^{-1}}{\left(4.18 \text{joules cal}^{-1} \times 10^7 \text{ergs joule}^{-1}\right)} = 95,300 \text{cal mole}^{-1} \]

\[ = 95.300 \text{k cal mole}^{-1} \]

(d). Calculate the energy in electron volts per molecule which corresponds to a wavelength of 3000 Å. Since 23,060 cal mole\(^{-1}\) corresponds to 1 electron volt, 95,300 cal mole\(^{-1}\) corresponds to

\[ \frac{95,300 \text{cal mole}^{-1}}{23,060 \text{cal mole}^{-1} \text{ev}^{-1}} = 4.13 \text{eV} \]

**Primary and secondary Reactions:**

If a molecule is dissociated as a consequence of absorbing a quantum of radiation, extensive secondary reactions may occur, since the fragments are often highly reactive atoms or radicals. Sometimes, also, the products of the primary fission processes are in excited states, as so-called hot atoms or hot radicals. Therefore, the overall photochemical reaction may consist of:

(a) primary reaction

(b) secondary reaction

For example, the decomposition of \( \text{HI} \) occurs as follows:

\[
\begin{align*}
\text{HI} + h\nu & \rightarrow \text{H} + \text{I} \quad \text{primary reaction} \\
\text{HI} + \text{H} & \rightarrow \text{H}_2 + \text{I} \quad \text{secondary reaction} \\
\text{I} + \text{I} & \rightarrow \text{I}_2 \quad \text{secondary reaction}
\end{align*}
\]

\[
\begin{align*}
2 \ \text{HI} + h\nu & \rightarrow \text{H}_2 + \text{I}_2 \quad \text{overall reaction}
\end{align*}
\]

Evidently, the primary reaction only obeys the law of photochemical Equivalence strictly. The secondary reactions have no concern with the law.

**QUANTUM EFFICIENCY (YIELD) AND ITS DETERMINATION:**

Quantum efficiency occupies a prominent place in studies of photochemical mechanisms. Quantum efficiency (or quantum Yield) is a measure of the efficiency of the use of light in a photochemical reaction. As mentioned above that not always a photochemical reaction obeys the law of photochemical Equivalence. The number of molecules formed or decomposed is often found to be markedly different from the number of quanta or photons of radiation absorbed.
in a given time. The quantum efficiency for the formation of a product ($\Phi_{\text{form}}$) is defined as the number of molecules of product formed per quantum of light absorbed.

$$\Phi_{\text{form}} = \frac{\text{number of molecules of product formed}}{\text{number of quanta absorbed}}$$

for disappearance of starting material ($\Phi_{\text{dis}}$) is defined as the number of molecules of starting material that disappear per quantum of light absorbed. If a photochemical reaction gives only one product, the quantum efficiency of formation and the quantum efficiencies of disappearance will be equal. If several products are formed, the sum of the quantum efficiencies formation will be equal to the quantum efficiency of disappearance. Quantum efficiencies for reactions that do not go through chain mechanisms have values of zero to one. Free radical chain processes have quantum efficiencies as high as several thousand. These high efficiencies arise from the fact that the photochemical reaction is the initiation step in a free radical chain process. The free radical chlorination of methane, or other alkanes has a high quantum efficiency, because the chain length is long. The chain propagation steps occur many times before the chain terminates. For example, the light chlorination of methane is given below:

$$\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl}^* \\
\text{Cl}^* + \text{C}_4 & \rightarrow \text{C}_3\text{H}^* + \text{HCl} \\
\text{C}_3\text{H}^* + \text{Cl}_2 & \rightarrow \text{C}_3\text{HCl} + \text{Cl}^* \\
2 \text{C}_3\text{H}^* & \rightarrow \text{C}_3\text{H}_2 - \text{C}_3\text{H}_3 \\
2 \text{Cl}^* & \rightarrow \text{Cl}_2
\end{align*}$$

It has a quantum yield often near $10^6$, because of the secondary chain reactions that follow the primary cleavage of the Cl – Cl bond.

In the photolysis of HI, for example, the processes are

$$\begin{align*}
\text{HI} + \text{hv} & \rightarrow \text{H} + \text{I}, \\
\text{H} + \text{HI} & \rightarrow \text{H}_2 + \text{I}, \\
2 \text{I} & \rightarrow \text{I}_2
\end{align*}$$

and so the quantum efficiency is two because the absorption of one photon leads to the destruction of two HI molecules. In a chain reaction the quantum efficiency may be very large, and values of
about $10^4$ are common. In these cases the chain reaction acts as a chemical amplifier of the initial absorption step.

It is important when quoting a value for a quantum yield to specify the process to which the value refers. The reason for this can be seen by considering the photochemical reaction between hydrogen and chlorine. The mechanism of this reaction is as follows:

1. $\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}'$  
   Photo - initiation

2. $\text{Cl}' + \text{H}_2 \rightarrow \text{HCl} + \text{H}$  
   Chain

3. $\text{H} + \text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$  
   Propagation

4. $\text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2 \text{(Wall)}$  
   Termination

The quantum yield for the primary process, viz; photo – initiation, cannot be greater than two since at maximum only 2 Cl atoms can be produced per quantum absorbed. On the other hand, the quantum yield for the consumption of $\text{Cl}_2$ and $\text{H}_2$ is extremely large ($\Phi > 10^6$) because of the chain reaction occurring in the second and third steps. Thus in this reaction, as in many other reactions, there are a number of process occurring each of which has a different quantum yield.

The absorption of light can lead to one or more of several processes: fluorescence, phosphorescence, energy transfer to another molecule, or chemical reaction. It is convenient to express the yield of each of these processes as a quantum yield $\Phi$. For a chemical reaction, it is equal to the reaction rate $\nu$ divided by the intensity of light absorbed $I_a$:

$$\Phi = \frac{\nu}{I_a} \quad (3.11)$$

$I_a$ represents the intensity of light absorbed by a system, expressed as the amount per unit volume per unit time, the amount is expressed in moles of photons. A mole of photons is frequently referred to as an einstein. The intensity $I_a$ is calculated from the radiant energy of a specific wavelength absorbed per unit volume per time dividing by $Nh\nu$. Where $N$ is Avogadro’s number ($6.023 \times 10^{23}$), $h$ is Planck’s constant ($6.626 \times 10^{-27}$ ergs sec or $6.626 \times 10^{-34}$ J S) and $\nu$ is the frequency of light.

For fluorescence or Phosphorescence it is the rate of emission of radiation divided by the intensity of light absorbed. The quantum yield of chemical reaction is sometimes expressed in terms of a particular reactant or product, but Equation (3.11) has the advantage that the quantum yield applies to a specific reaction. The $\Phi$ of a process can also be defined as
\[
\Phi = \frac{\text{number of molecules reacting in a given time}}{\text{number of quanta of light absorbed in the same time}}
\]

\[
\Phi = \frac{\text{number of moles reacting in a given time}}{\text{number of einstein of light absorbed in the same time}} \tag{3.12}
\]

and gives the number of molecules observed to undergo chemical transformation per quantum of absorbed energy. An einstein of energy \( E_e \) is given by

\[
E_e = N h \nu = N h \frac{c}{\lambda}
\]

\[
= \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-27} \times 3 \times 10^{10}}{\lambda}
\]

\[
= \frac{1.196 \times 10^8}{\lambda} \text{ erg mole}^{-1} \tag{3.13}
\]

If magnitude for wavelength \( \lambda \) in \( \overset{o}{\text{Å}} \) is given by

\[
E_e = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mole}^{-1}
\]

or

\[
= 2.859 \times 10^8 / \lambda \text{ cal mole}^{-1} \tag{3.14}
\]

**EXPERIMENTAL DETERMINATION OF QUANTUM YIELD (EFFICIENCY)**

The quantum yield (efficiency) \( \Phi \) of photochemical reaction is the number of molecules of reactant consumed or product formed per quantum of light absorbed. For practical purposes the \( \Phi \) may be expressed in the following forms:

\[
\Phi = \frac{\text{number of molecules reacting in a given time}}{\text{number of quanta of light absorbed in the same time}}
\]

\[
\Phi = \frac{\text{number of moles reacting in a given time}}{\text{number of einstein of light absorbed in the same time}}
\]

\[
= \frac{\text{Rate of chemical reaction}}{\text{number of quanta absorbed per second}}
\]

The number of quanta absorbed per second is the absorbed intensity \( (I_a) \), so that
\[ \Phi = \frac{\text{Rate of chemical reaction}}{I_a} \quad (3.15) \]

To determine the \( \Phi \) of the reaction it is necessary to measure the rate of reaction and the amount of radiation absorbed \( (I_a) \). The rate of reaction is measured in any convenient way. Fig 3.1 shows a typical arrangement for measuring the absorbed intensity.

Photochemical reactions require a light source that emits wavelengths corresponding to an electronic transition in the reactant. The emitted light must of course reach the target functional group without being blocked by the reactor, medium, or other functional groups present. For many applications, quartz is used for the reactors as well as to contain the lamp. Pyrex absorbs at wavelengths shorter than 275 nm. The solvent is an important experimental parameter. Solvents are potential reactants and for this reason, chlorinated solvents are avoided because the C – Cl bond can lead to chlorination of the substrate. Strongly, absorbing solvents prevent photons from reaching the substrate. Hydrocarbon solvents absorb only at short wavelengths and are thus preferred for photochemical experiments requiring high energy photons. Solvents containing unsaturation absorb at longer wavelengths and can usefully filter out short wavelengths. For example, cyclohexane and acetone “cut off” at wavelengths shorter than 215 and 330 nm respectively.

To measure the rate of a photochemical reaction it is necessary to irradiate a reaction mixture with light of a selected wavelength and to observe the manner in which the concentration of reactants or products varies with time. In the diagram (Fig. 3.1). A is a light source (tungsten filament or mercury vapour lamp) emitting radiation of suitable intensity in the desired spectral range. To select radiation of only a single wavelength or to confine the radiation to an arrow band, the light is rendered parallel by passing through the lens B into a monochromator or filter at C which yields light of one wavelength only. From C and after passing through the slit the light enters the cell D immersed in a thermostat and containing the reaction mixture. The reacting system is placed in quartz cell provided with clear polished windows. Finally, the light transmitted through D falls on some suitable recorder E (thermopile), where its intensity is determined. The reacting system is confined to a cell. The intensity of the transmitted beam is measured with the reaction cell empty and with the cell filled with the reaction mixture. It is still better to use two identical cells, one to contain the chemically reacting material and one to act as a blank for obtaining the light intensity. The thermopile which acts as a detector is a set of junctions
of dissimilar metals covered with a blackened metal foil. All the radiation is absorbed on the blackened metal and the energy of the radiation is converted to a temperature increase, the temperature increase is converted to potential difference by the thermopile. The device must be calibrated against a standard light source. It has the advantage of being usable for light of any frequency. Photoelectric cells are convenient detectors but, since the response varies with frequency, they must be calibrated for each frequency. The amount of radiation may also be measured with a chemical actinometer, in which the amount of chemical change is determined. The quantum yields of a few photochemical reactions are summarized in Table 3.1.

Fig. 3.1: Schematic diagram for study of photochemical reactions

As mentioned above the intensity of the transmitted beam is measured with the reaction cell empty and with cell filled with the reaction mixture. The difference between these readings is the total energy absorbed by the reaction mixture in the given time. If this time is 1 second, the total energy absorbed divided by the volume of the reaction mixture is \( I_a \), the intensity of the radiation absorbed.

**Table 3.1:** \( \Phi \) in Photochemical Reactions at Room Temperatures.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Approx. Wavelength (nm)</th>
<th>( \Phi )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 2 HI ( \rightarrow ) H(_2)+I(_2)</td>
<td>300 – 280</td>
<td>2</td>
<td>Same value of ( \Phi ) at low and high pressures.</td>
</tr>
<tr>
<td>2. C(<em>{14})H(</em>{10}) ( \leftarrow ) ( \frac{1}{2} ) (C(<em>{14})H(</em>{10}))</td>
<td>&lt; 360</td>
<td>0 – 1</td>
<td>Reverse chemical reaction can occur.</td>
</tr>
<tr>
<td>3. CH(_3)CHO ( \rightarrow ) CO+CH(_4) ((+C_2H_6+H_2))</td>
<td>310</td>
<td>0.5</td>
<td>Products given in Parentheses are present also but in small amounts.</td>
</tr>
<tr>
<td>4. NH(_3) ( \frac{1}{2} ) ( \rightarrow ) N(_2) + ( \frac{3}{2} ) H(_2)</td>
<td>210</td>
<td>0.2</td>
<td>Depends on pressure.</td>
</tr>
<tr>
<td>5. Cl(_2)+H(_2) ( \rightarrow ) 2 HCl</td>
<td>400</td>
<td>( 10^5 )</td>
<td>Chain reaction varies with pH(_2)&amp; impurities.</td>
</tr>
</tbody>
</table>


The rate of the chemical reaction taking place in the system is ascertained in the usual manner. For this purpose the change in some physical property can be followed, or samples can be removed periodically from the cell and analyzed. It is thus possible to collect data on the rate of the chemical reaction and the light intensity, from which the rate law and the quantum yield may be deduced.

Consider, for example, an experiment on the photolysis of gaseous HI with light of 253.7 nm wavelength. $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$

It was found that absorption of 307 J of energy decomposed $1.30 \times 10^{-3}$ mol of HI. The energy of the 253.7 nm quantum is $h \nu = hc / \lambda = (6.62 \times 10^{-34}) (3.0 \times 10^{10}) / (2.537 \times 10^{-5}) = 7.84 \times 10^{-19}$ J. The HI has therefore, absorbed $307 / 7.84 \times 10^{-19} = 3.92 \times 10^{20}$ quanta. One Einstein is defined as $N_A = 6.02 \times 10^{23}$ quanta, so that $3.92 \times 10^{20} / 6.02 \times 10^{23} = 6.51 \times 10^{-4}$ Einsteins were absorbed. The quantum yield $\Phi$ is the number of moles reacted per Einstein absorbed. Hence, $\Phi = 1.30 \times 10^{-3} / 0.651 \times 10^{-3} = 1.99$ for the photolysis of the HI.
Exercise

A. Fill in the blanks with suitable words:

1. Photoelectric cells are convenient detectors but, since the response varies with ________________
2. The quantum yield $\Phi$ is the number of moles reacted per ________________ absorbed.
3. The amount of radiation may also be measured with a ____________________.
4. Photochemical reactions require ________________ source that emits wavelengths corresponding to an electronic transition in the reactant.
5. In the primary photochemical process, each molecule is ________________ by the absorption of one photon.

B. Define the following terms:

a. Quantum yield
b. Einstein
c. Photolysis
d. Quantum
e. Photoelectric cells
f. Primary Reactions
g. Secondary Reactions
h. Electron Volt

C. Discuss and explain the following laws of photochemistry:

1. Grotthus – Draper Law

CHAPTER 4
PHOTOCHEMICAL KINETICS:

The kinetics of photochemical reaction is more complicated than the kinetics of thermal reactions because more variables are involved. The intensity of light and the size and shape of the vessel may affect the rate of the reaction. A photochemical reaction may be accompanied by a thermal reaction, identical with the photochemical reaction, or opposite to it, or entirely different in character. A photochemical reaction may produce a catalyst which then causes thermal reaction to proceed at a measurable rate. Sometimes an induction period is necessary while a sufficient quantity of catalyst is being accumulated to make the reaction proceed with a measurable velocity. Again, a thermal reaction once started may continue after the illumination is stopped, giving an aftereffect. The energy available in a photochemical reaction is much greater than in the thermal reaction, and this fact often changes the nature of the reaction.

Not only second – order and first – order reactions but also zero order reactions are found in photochemistry. A zero – order reaction is one in which the rate is entirely independent of the concentration. For example, if the concentration is high and the light intensity is weak, the light intensity may be the limiting factor in the reaction rate and the concentration may be without influence on the rate.

Consider first a hypothetical reaction \( A_2 \rightarrow 2A \) which proceeds by photochemical activation. Assume further that the reaction follows the mechanism:

(a). \( A_2 + h\nu \rightarrow A_2^* \) (Activation) \( k_1 \)

(b). \( A_2^* \rightarrow 2A \) (Dissociation) \( k_2 \)

(c). \( A_2^* + A_2 \rightarrow 2A_2 \) (Deactivation) \( k_3 \)
The first stage in this sequence is the absorption of a quantum of light by \( A_2 \) with the formation of an activated molecule. This activation molecule may undergo new dissociation according to reaction (b), or it may be deactivated by collision with an inactive molecule of \( A_2 \) according to reaction (c). The rate constants with which these reactions occur are indicated to the right of each step.

The final product \( A \) is formed only in reaction (b). Consequently, the rate of formation of \( A \) must be given by

\[
\frac{dC_A}{dt} = k_2 C_{A_2^*} \tag{4.1}
\]

To eliminate from this rate expression the unavailable concentration of active molecules, we resort to the concept of the stationary state. If we apply this concept to the intermediate \( A_2^* \), we observe that \( A_2^* \) is formed by reaction (a) and that it disappears by reactions (b) and (c). For reaction (a) the rate is determined only by the rate at which the light is absorbed, i.e., the rate is directly proportional to the intensity of the absorbed light \( I_a \). We obtain thus

\[
\frac{dC_{A_2^*}}{dt} = k_1 I_a \tag{4.2}
\]

The rate of disappearance of \( A_2^* \) is given in turn by the sum of the rates of reactions (b) and (c) namely,

\[
- \frac{dC_{A_2^*}}{dt} = k_2 C_{A_2^*} + k_3 C_{A_2^*} A_2 \tag{4.3}
\]

Equating (4.2) and (4.3) to obtain the condition for the stationary state, we find that

\[
k_1 I_a = k_2 C_{A_2^*} + k_3 C_{A_2^*} A_2
\]

or

\[
k_1 I_a = C_{A_2^*} \left( k_2 + k_3 C_{A_2} \right)
\]

\[
C_{A_2^*} = \frac{k_1 I_a}{k_2 + k_3 C_{A_2}} \tag{4.4}
\]

Substituting the value of \( C_{A_2^*} \) from Eq (4.4) into Eq (4.1), the rate of formation of \( A \) is seen to be

\[
\frac{dC_A}{dt} = k_2 C_{A_2^*} = \frac{k_2 k_1 I_a}{k_2 + k_3 C_{A_2}} \tag{4.5}
\]
Finally, since for every two molecules of $A$ formed one molecule of $A_2$ reacts, the photochemical efficiency of the process $\Phi$ will be

$$\Phi = \frac{1}{2I_a} \frac{dC_A}{dt} = \frac{1}{2} \left[ \frac{k_2k_1}{k_2 + k_3C_{A_2}} \right]$$ (4.6)

For example the kinetics of the photochemical reaction of chlorine with chloroform in the gas phase,

$$\text{Cl}_2 + \text{CHCl}_3 \xrightarrow{\text{hv}} \text{CCl}_4 + \text{HCl}$$ (4.7)

For this reaction the rate of formation of $\text{CCl}_4$ is given by the expression

$$\frac{dC_{\text{CCl}_4}}{dt} = kC_{\text{Cl}_2}^{1/2}I_a^{1/2}$$ (4.8)

To account for this rate, the following mechanism has been proposed:

a. $\text{Cl}_2 + \text{hv} \longrightarrow 2 \text{Cl}$ \quad $k_1I_a$

b. $\text{Cl} + \text{CHCl}_3 \longrightarrow \text{CCl}_3 + \text{HCl}$ \quad $k_2C_{\text{Cl}}C_{\text{CHCl}_3}$

c. $\text{CCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{Cl}$ \quad $k_3\text{CCl}_3\text{CCl}_2$

d. $2\text{CCl}_3 + \text{Cl}_2 \longrightarrow 2 \text{CCl}_4$ \quad $k_4\text{CCl}_3\text{CCl}_2$

To the right of each reaction is given the rate at which it proceeds. In these reactions $\text{CCl}_4$ is formed only in steps (c) and (d) and hence the rate of formation of this substance must be

$$\frac{dC_{\text{CCl}_4}}{dt} = k_3C_{\text{CCl}_3}C_{\text{Cl}_2} + k_4C_{\text{CCl}_3}^2C_{\text{Cl}_2}$$ (4.9)

To eliminate from this expression $\text{CCl}_3$, we assume first a stationary state for this species. Since $\text{CCl}_3$ is formed only in step (b) and it is removed in step (c) and (d), the rate of the former must be equal to the sum of the rates of the latter two, namely,

$$k_2C_{\text{Cl}}C_{\text{CHCl}_3} = k_3C_{\text{CCl}_3}C_{\text{Cl}_2} + k_4C_{\text{CCl}_3}^2C_{\text{Cl}_2}$$ (4.10)

Further, since Cl is also a short-lived intermediate, a stationary state may be assumed for it as well. This means that the rate of steps (a) and (c) equals the rate of step (b) or

$$k_1I_a + k_3\text{CCl}_3\text{CCl}_2 = k_2C_{\text{Cl}}C_{\text{CHCl}_3}$$ (4.11)
Adding Equations (4.10) and (4.11), we obtain
\[ k_1 I_a + k_3 C_{CCl_3} C_{Cl_2} = k_2 C_{Cl} C_{CHCl_3} + k_3 C_{Cl} C_{Cl_2} + k_4 C_{CCl_3} C_{Cl_2} \]

or \( k_1 I_a = k_4 C_{CCl_3}^2 C_{Cl_2} \)

and \( C_{CCl_3}^2 = \frac{k_1 I_a}{k_4 C_{Cl_2}} \)

\( C_{CCl_3} = \sqrt{\frac{k_1 I_a}{k_4 C_{Cl_2}}} = \left( \frac{k_1 I_a}{k_4 C_{Cl_2}} \right)^{\frac{1}{2}} \) (4.12)

Substituting \( C_{CCl_3} \) from Eq (4.12) into Eq (4.9), the rate of formation of \( CCl_4 \) follows as

\[
\frac{dC_{CCl_4}}{dt} = k_3 \left[ \frac{k_1 I_a}{k_4 C_{Cl_2}} \right]^{\frac{1}{2}} C_{Cl_2} + k_4 \left[ \frac{k_1 I_a}{k_4 C_{Cl_2}} \right] C_{Cl_2}
\]

(4.13)

where \( k = k_3 \left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} \). If it is assumed now that the second term on the right in Eq (4.13) is negligible compared with the first term, Eq (4.13) reduces to

\[
\frac{dC_{CCl_4}}{dt} = kI_a^{\frac{1}{2}} C_{Cl_2}^{\frac{1}{2}}
\]

(4.14)

which is identical with the observed rate, Eq (4.8).

In photochemical rate equations time is generally expressed in seconds, concentrations either in molecules or moles per cc. For the first of these concentration units \( I_a \) must be expressed in quanta of light absorbed \( \text{cm}^{-3} \) per second i.e; the total number of quanta absorbed in 1 second divided by the volume of the absorbing medium. For the second concentration unit, on the other hand, \( I_a \) must be taken in einsteins absorbed per \( \text{cm}^{-3} \) per second, namely, the total number of Einstein absorbed in 1 second divided by the volume in \( \text{cm}^3 \).

**TYPICAL PHOTOCHEMICAL REACTIONS:**

A few typical photochemical reactions are summarized in Table 4.2.
Table 4.2: Typical photochemical reactions and their $\Phi$ at R.T.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reactions</th>
<th>$\sim \lambda$ (Å)</th>
<th>Approx. $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$2 \text{ H I} \rightarrow \text{H}_2 + \text{I}_2$</td>
<td>3000-2800</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>$S_2 \text{O}_8 + \text{H}_2\text{O} \rightarrow 2 \text{SO}_4^2 + 2\text{H}^+ + \frac{1}{2}\text{O}_2$</td>
<td>3000-2500</td>
<td>1</td>
</tr>
<tr>
<td>3.</td>
<td>$\text{C}<em>{14}\text{H}</em>{10} \rightleftharpoons \frac{1}{2}(\text{C}<em>{14}\text{H}</em>{10})_2 \rightarrow \text{Anthracene}$</td>
<td>$&lt; 3600$</td>
<td>1 – 0</td>
</tr>
<tr>
<td>4.</td>
<td>$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$</td>
<td>4350- 3660</td>
<td>0-2</td>
</tr>
<tr>
<td>5.</td>
<td>$\text{CH}_3\text{CHO} \rightarrow \text{CO}+\text{CH}_4 (+\text{C}_2\text{H}_6+\text{H}_2)$</td>
<td>3100--2537</td>
<td>0.5-1</td>
</tr>
<tr>
<td>6.</td>
<td>$(\text{CH}_3)_2\text{CO} \rightarrow \text{CO}+\text{C}_2\text{H}_6 (+\text{CH}_4)$</td>
<td>$&lt;3300$</td>
<td>0.2</td>
</tr>
<tr>
<td>7.</td>
<td>\text{Crotonaldehyde} (CH3 CH: CHCHO)</td>
<td>$&lt;3100$</td>
<td>0.0</td>
</tr>
<tr>
<td>8.</td>
<td>$\text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2$</td>
<td>2100</td>
<td>0.2</td>
</tr>
<tr>
<td>9.</td>
<td>$\text{H}_2\text{C}_2\text{O}_4 (+\text{UO}_2^{++}) \rightarrow \text{CO}+\text{CO}_2+\text{H}_2$</td>
<td>4300-2500</td>
<td>0.5–0.6</td>
</tr>
<tr>
<td>10.</td>
<td>$2 \text{NO}_3 \rightarrow 2 \text{NO}_2 + \text{O}_2$</td>
<td>3000-2500</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>11.</td>
<td>$\text{Cl}_2 + \text{H}_2 \rightarrow 2 \text{HCl}$</td>
<td>4000</td>
<td>$10^5$</td>
</tr>
<tr>
<td>12.</td>
<td>$\text{Br}_2+\text{C}_6\text{H}_5\text{CH}=$CH$\text{COOH} \rightarrow \text{C}_6\text{H}_5\text{CH Br CH Br COOH}$</td>
<td>$&lt;5500$</td>
<td>100 – 1</td>
</tr>
<tr>
<td>13.</td>
<td>$\text{C}_2\text{H}_2 \rightarrow \frac{1}{n}(\text{C}_2\text{H}_2)_n$</td>
<td>2000</td>
<td>7</td>
</tr>
<tr>
<td>14.</td>
<td>$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$</td>
<td>4000-4360</td>
<td>1000</td>
</tr>
</tbody>
</table>

Reaction 1 is one of the most exact photochemical reactions, and it has the same value of $\Phi$ from 2800 to 3000 Å, at low pressure and high pressures, in the liquid state or in solution in hexane. The primary process $\text{HI} + h\nu \rightarrow \text{H}+\text{I}$ is followed by the thermal reactions $\text{H}+\text{HI} \rightarrow \text{H}_2+\text{I}$ and $\text{I} + \text{I} \rightarrow \text{I}_2$, thus giving two molecules of HI decomposed for each photon.
absorbed. Reaction 2 has the quantum yield of 1. Reaction 3 dimerization has a $\Phi$ of unity initially, but the reverse thermal process reduces it as the product accumulates. In reaction 4 at 3660 Å the photo process is completely efficient ($\Phi = 2$) if correction is made for internal screening by the accompanying N$_2$O$_4$, which absorbs some light at 3660 Å. The reactions are, $\text{NO}_2 + \text{hv} \rightarrow \text{NO}_2^*$, $\text{NO}_2^* + \text{NO}_2 \rightarrow \text{2NO} + \text{O}_2$, where the asterisk indicates an activated molecule. At longer wavelengths the spectrum is of a different type and at 4350 Å no reaction occurs when the radiation is absorbed. Reaction 5 shows a greater quantum yield at shorter wavelengths. This reaction is interesting because at 300 °C $\Phi$ has a value of more than 300, indicating that the free radicals that are first produced by the absorption of light are able to propagate a chain reaction at the higher temperatures. At room temperature the reactions involved in the chain do not go fast enough to be detected. The products given in parentheses are present also but in small amounts.

Reaction 6 is an example of the fact that the absorption of light in a particular bond does not necessarily cause the rupture of that bond. Acetone, like other aliphatic ketones, absorbs UV light at about 2800 Å. The C=0 bond, which we designate as the chromophore, is very strong and does not break to give atomic oxygen. Instead, the absorption energy leads to the cleavage of an adjacent –C–bond that is weaker; thus,

$$\text{CH}_3\text{C}=\text{O} + \text{hv} \rightarrow \text{CH}_3^* + \text{CH}_3\text{C}=\text{O}$$

$\text{CH}_3$

$\text{C} = \text{O} + \text{hv}$

$\text{CH}_3\text{C}=\text{O} + \text{hv}$

$\text{CH}_3\text{C}=\text{O}$

$\text{CH}_3$

$\text{CH}_3^*$

$\text{CH}_3\text{C}=\text{O}$

$\text{CH}_3\text{C}=\text{O}$

$\text{CH}_3$

$\text{CH}_3$

$\text{CH}_3$

giving a methyl radical and an acetyl radical. The acetyl radical can then decarbonylate, giving CO and CH$_3$ or it can react with CH$_3^*$ to give back acetone. The methyl radicals can couple to form ethane. In reaction 7, in crotonaldehyde (a colorless flammable liquid, CH$_3$CH:CHCHO) no photochemical decomposition is observed, probably because the molecule is so complex that the energy taken up from the light is dissipated through the vibrations of many different atom – pairs within the molecule before it can become localized for the breaking of a bond. In the photolysis of NH$_3$, reaction 8, hydrogen atoms are split off, and the low yield is probably due to partial recombination of the fragments. The $\Phi$ varies with pressure and reaches a maximum at 0.6 to 0.7 Pa (80-90 mm).
Reaction 9 illustrates a photosentized reaction. The photodecomposition of oxalic acid, sensitized by uranyl ion, is so reproducible that it is suitable for use as a chemical actinometer. In the uranyl oxalate actinometer the light is absorbed by the colored uranye ion, and the energy is transferred to the colorless oxalic acid and which then decomposes. The uranyl ion remains unchanged and can be used indefinitely as a sensitizer. The fact that the molar absorption coefficient of uranyl ion is increased by the addition of colorless oxalic acid indicates the formation of a complex. The formation of a chemical complex is often necessary for photosensitization. Reaction 11 is the best known example of a chain reaction. About $10^5$ molecules react for each quantum absorbed. The molecules of HCl formed undergo further reaction with the hydrogen and chlorine atoms produced. The measurement of the number of molecules per photon, gives a measure of the average number of molecules involved in the chain. Initiation of the reaction with a flash of light can result in an explosively fast reaction. Oxygen and certain other substances act as inhibitors by combining with the chlorine or hydrogen atoms, thus stopping the propagation of the chain and reducing the quantum yield.

The addition of bromine to cinnamic acid, reaction 12, is a chain reaction, the length of the chains depending on the temperature, the concentration of bromine, and the amount of dissolved oxygen. The reaction can be split up into the primary photo process, which is not affected by temperature and the subsequent thermal reaction which has a large temperature coefficient. When oxygen is removed, the breaking of chains is less frequent and the $\Phi$ is of the order of hundreds and more. The polymerization of acetylene, reaction 13 to give an insoluble substance called cuprene is effected by short UV light with a $\Phi$ of about 7, showing that the primary process is followed by a short chain reaction. Reaction 14 varies with the pressure of CO and Cl$_2$ and like all chain reactions, is sensitive to impurities.
Exercise

A. Fill in the blanks with suitable words:
1. The photodecomposition of oxalic acid, sensitized ________________, is so reproducible that it is suitable for use as a chemical actinometer.
2. Not only second – order and first – order reactions but also ________________ reactions are found in photochemistry.
3. The addition of bromine to ________________, is a chain reaction.
4. The formation of a ________________ is often necessary for photosensitization.
5. The kinetics of photochemical reaction is more complicated than the kinetics of ________________.

B. Write short answers to following questions.
   a. Why the kinetics of photochemical reaction is more complicated than the kinetics of thermal reactions?
   b. Under what conditions cuprene is formed?
   c. Give some example of a chain reaction.
   d. What is quantum yield?
   e. What is a photosentized reaction? Give some examples.
   f. Explain dimerization with an example.

C. Long questions
   1. Discuss various kinds of photochemical reactions with the help of various examples.
   2. Explain in detail photochemical kinetics.
CHAPTER 5

PHOTOCHEMICAL REACTIONS:

Photo-excited molecules are highly energetic and have the potential for internal arrangement or reaction with other molecular species in the system. The products of photochemical reactions frequently differ from those of thermal reactions and there are many examples where products obtained photochemically could not be prepared by any other synthetic route. The application of photochemistry to organic synthesis is rapidly increasing and the number of photochemical reactions now characterized is very large. As knowledge of photochemical principles develops so many of the apparently unique reactions are seen to be examples of general photochemical reaction processes. A number of general types of photochemical reactions are considered viz; photo reduction, photo dimerization, photo addition, photo oxidation and photo rearrangement. Many reactions can be initiated by the absorption of light. The most important of all are photochemical processes that capture the sun’s radiant energy. These range from the ones that lead to the heating of the atmosphere during the day time by absorption in the UV region as a result of reactions (such as these depicted in

**Fig.5.1:** The temperature profiles through the atmosphere some of the reactions that occur in each region.

(Fig. 5.1) to the absorption of red and blue light by chlorophyll and its subsequent use of the energy to bring about the synthesis of carbohydrates. Photochemical processes are also the basis of undesirable effects, such as the degradation of polymers and the formation of smog, and of leisure activities, such as photography. Without photochemical processes the world would be simply a warm sterile rock. The photochemical reaction is also responsible for the destruction of ozone in the ozone layer of the atmosphere, which protects the earth from harmful UV radiation by trapping these radiations. This ozone layer has been thinning gradually and poses potential health hazards for the future. The thinning of ozone layer has been attributed to the presence of chlorofluoro hydrocarbons like CF Cl₃ and CF₂ Cl₂ in the atmosphere. These chemicals have been used as aerosol propellants and cooling mixtures in refrigerators. These chemicals affect ozone concentration with the equations given below:

\[
\text{(i). } \quad \text{CF}_2 \text{Cl}_2 + h\nu \xrightarrow{} \text{CF}_2 \text{Cl} + \text{Cl}
\]
Chlorine atom is highly reactive and reacts with ozone (O₃).

(ii). \[ \text{O}_3 + \text{Cl} \rightarrow \text{ClO} + \text{O}_2 \]

The monoxide of chlorine further reacts with another molecule O₃.

(iii). \[ \text{ClO} + \text{O}_3 \rightarrow \text{Cl} + 2\text{O}_2 \]

The chlorine atom so obtained reacts with another ozone molecule. Hence, steps (ii) and (iii) are repeated again and again and, lead to the depletion of concentration of ozone.

The photochemical reactions are studied with a view to discover the mechanisms of chemical changes which take place when a system is exposed to light. Generally these reactions are complex in nature and have not been fully understood in many cases. Only reactions produced directly by absorption of light, obey Einstein Law of photochemical Equivalence, where \( \Phi \) is unity or close to unity. Such reactions are termed as primary reactions. The reactions that proceed by the products of primary reactions or the reactions which occur as secondary effects of light absorption are called secondary reactions. Secondary reactions are usually thermal (dark) reactions. In these reactions total number of moles reacting for each Einstein of the radiations absorbed may differ from unity. Although \( \Phi \) of primary reactions is unity but overall yield determined from ultimate results may be quite different. This makes it possible to understand the nature of secondary process.

**PHOTOCHEMICAL GAS REACTIONS:**

Quantum yields of photochemical gas reactions vary within very wide limits, as from 0.25 for ammonia decomposition to \( 10^6 \) for the combination of chlorine and hydrogen. Some of the photochemical gas reactions are discussed below to illustrate some of the mechanisms by which they proceed.

**THE PHOTOLYSIS OF NH₃**

The photolysis or photochemical decomposition of NH₃ was studied by Wiig, who found that the reaction proceeds quantitatively according to

\[ 2 \text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \]

with an average \( \Phi \) of 0.25 up to 500 mm pressure of NH₃. The following mechanism has been proposed to explain these results.

\[ \text{a. } \text{NH}_3 + h\nu \rightarrow \text{NH}_2 + \text{H} \]
\[ \text{b. } \text{NH}_2 + \text{H} \rightarrow \text{NH}_3 \]
From this mechanism it can be shown that the $\Phi$ should be small and it would vary with pressure. These conclusions are in accord with the observed results. The $\Phi$ of the photolysis of NH$_3$ varies with the temperature, e.g; 0.15 at 20°C to 0.5 at 40°C with light of 2144 Å; and increases and then decreases with increasing pressure. The low $\Phi$ is not due to deactivating collisions, because it remains small at very low pressures, and so it must be attributed to partial recombination of the fragments. The $\Phi$ yield varies with pressure and reaches a maximum at 80 – 90 mm. The final products of photolysis are N$_2$, H$_2$ and N$_2$H$_4$ (hydrazine).

**THE PHOTOCHEMICAL REACTION BETWEEN H$_2$ AND Br$_2$**

The photochemical reaction between H$_2$ and Br$_2$ follows a kinetic law which resembles that for the thermal reaction in contrast to the decomposition of HI, where the kinetics are quite different. Using light of wavelength less than 5110 Å the mechanisms of the photochemical reaction between H$_2$ and Br$_2$ is

\[
\begin{align*}
k_1 & : \text{Br}_2 + \text{hv} \xrightarrow{k_1} 2 \text{Br}, \quad \text{(Primary Process)} \\
k_2 & : \text{Br} + \text{H}_2 \xrightarrow{k_2} \text{HBr} + \text{H} \quad \text{Secondary Process} \\
k_3 & : \text{H} + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br} \\
k_4 & : \text{H} + \text{HBr} \xrightarrow{k_4} \text{H}_2 + \text{Br} \\
k_4 & : 2 \text{Br} \xrightarrow{k_5} \text{Br}_2
\end{align*}
\]

The rate of formation of HBr is the same as that for the thermal reaction

\[
\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr]
\] (5.1)

The steady – state conditions for H atoms and Br atoms are

\[
\begin{align*}
\frac{d[H]}{dt} & = 0 = k_2[Br][H_2] - k_3[Br_2] - k_4[H][HBr] \\
\frac{d[Br]}{dt} & = 0 = 2I_a - k_2[Br][H_2] + [H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2
\end{align*}
\]
Addition of these two equations yields $2k_5[Br]^2 = 2I_a$ so that

$$[Br] = \frac{2I_a}{2k_5} = \frac{I_a}{k_5}$$

or

$$[Br] = \left(\frac{I_a}{k_5}\right)^{\frac{1}{2}}$$

This results in either of the steady – state equations yields ultimately

$$[H] = \frac{(k_2)}{(k_5^{1/2})} I_a^{1/2}/k_3[Br_2] + k_4[HBr]$$

which on substitution into equation (5.1), finally gives

$$d[HBr] = \left[\frac{2k_2}{k_5^{1/2}}\right] I_a^{1/2} \left[H_2\right]$$

$$1 + \frac{k_4[HBr]}{k_3[Br_2]}$$

The expression in Eq (3.16) is very similar to that for the thermal reaction where the factor $I_a^{1/2}$ is replaced by $k_1^{1/2}(Br_2)^{1/2}$. This means that the bromine atom concentration is maintained by the photochemical dissociation of bromine rather than the thermal dissociation. The dependence on the square root of the intensity is notable, since it has the consequence that the $\Phi$ is inversely proportional to the square root of the intensity:

$$\Phi = \frac{d[HBr]}{dt} = \frac{(2k_2)}{k_5^{1/2}} \left[H_2\right] I_a^{1/2} \left\{1 + \frac{k_4[HBr]}{k_2[Br_2]}\right\}$$

As the intensity increases, a greater proportion of the bromine atoms formed are converted to $Br_2$ instead of entering the chain; most of the additional quanta therefore, are wasted and the process is less efficient. Because $k_2$ is very small, the $\Phi$ is less than unity at room temperature in spite of the fact that the HBr is formed in a chain reaction. As the temperature increases, the increase in $k_2$ increases the $\Phi$ ($k_5$ is nearly independent of temperature).
The Photochemical Reaction between H₂ and Cl₂:

If a molecule is dissociated as a consequence of absorbing a quantum of radiation, extensive secondary reactions may occur, since the fragments are often highly reactive atoms or radicals. Sometimes, also the products of the primary fission process are in excited states as so called hot atoms or hot radicals.

The combination of hydrogen and chlorine is a classical example of photochemical reaction which was first observed by Gay Lussac and Thenard in 1809. The hydrogen chloride actinometer is based on this reaction. For example if a mixture of chlorine and hydrogen is exposed to light in the continuous region of the absorption spectrum of chlorine (λ < 480 nm, a rapid formation of hydrogen chloride ensues. The quantum yield Φ is 10⁴ to 10⁶. In 1918, Nernst explained the high value of Φ in terms of a long reaction chain. The mechanism for this reaction is as follows:

1. \( \text{Cl}_2 + \text{hv} \xrightarrow{k_1} 2\text{Cl} \)  \( \text{Photo – initiation} \)
2. \( \text{Cl} + \text{H}_2 \xrightarrow{k_2} \text{HCl} + \text{H} \)  \( \text{Chain} \)
3. \( \text{H} + \text{Cl}_2 \xrightarrow{k_3} \text{HCl} + \text{Cl} \)  \( \text{Propagation} \)
4. \( \text{Cl} \xrightarrow{k_4} \frac{1}{2} \text{Cl}_2 \)  \( \text{(Wall)} \)  \( \text{Termination} \)

The quantum yield for the primary process, viz; photo – initiation, cannot be greater than two since at maximum only 2Cl atoms can be produced per quantum absorbed. On the other hand, the Φ for the consumption of Cl₂ and H₂ is approximately 10⁶ because of the chain reaction occurring in the second and third steps. The reactions (2) and (3) repeat alternately many times and the cycle continues, so that by a long chain of these reactions the combination of millions of molecules takes place. The chain reaction does not stop until the entire reactants are consumed. In many cases the chain may be broken when molecules or atoms in the chain collide with the wall of the containing vessel or some inert molecule. Such photochemical reactions in which chain of reactions are set up and thus millions of molecules react for each quantum of light absorbed are generally called chain reactions. The rate of formation of HCl can be deduced as below:

Chlorine atoms are formed in reaction (1) and (3) are removed by (2) and (4) so that in the stationary state

\[
k_1 I_{abs} + k_3 C_H C_{Cl_2} = k_3 C_{Cl} C_H + k_4 C_{Cl}
\]

(5.4)
The assumption is made that reaction (4) is a first–order reaction. Similarly, considering the stationary state for hydrogen atoms, it is seen that

\[ k_2 C_{Cl} C_{H_2} = k_3 C_H C_{Cl_2} \]  

(5.5)

now, from Eqs (5.4) and (5.5),

\[ k_1 I_{abs} = k_4 C_{Cl} \]  

(5.6)

\[ C_{Cl} = k_1 I_{abs} / k_4 \]  

(5.7)

The total rate of formation of HCl, by reactions (5.5) and (5.6) is represented by

\[ \frac{dC_{HCl}}{dt} = k_2 C_{Cl} C_{H_2} + k_3 C_H C_{Cl_2} \]  

(5.8)

\[ = 2k_2 C_{Cl} C_{H_2} \]  

(5.9)

[From Eq (5.5)]

Introducing the value for \( C_{Cl} \) given by Eq (5.7) it follows that

\[ \frac{dC_{HCl}}{dt} = \frac{2k_1 k_2 I_{abs} C_{H_2}}{k_4} \]  

(5.10)

At moderate gas pressures and with comparable preparations of chlorine to hydrogen, Bodenstein and Unger and others found that the rate of formation of HCl is given by Eq (5.10).

**THE PHOTOLYSIS OF HI:**

The photolysis of HI is an example of a photochemical process brought about by radiation in the region of continuous absorption and so involves dissociation into atoms as the primary stage. Spectroscopic studies revealed that HI molecule absorbs radiation in the range 2100 – 2820 Å for the primary act of excitation. The absorption of the requisite photon produces a hydrogen and an excited iodine atom as

\[ HI + h\nu \rightarrow H + I^* \]  

(i)

Rate = \( I_a \)  

(Excited)

The primary act of excitation is followed by the following steps of secondary reactions.

\[ HI + I \rightarrow I_2 + H \]  

(endothermic)  

\( \Delta H = 146 \text{ kJ mol}^{-1} \)  

(ii)
\[ \text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I} \quad \Delta H = -134 \text{ kJ mol}^{-1} \quad (\text{iii}) \]

\[ \text{H} + \text{H} \rightarrow \text{H}_2 \quad \text{(highly exothermic)} \quad (\text{iv}) \]
\[ \text{I} + \text{I} \rightarrow \text{I}_2 \quad (\text{v}) \]
\[ \text{I} + \text{H} \rightarrow \text{HI} \quad \text{(highly exothermic)} \quad (\text{vi}) \]

of these secondary reactions, (ii) is strongly endothermic and does not take place at ordinary
temperature (iv) and (vi) are highly exothermic so much so that the products formed are unstable.
This leaves the possibility of the reactions (iii) and (v) as the only secondary reactions taking
place at ordinary temperature. The overall reaction can be written as
\[ \text{HI} + h\nu \rightarrow \text{H} + \text{I}, \quad \text{Rate} = I_a \]
\[ \text{HI} + \text{H} \rightarrow \text{H}_2 + \text{I}, \quad \text{Rate} = k_2 [\text{H}] [\text{HI}] \]
\[ 2 \text{I} \rightarrow \text{I}_2, \quad \text{Rate} = k_3 [\text{I}]^2 \]

The sum:
\[ 2 \text{H I} + h\nu \rightarrow \text{H}_2 + \text{I}_2 \]

The rate of disappearance of HI is
\[ -\frac{d[\text{HI}]}{dt} = I_a + k_2 [\text{H}][\text{HI}] \quad (5.11) \]

where \( I_a \) is intensity of light absorbed. The steady – state requirement for H
atom gives
\[ \frac{d[\text{HI}]}{dt} = 0 = I_a - k_2 [\text{H}][\text{HI}] \quad (5.12) \]

Therefore,
\[ I_a = k_2 [\text{H}][\text{HI}] \quad (5.13) \]

Now, substitute the value of \( I_a \) from Eq (5.13) in Eq (5.11)
\[ -\frac{d[\text{HI}]}{dt} = 2I_a \quad (5.14) \]
By definition the quantum yield is

\[ \Phi = \frac{(-d[H I]/dt)}{I_a} \]

so that, from Eq (5.14) we find that \( \Phi = 2 \). Evidently a photon of light radiation causes the decomposition of two molecules of HI, thereby giving the quantum yield (\( \Phi \)) of the reaction as 2. In a variety of experimental situations the observed value of \( \Phi \) is 2.

The interesting point about the gas – phase photochemical decomposition of hydrogen iodide into hydrogen and iodine is that the rate, by Eq(5.14) is simply twice the absorbed intensity and is not directly dependent on the concentration of HI. This fact implies that the reaction is very slow, since even fairly intense light sources do not produce a very large number of quanta per second. The dependence of rate on intensity can be readily verified by altering the distance between the system and the light source. The incident intensity varies inversely as the square of the distance, so for a given cell and given concentration of HI, the absorbed intensity must vary in the same way. Indirectly, the rate depends on the concentration of HI, since the absorbed intensity is dependent on concentration through Beer’s law.

The photolysis of HI is one of the most exact photochemical reaction and it has the same value of \( \Phi \) from ~ 2070 to 3000Å at low pressures and high pressures in the liquid state or in solution in hexane. Since no fluorescence is observed even at the lowest pressures, it is unlikely that any excited HI molecules are involved in the mechanism. This is a good example of a photochemical dissociation process.
Exercise

A. Fill in the blanks with suitable words:

1. The most important of all photochemical processes that capture the .
2. The thinning of ozone layer has been attributed to the presence of like CF Cl₃ and CF₂ Cl₂ in the atmosphere.
3. The final products of photolysis are N₂, H₂ and N₂ H₄ (hydrazine).
4. The bromine atom concentration is maintained by the photochemical dissociation of bromine rather than the .
5. The photochemical reactions discovered the mechanisms of which take place when a system is exposed to light.
6. The Φ of the photolysis of NH₃ varies with the________________________

B. Provide short answers to the following questions.

1. What are the general types of photochemical reactions?
2. Which types of light rays are utilized for Carbohydrate synthesis?
3. How photochemical processes are responsible for the destruction of ozone layer?
4. Write short note on Quantum yields of photochemical gas reactions?
5. Why photolysis of HI is one of the most exact photochemical reactions?
6. What is application of Einstein Law of photochemical Equivalence on photochemical reactions?

C. Briefly describe the following

1. Differentiate between the primary and secondary photochemical reactions
2. Write equation for Quantum yield of photochemical reactions
3. Write short note on classical example of photochemical reactions
4. Types of wave lengths Involved in photolysis of Hydrogen and Bromine
CHAPTER 6

QUENCHING

When a photochemically excited atom undergoes collision with another atom or molecule before it has a chance to fluoresce, the fluorescence may be quenched, i.e.; the intensity of the fluorescent emission may be diminished or stopped. The quenching of fluorescence is due to transfer of energy from the excited atom to the particle with which it collides. As a result of this energy transfer the following changes may occur:

1. An excited atom may activate another atom with which it collides. An example is the activation of thallium atom by excited mercury vapor, viz;
   \[ \text{Hg}^* + \text{Tl} \rightarrow \text{Hg} + \text{Tl}^* \]  
   (6.1)
   The asterisk denotes the activated or excited particle.

2. The excited atom may collide with a molecule and activate it. An instance is the activation of hydrogen by excited cadmium atoms.
   \[ \text{Cd}^* + \text{H}_2 \rightarrow \text{Cd} + \text{H}_2^* \]  
   (6.2)

3. An excited atom may react with the colliding molecule. Such a process is the reaction
   \[ \text{Hg}^* + \text{O}_2 \rightarrow \text{HgO} + \text{O} \]  
   (6.3)

4. Finally, an excited atom may collide with a molecule and by energy exchange cause the molecule to dissociate. A dissociation thus brought about by an excited atom is called photosensitization. It is exemplified by the photosensitized dissociation of hydrogen gas by excited mercury vapor, namely,
   \[ \text{Hg}^* + \text{H}_2 \rightarrow \text{Hg} + 2 \text{H} \]  
   (6.4)

Whether or not fluorescence will be quenched depends greatly on the concentration of the fluorescent atoms and of the quenching substance. In a gas at low pressure the time interval between collisions is usually greater than the life of the excited atoms and hence very little quenching will occur. At higher pressures the time interval between collisions is shorter and consequently appreciable quenching will take place. Since in liquid medium collisions are very frequent, the fluorescence emitted by liquid media will generally be appreciably quenched. Further, the quenching of fluorescence is to a large degree specific. Thus in the quenching of mercury fluorescence oxygen gas is most effective, followed by hydrogen and CO, while helium and organ are very inefficient quenchers at the same pressure.
The photochemical importance of the quenching of fluorescence lies in the fact that excited atoms or molecules resulting from the quenching process may react further to continue the photochemically initiated change. Thus in reactions such as (1) and (2) the activated products may combine with other reactants to yield new products. Similarly, the atoms formed in reactions (3) and (4) may enter further reaction. Nevertheless, the absorbed light is involved only in the initial activation of some atom. Any succeeding reactions are generally thermal in character.

Quenching is useful probe for determination of mechanism. As mentioned above it is possible to quench reactions and to quench light emission from excited states. Both kinds of quenching are important in the study of reaction mechanism. If we consider a simple mechanism of the type shown below, assumption of a steady-state concentration for the reactive excited state \((M^*)\) permit analysis of the kinetics of the system in terms of the quantum efficiency of the reaction in presence and absence of a quencher. The steady-state

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>excitation</td>
<td>(M \xrightarrow{hv} M^*) I_o (\Phi) I_o = number of quanta</td>
</tr>
<tr>
<td>deactivation</td>
<td>(M^* \xrightarrow{kd} M) k_d ([M^*]) absorbed by (M) per unit time</td>
</tr>
<tr>
<td>reaction</td>
<td>(M^* \xrightarrow{kr} ) products k_r ([M^<em>]) (\Phi) = efficiency of production of the reactive excited state ([M^</em>])</td>
</tr>
<tr>
<td>quenching</td>
<td>(M^* + Q \xrightarrow{k_q} M + Q^<em>) k_q ([M^</em>]) ([Q])</td>
</tr>
</tbody>
</table>

Concentration of \(M^*\) will be achieved when the rate of production of \(M^*\) is equal to the sum of the rates of destruction. This relationship can be solved for the concentration of \(M^*\). This value

\[
I_o \Phi = k_d [M^*] + K_r [M^*][Q]
\]

\[
[M^*] = \frac{I_o \Phi}{k_d + k_r + k_q [Q]}
\]

(6.5)

can be used to obtain an expression for the quantum efficiency of the process. In the absence of a quencher, the term \(k_q [Q]\) is zero. We can then

\[
\Phi = \frac{\text{rate of product formation}}{\text{rate of absorption of quanta}}
\]
\[ \Phi = \frac{k_r[M^*]}{I_o} = \frac{k_r\Phi}{k_d + k_r + k_q[Q]} \]  \hspace{1cm} (6.6)

take a ratio of the quantum efficiency in the absence of quencher to that in the presence of a quencher. The resulting equation predicts a

\[
\frac{\left(\Phi_{prod}\right)_o}{\left(\Phi_{prod}\right)_q} = \frac{k_r\Phi}{k_d + k_q[Q]} \]  

\[ = \frac{k_d + k_r + k_q[Q]}{k_d + k_r} \]

\[ = \frac{k_d + k_r + k_q[Q]}{k_d + k_r} \]  \hspace{1cm} (6.7)

linear plot of the ratio of the quantum efficiencies for unquenched and quenched reactions \( \left(\Phi_o/\Phi_q\right) \) as function of the quencher concentration; this is known as stern-volmer plot. Eq (6.8) is known as stern-volmer equation. The arrangement of 4,4 dimethyl-2-cyclohexanone may be used as an example of quenching of a reaction. Di-tertiary-butyl nitroxide is used as a quencher because it is an efficient quencher for triplet excited states and because it does not absorb strongly the 3130 Å light used in the irradiation of 4,4-dimethyl-2-cyclohexanone. This system gives a linear stern-volmer plot \( \left(\Phi_o/\Phi_q\right) \) vs. \([Q]\) (Fig. 6.1). The slope of a stern-volmer plot is equal to \( k_q\tau \), where \( \tau \) is the mean lifetime of the reactive excited state.
state being quenched. The value of $k_q$ can be estimated from the Debye equation for diffusion controlled rates. Quenching thus provides a kinetic method for estimating excited state lifetimes.

Quenching of light emission from an excited state can be useful in the study of mechanism, especially in identifying reactive singlet excited states. Irradiation of trans-stilbene in the presence of tetraethylene (4M) gives a 1:1 adduct with a quantum efficiency of 0.54 at room temperature. The photocyclo addition is:

$$\text{Trans-stilbene} + \text{Ethylene} \rightarrow \text{Adduct}$$

Fig. 6.1: 

```
[ di – tertiary – butyl nitroxide] moles / liter. of trans-stilbene to tetramethyethylene competes with trans to cis isomerization of the stilbene. When the reaction is sensitized with thioxanthone, only trans to cis isomerization is observed. This implies, but does not prove, that it is the low – lying singlet excited stat of trans – stilbene which adds to tetramethyylene. Fortunately, trans – stilbene emits light from its low – lying singlet; i.e; it fluoresces. If tetramethylethylene is adding to the S, state of trans-stilbene; it must quench the fluorescence. This is found to be true, and the quenching again follows the stern-volmer equation (Fig 6.2). Notice that much higher quencher concentrations are required to quench the excited
```
singlet state than were required for quenching the triplet excited state in 4,4-admethyl -2-cyclohexanone.

![Graph showing quenching of trans-stilbene fluorescence by tetramethylethylene](image)

**Fig. 6.2:** The quenching of trans-stilbene fluorescence by tetramethylethylene is a consequence of exciplex formation.

The effectiveness of a molecule in quenching fluorescence increases as the number of internal modes of motion increases. For example, if a helium atom or argon atom collides with an activated molecule the excess energy can only be drained off into translational energy of the colliding atom. Looking at the diatomics, we find that H\(_2\) is relatively ineffective while O\(_2\) and N\(_2\) are only slightly more effective. Although these molecules do have a vibrational mode, the vibrational quantum is so large that it is not effective in quenching. Molecules with small spacings between the vibrational and rotational energy levels are more effective than those with larger spacing. Consequently, molecules with more modes of motion and heavier atoms are noticeably more effective. Heavy atoms lower the size of the vibrational and rotational energy quanta; similarly complex molecules have bending vibrational modes, which have low energy quanta. Polar molecules, such as water, are particularly effective.

**PHOTOSENSITIZATION:**

When a reaction mixture is exposed to light to which the reactants are insensitive, no reaction will take place. However, it is possible to introduce into the reaction mixture molecules or atoms which will absorb the light, become excited and then pass on this energy to one of the reactants and thereby activate it for reaction. A substance acting in this manner is called a
photosensitizer (sensitizer) while the reaction resulting is said to be photosensitized and the phenomenon is termed photosensitization.

Photosensitization was first discovered by Cario and Franck (1922), who demonstrated the formation of hydrogen atoms from hydrogen molecules and excited mercury, detecting them by their chemical reactivity. They described a collision between the excited mercury atom and the molecule as a “Stoss Zweiter Art” (“collision of the second kind”). Later Taylor and his coworkers (1926) used the method to investigate the reactions of atomic hydrogen, which they caused to react with CO, N₂O, hydrocarbons, and other substances.

**Examples**

**PHOTOSENSITIZED GAS REACTIONS**

An example is the reaction often used to generate atomic hydrogen by irradiation of hydrogen containing a trace of mercury using 254 nm light from a mercury discharge lamp. The mercury atoms are excited by resonant absorption of the radiation and then collide with hydrogen molecules. Two reactions then take place.

\[
\text{Hg} + \text{hv} \rightarrow \text{Hg}^* \quad \text{(Activation of the Hg vapours)}
\]

(i) \[
\text{Hg}^* + \text{H}_2 \rightarrow \text{Hg} + 2\text{H} \quad \text{Transfer of the active energy}
\]

(ii) \[
\text{Hg}^* + \text{H}_2 \rightarrow \text{HgH} + \text{H} \quad \text{to a hydrogen molecule.}
\]

The reaction (ii) which is monitored by detecting the HgH spectroscopically accounting for 67% of the process (but 76% when deuterium is used in place of hydrogen). This reaction is the initiation step for other mercury – photosensitized reactions, such as the synthesis of formaldehyde (HCHO) and some glyoxal from CO and hydrogen

\[
\begin{align*}
\text{(a)} \quad \text{H} + \text{CO} & \rightarrow \text{HCO} \\
\text{(b)} \quad \text{HCO} + \text{H}_2 & \rightarrow \text{HCHO} + \text{H} \\
\text{(c)} \quad 2 \text{ HCO} & \rightarrow \text{HCHO} + \text{CO} \\
\text{(d)} \quad 2 \text{ HCO} & \rightarrow \text{HCO} – \text{CHO} \quad \text{(glyoxal)}
\end{align*}
\]

Decomposition of ozone into oxygen is photosensitized by chlorine. Bonhoeffer suggested the following reaction mechanism:

\[
\text{Cl}_2 + \text{hv} \rightarrow \text{Cl}^*_2 \quad \text{(activated Cl}_2)\]

Chlorine absorbs continuously below 478.5 nm

\[
\begin{align*}
\text{Cl}^*_2 + \text{O}_3 & \rightarrow \text{Cl}_2 + \text{O}_2 + \text{O} \\
\text{O} + \text{O} & \rightarrow 2\text{O}_2
\end{align*}
\]
or

\[ \text{Cl}_2^* + \text{O}_3 \rightarrow \text{Cl}_2\text{O}^* + \text{O}_2 \]

\[ \text{Cl}_2\text{O}^* + \text{O}_3 \rightarrow \text{Cl}_2 + 2 \text{O}_2 \]

\( \text{O}_3 \) is stable under irradiation by visible light. The absorption continuum begins at about 290 nm.

In the presence of a little chlorine, ozone decomposes rapidly. The chlorine atoms react with ozone in a complex chain mechanism. Bromine is also effective as a sensitizer for this decomposition.

Many mercury – photosensitized reactions have been investigated. These include decompositions of \( \text{H}_2 \), \( \text{NH}_3 \), \( \text{H}_2\text{O} \), \( \text{PH}_3 \), \( \text{AsH}_3 \), various hydrocarbons, alcohols, ethers, acids and amines; hydrocarbons such as that of ethylene propylene and butylene, combinations, such as that of oxygen and hydrogen to water, oxygen to ozone and hydrogen and nitrogen to ammonia; and polymerizations, such as that of ethylene. The dissociation of hydrogen is sensitized also by xenon, the polymerization of ethylene by cadmium vapor. The latter is effective as well in the decomposition of ethane and propane into hydrogen, methane and higher hydrocarbons. The halogens have also been employed frequently as sensitizers. Thus chlorine, bromine and iodine sensitize the decomposition of ozone; bromine that of \( \text{Cl}_2\text{O} \), while chlorine promotes the combination of oxygen and hydrogen to form water and of CO and oxygen to form \( \text{CO}_2 \).

In Table 2 are given several photosensitized gas reactions along with their quantum yields and the wavelengths at which these were obtained.

**Table 2.6:** Some photosensitized Gas Reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Sensitizer</th>
<th>Wave Length (Å)</th>
<th>( \Phi )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \text{O}_3 )</td>
<td>( 3 \text{O}_2 )</td>
<td>Cl(_2)</td>
<td>4300</td>
<td>2-3</td>
</tr>
<tr>
<td>( 2 \text{H}_2 + \text{O}_2 )</td>
<td></td>
<td>2( \text{H}_2\text{O} )</td>
<td>Cl(_2)</td>
<td>4300</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{CO} )</td>
<td></td>
<td>HCHO</td>
<td>Hg</td>
<td>2537</td>
</tr>
<tr>
<td>( 2 \text{CO} + \text{O}_2 )</td>
<td></td>
<td>2( \text{CO}_2 )</td>
<td>Cl(_2)</td>
<td>4050-4360</td>
</tr>
</tbody>
</table>
PHOTOSENSITIZED LIQUID REACTION

One of the most reproducible photochemical reactions is the decomposition of oxalic acid photosensitized by uranyl ion is a common actino-metric reaction. The uranyl ion \( (UO_2^{2+})^* \) absorbs radiation from 250 to 450 nm, becoming an excited ion \( (UO_2^{2+})^* \), which transfers its energy to a molecule of oxalic acid, causing it to decompose. This reaction may be written:

\[
UO_2^{2+} + \text{hv} \rightarrow (UO_2^{2+})^*
\]

\[
(UO_2^{2+})^* + (COOH)_2 \rightarrow UO_2^{2+} + CO_2 + CO + H_2O
\]

The quantum yield depends on the frequency of the light, varying between about 0.5 and 0.6. After a measured period of time, the light is turned off and the residual oxalic acid determined by titration with \( \text{KMnO}_4 \). From these data and knowing the original amount of oxalic acid, the intensity is calculated using the value of the quantum yield appropriate to the frequency of light used. A quartz vessel filled with the uranyl–oxalate mixture can be used instead of a thermopile to measure the number of quanta absorbed, from the oxalic acid decomposed and the known quantum yield.

IMPORTANCE OF PHOTOSENSITIZATION

If a mixture of hydrogen, oxygen and mercury vapor is exposed to UV light, the mercury vapor absorbs strongly at 253.7 nm with the formation of an excited mercury atom, \( \text{Hg}^* \):

\[
\text{Hg} + \text{hv} \rightarrow \text{Hg}^*
\]

The energy corresponding to this wavelength is 471.5 k J / mol. The energy required to dissociate a molecule of hydrogen in its ground state to two hydrogen atoms in their ground state is 432.0 k J / mol. The dissociation of oxygen requires 490.2 k J / mol. The energy possessed by the excited mercury atom is more than enough to dissociate \( \text{H}_2 \) but not enough to dissociate \( \text{O}_2 \). The quenching reaction

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

introduces \( \text{H} \) atoms into the mixture which can initiate chains to form \( \text{H}_2\text{O} \) by the usual mechanism.

The importance of photosensitization derives from the fact that reaction is produced in the presence of the sensitizer in circumstances where the direct photochemical dissociation is not possible. The example just cited is a case in point. Radiation of wavelength 253.7 nm was absorbed by a mercury atom. The excited mercury atom dissociated a molecule of hydrogen by
transferring the excitation energy in a collision. The mercury atom had 471.5 k J; of this 432.0 k J were needed for the dissociation; 39.5 k J are left over and go into additional translational energy of the two hydrogen atoms and the mercury atom. If the attempt is made to dissociate H₂ directly by the process:

$$H_2 + hv \rightarrow H + H$$

We find that light of $\lambda = 253.7$ nm will not produce any dissociation even though it still has the 471.5 k J which is more than enough if we consider only the thermodynamics of the process. For the direct absorption to produce dissociation, the wavelength must lie in the absorption continuum; for H₂ the continuum begins at 84.9 nm. The absorption of light in the continuum produces at least one atom in an excited state:

$$H_2 + hv \rightarrow H + H^*, \quad \lambda \leq 84.9 \text{ nm}.$$  

The selection rules that govern the absorption of radiation forbid the direct absorption of a quantum by H₂ to yield two H atoms in their ground state, thus a quantum of light does not necessarily produce dissociation even though it may have sufficient energy. The quantum must have enough energy to produce the dissociation in the special way required by the selection rules. The transfer of energy in a collision is not limited by this requirement and so sensitization can produce dissociation. A practical example of photosensitization is in the use of certain dyes in photographic film to render the emulsion sensitive to wavelengths that are longer than those to which it ordinarily responds, e.g; infrared spectroscopy which permits photographs of objects in the absence of visible light.

**PHOTOCHEMICAL REACTION IN THE LIQUID PHASE**

Many substances undergo photochemical reactions when liquefied or dissolved in a solvent. Again such reactions may be initiated by direct light absorption on the part of the reactant or they may be photosensitized. It may be anticipated that the quantum yield of a photochemical process will be less in the liquid phase than for the same reaction in the gas phase. The reason for this is that in the liquid phase an active molecule or atom may readily be deactivated by frequent collisions with other molecules or by reaction with the solvent. Furthermore, because of the very short mean free path in the liquid phase, free radicals or atoms when formed photochemically will tend to recombine before they have a chance to get very far from each other. The net effect of these processes will be to keep the quantum yield relatively low. In fact, only those reactions may be expected to proceed to any extent for which the primary
products of the photochemical act are relatively stable particles. Otherwise the active intermediates will tend to recombine or react with the solvent and thereby, keep the yield low. For example, it has been estimated that for dissociation of iodine in hexane solution, the probability that the original pair recombines is about 0.5. This kind of recombination of pair that comes originally from the same parent molecule is called geminate recombination.

![Diagram](image)

The course of the reaction can be influenced by the addition to the solution of a scavenger or radical trap, i.e; a substance combining readily with free radicals. Scavengers frequently used have included iodine, vinyl monomers and diphenylpicryl-hydrazyl (DPPH).

The typical mechanism for a photolysis in a liquid in the presence of a scavenger S can thus be written as follows:

1. \( AB + h\nu \rightarrow (A + B) \) dissociation
2. \( (A + B) \rightarrow AB \) geminate recombination
3. \( (A + B) \rightarrow A + B \) separation by diffusion
4. \( A + S \rightarrow AS \) scavenging of radicals
   \( B + S \rightarrow BS \)
5. \( A + B \rightarrow AB \) recombination
6. \( A + X \rightarrow \) product, \( 2A \rightarrow A_2 \) reaction of Radicals
   \( B + X \rightarrow \) product, \( 2B \rightarrow B_2 \)

Table 6.1 gives the quantum yields of many instances in the gas and liquid phases. In every case except the last the yield is lower in the liquid phase than in the gas for the same
wavelength of irradiating light. However, in a number of reactions of which the photolysis of Ni (CO)₄ is an example, just the reverse is true. This reversal may be due to formation of intermediates of kinetic energy sufficiently high to separate them rapidly, thereby preventing their combination or to the specific effect of solvent which makes it inefficient as a deactivator. That solvents may exert specific effects is borne out by the observation that the same reaction conducted in different media may have different quantum efficiencies under the same conditions. Thus for the photolysis of ClO₂ at 4358 Å Φ = 1.0 in CCl₄ and only 0.20 in water.

Similarly the photolysis of N₂CH₂ COO C₂H₅ at 2600 Å gives Φ = 1.1 in heptane, 1.42 in methyl alcohol and 2.8 in water.

**Table 6.1**: Comparison of Φ in the gas and liquid phases.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Wave length Å</th>
<th>Quantum Yield</th>
<th>Gas</th>
<th>Liquid Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 NH₃ → N₂+3H₂</td>
<td>2100</td>
<td>0.14-0.32</td>
<td>0 (in liq NH₃)</td>
<td></td>
</tr>
<tr>
<td>CH₃ COOH → CH₄+CO₂&lt;2300</td>
<td></td>
<td>1</td>
<td>0.45 (in H₂O)</td>
<td></td>
</tr>
<tr>
<td>Cl₂O → Cl₂+ ½ O₂</td>
<td>4358</td>
<td>3.2</td>
<td>1.8 (in CCl₄)</td>
<td></td>
</tr>
<tr>
<td>NO₂ → NO+ ½ O₂</td>
<td>4050</td>
<td>0.50</td>
<td>0.03 (in CCl₄)</td>
<td></td>
</tr>
<tr>
<td>Pb (CH₃)₄ → Pb + 2C₂H₆</td>
<td>2357</td>
<td>1.1</td>
<td>0.4 (in hexane)</td>
<td></td>
</tr>
<tr>
<td>Ni (CO)₄ → Ni + 4CO</td>
<td>3010-3135</td>
<td>0</td>
<td>2.8 (in CCl₄)</td>
<td></td>
</tr>
</tbody>
</table>

In table 6.2 are given results for several other sensitized and non – sensitized reactions in solution.

**Table 6.2**: Further example of photochemical reactions in solution:

<table>
<thead>
<tr>
<th>Reaction Remarks</th>
<th>Solvent</th>
<th>Wave Length (Å)</th>
<th>Quantum Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 HI</td>
<td>H₂O</td>
<td>2070</td>
<td>0.34</td>
<td>Depends on Conc. and Wavelength</td>
</tr>
<tr>
<td>Cis-C₄H₆+I₂</td>
<td>CHCl₃</td>
<td>4360</td>
<td>2.48</td>
<td>each reactant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>At – 55°C</td>
</tr>
<tr>
<td>2 Fe⁺⁺⁺+I₂</td>
<td>H₂O</td>
<td>5790</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
ClCH₂COOH + H₂O → HOCH₂COOH, H₂O  
+HCl

H₂C₂O₂ → H₂O+CO+CO₂  
H₂O  

2 H₂O₂ → 2 H₂O+O₂  
H₂O  

<table>
<thead>
<tr>
<th>Sensitized</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>
| H₂C₂O₄     | → H₂O+CO+CO₂  
H₂O | 2540-4350 | 0.49-0.60 | 0.05 molar acid 0.01 molar UO⁺⁺ as sensitizer |
| 2 CCl₃Br+O₂ | → 2COCl₂+Br₂  
CCl₃Br | 4070-4360 | 0.9 Br₂ as Sensitizer |
| Maleic ester | → Fumaric ester  
CCl₄ | 4360 | 295 |

The mechanisms for some of these may be indicated. The quantum efficiency of unity for the Chloracetic acid reaction may be accounted by the simple sequence.

Cl CH₂ COOH + hν → Cl CH₂ COOH⁺
Cl CH₂ COOH⁺ + H₂O → HO CH₂ COOH + HCl

For the cis – butene iodination Forbes and Nelson found the rate to be

\[
\frac{dC_{C₄H₈I₂}}{dt} = kC_{C₄H₈I₂}C_{I₂}
\]

(6.1)

To deduce this rate law it is necessary to assume that the mechanism involved is

(a) I₂ + hv → 2 I
(b) I + C₄H₈ → C₄H₈I
(c) C₄H₈I + I₂ → C₄H₈I₂ + I
(d) C₄H₈I₂ + I → C₄H₈I + I₂
(e) I → \(\frac{1}{2}I₂\)

The reaction is initiated by formation of iodine atoms which subsequently become involved in reactions (b), (d) and (e). Step (c) however, operates to regenerate these. Further, it is necessary to postulate that step (b) proceeds in both directions. From these equations an expression Equivalent to the observed relation (6.1) may be derived.
PHOTOCHEMICAL EFFECTS (REACTIONS) IN SOLIDS

Solid substances may also be affected by light. Thus silver salts exposed to light tend to darken and sodium chloride crystals in UV light develop a yellowish tinge which can be removed by heating and dyes tend to fade in sunlight. e.g:

\[
\text{Ag Br: } \text{Ag} \quad \text{Br} + \text{hv} \quad \text{Ag} \quad \text{Br} \\
\]

The outstanding application of photolysis in the solid state is in photography. A photographic emulsion is a dispersion of finely divided silver chloride or bromide in a gelatin base. When such an emulsion is exposed to light the halides are acted upon to form an invisible latent image of density proportional to the light intensity. To make the image visible, it must be developed by treatment with a reducing agent which acts primarily on the exposed portion of the emulsion to yield a finely deposit of silver. A photographic plate thus developed is treated with a fixing agent, such as \( \text{Na}_2\text{S}_2\text{O}_3 \), to dissolve the undeveloped silver halide, but not the part exposed. On the resulting negative the portions that were lightest on the object photographed appear darkest and vice versa. To obtain from the negative a print in which the light densities are rectified the above process is repeated by photographing the negative. The exposure thus obtained will have when developed the light and dark portions of the negative reversed and these will correspond therefore, to the relative light and dark shadings of the original object.

Photographic emulsions consisting of silver halides alone are sensitive only to light near the UV to extend the range of sensitivity to longer wavelengths, various dyes which absorb in the yellow and red are incorporated into the emulsion. Photographic emulsions have also been developed which are sensitive to near – infrared radiation and thus make possible night photography.

The following effects were observed on irradiating thin nylon films (20 \( \mu \) thick) with UV light in the presence of oxygen:

a. Products formed in the “Thermal” (dark) and photochemical reactions are identical.

b. A new absorption band appears centered around 2,900 Å which continues to increase in intensity even in the dark.

c. On re – irradiation the band intensity falls rapidly to a value corresponding to that prior to the dark period. The isomerization of solid o-nitrobenzaldehyde to o-
nitrosobenzoic acid is a photo reaction with the efficiency 0.5, the effective radiation is in the range from 4360 to 3130 Å.

**EFFECT OF TEMPERATURE ON PHOTOCHEMICAL REACTION**

The effect of temperature on photochemical reactions is quite different from that on thermal ones. On thermal reactions an increase of 10°C in temperature generally leads to a two- or threefold increase in the rate. In photochemical reactions the same increase in temperature results as a rule in only a very small increase in rate. For most such reactions the temperature coefficient is not far from unity. Occasionally it does approach a value close to that for a thermal reaction as in the potassium oxalate–iodine reaction but such behavior is exceptional. Further, in some photochemical reactions of which the chlorination of benzene is an example, the unusual phenomenon of decrease in rate with temperature is encountered.

The primary light absorption process should be practically temperature-independent. Again, since secondary reactions in photochemical processes are thermal in character, there should have temperature coefficient akin to those of ordinary reactions. Most secondary reactions in photochemical processes involve interaction between atoms or free–radicals or of there with molecules. For such reactions the energy of activation is usually small or even zero. As the temperature coefficient of a reaction is determined by the magnitude of the activation energy, we may conclude that even for the secondary reactions the temperature coefficient should be smaller than for thermal ones involving only molecules. The net result should be, therefore, a small temperature coefficient for the overall process.

When a large temperature coefficient is observed in a photochemical reaction it is an indication that one or more of the intermediate steps have high activation energy. Another possibility is that some steps in the reaction sequence is an equilibrium whose variation with temperature involves an appreciable positive heat of reaction. Thus suppose that an observed velocity constant $k$ is composed of the product of a rate constant $k_1$ and an Equilibrium constant $K$

\[ k = k_1 K \]  \hspace{1cm} (6.2)

Take logarithms of both sides of Eq (6.2)

\[ \ln k = \ln k_1 K \]  \hspace{1cm} (6.3)

Differentiating with respect to temperature Eq (6.3) yields
\[
\frac{d \ln k}{dt} = \frac{d \ln k_1}{dt} + \frac{d \ln K}{dt}
\]  \hspace{1cm} (6.4)

The first term on the right of Eq (6.3) is \( \frac{E_a}{RT^2} \), where \( E_a \) is the energy of activation of the step involving \( k_1 \). Again, the second term is \( \frac{\Delta H}{RT^2} \), where \( \Delta H \) is the heat of the reaction for which \( K \) is the Equilibrium constant. Substitution of there into Eq(6.4) gives

\[
\frac{d \ln k}{dt} = \frac{E_a}{RT^2} + \frac{\Delta H}{RT^2}
\]

Or

\[
\frac{d \ln k}{dt} = \frac{E_a + \Delta H}{RT^2}
\]  \hspace{1cm} (6.5)

If \( E_a \) is small then a large positive \( \Delta H \) will give a large value for the quantity on the right in Eq (6.5) and hence the temperature coefficient will be large. On the other hand if \( \Delta H \) is negative and numerically greater than \( E_a \), then \( (E_a + \Delta H) \) will be negative and so will \( \frac{d \ln k}{dt} \), Under these conditions the reaction will have a negative temperature coefficient. This is the explanation for the decrease in rate with temperature observed in the photochemical chlorination of benzene and some other reactions of this type.

**PHOTOCHEMICAL EQUILIBRIUM**

If either or both the reactions in a reversible chemical change are sensitive to light a photochemical equilibrium or photo stationary state will be set up when the rates of direct and reverse reactions are equal. The position of the equilibrium will be different from the normal thermal equilibrium, since energy is being added to the system by the absorbed radiation, the photochemical equilibrium state will therefore, depend on the intensity and wavelength of the absorbed light. After the equilibrium condition is reached the absorbed light can produce no further chemical change and so it is converted into heat. A number of cases of the photochemical stationary state have been studied, they fall into two categories depending on whether light affects one or both of the reactions concerned.

Consider a reaction

\[
A + B \xrightarrow{\text{light}} C + D
\]  \hspace{1cm} (1)
Suppose, that the products are not photosensitive but that they combine in a thermal reaction to reform the reactants, namely,

\[ C + D \xrightarrow{\text{thermal}} A + B \]  

(2)

As there reactions proceed a state will eventually be reached in which thermal of the two become equal and the equilibrium

\[ A + B \xrightarrow{\text{light}} C + D \xrightarrow{\text{thermal}} \]

(3)

is established. Similarly, both forward and reverse reactions may be light sensitive in which case an equilibrium of the typ

\[ A + B \xrightarrow{\text{light}} C + D \]  

(4)

is attained. Equilibria such as (3) or (4) resulting from opposing processes in which one or both reactions are photosensitive are called photochemical equilibria. An example of the first of these is the dimerization of anthracene

\[ 2 \text{C}_{14}\text{H}_{10} \xrightarrow{\text{light}} \text{C}_{28}\text{H}_{20} \text{N}_{\text{thermal}} \]

(5)

and of the second the decomposition of SO\textsubscript{3}

\[ 2 \text{SO}_3 \xrightarrow{\text{light}} 2 \text{SO}_2 + \text{O}_2 \text{N}_{\text{light}} \]

(6)

The Equilibrium constants for photochemical equilibria are constants only for a given light intensity and vary as the latter is changed. Further, they do not correspond to the equilibrium constants obtained for the reactions under purely thermal conditions. For instance, thermal equilibrium calculations show that to obtain 30 percent dissociation of SO\textsubscript{3} at 1 atm pressure this substance must be heated to 630°C. On the other hand photochemically SO\textsubscript{3} may be dissociated about 35 percent at 45°C. Again, whereas the thermal equilibrium constant varies very markedly with temperature, the photochemical equilibrium constant was found at constant light intensity to be temperature – independent between 50 and 800°C. It is evident that the usual equilibrium considerations do not apply to photochemical reactions.

When NO\textsubscript{2} vapor is exposed to light of wavelength less than 3700Å, it decomposes into NO and O\textsubscript{2} the combination of these products is a simple thermal or dark, reaction and so the equilibrium

\[ 2 \text{NO}_2 \xleftrightarrow{\text{light}} 2 \text{NO} + \text{O}_2 \]
is set up. The pressure of the gas rises at first due to decomposition of the dioxide and then becomes constant when the stationary state is attained part of the increase of pressure is the result of an increase of temperature.

A number of other reversible processes in which one or both reactions are photochemical have been studied for example,

\[
\text{CO} + \text{Cl}_2 \leftrightarrow \text{COCl}_2; \quad 2 \text{CO} + \text{O}_2 \leftrightarrow 2 \text{CO}_2; \\
2 \text{H} \text{X} \leftrightarrow \text{H}_2 + \text{X}_2,
\]

where X is a halogen;

\[
\text{SO}_2 + \text{Cl}_2 \leftrightarrow \text{SO}_2\text{Cl}_2, \text{ and}
\]

fumaric acid \(\leftrightarrow\) maleic acid.

\[
\text{HOO\-CH} \quad \text{HC\-COOH}
\]

\[
\text{H} \text{C\-COOH} \quad \text{H} \text{C\-COOH}
\]

Fumaric acid \(\leftrightarrow\) Maleic acid.

In thermal equilibrium we are concerned only with the normal free energy relations of products and reactants as they apply to the conditions of these at the temperature and pressure in question. In photochemical equilibria these free energy relations are modified by the free energy supplied by the light. Addition of the latter changes the \(\Delta G^o\) of the reaction and thereby also the equilibrium constant.

**PHOTOSYNTHESIS IN PLANTS**

The most important photochemical reaction in the world is the union of \(\text{CO}_2\) and \(\text{H}_2\text{O}\) in plants through the agency of sunlight and chlorophyll. Chlorophyll which gives plants their green color is a complex organic compound containing magnesium. It absorbs red and blue light and to a lesser extend green light. The activated chlorophyll thus formed is responsible for the production of carbohydrates from \(\text{CO}_2\) and \(\text{H}_2\text{O}\) of the starting material of all plants growth.

The important primary reaction involved in the growth of plants may be represented by the equation

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{light} + \text{chlorophyll} \rightarrow \frac{1}{n} \left(\text{CH}_2\text{O}\right)_n + \text{O}_2 + \text{Chlorophyl}
\]
Where \((CH_2O)\) represents a carbohydrate such as cellulose or sugar. When cellulose is burnt the reaction is

\[
\left[ \frac{1}{n} \right] (CH_2O)_n + O_2 \rightarrow CO_2 + H_2O \quad \Delta H = -112 \text{ k cal mol}^{-1}
\]

The endothermic formation of carbohydrates from \(CO_2\) and \(H_2O\) must require therefore, the absorption of 112 k cal mol\(^{-1}\), and the activation energy must be at least as great as this. The activation energy is equivalent to radiation 2300 Å or less. There is no radiation as short as this in the sunlight that reaches the earth’s surface and moreover, \(CO_2\) and \(H_2O\) are both transparent down to even shorter wavelengths.

Chlorophyll, acts as a photosensitizer, absorbing visible light and making it available for photosynthesis in the plant. But there is something unique about the reaction. Red light will cause photosynthesis, but red light corresponds to only 40,000 calories per mole and more than 112,000 calories are required to bring about the reaction obviously three or more photons must be utilized. The reaction takes place in steps. Laboratory experiments with algae have shown that normally about light photons are required for each \(CO_2\) molecule utilized and each \(O_2\) molecule evolved in photosynthesis.

Green plants as well as certain protozoa and bacteria, can carry out photochemical reactions having as a net result the conversion of solar radiant energy to chemical free energy stored in the form of carbohydrates and other products. It has been estimated that the annual photosynthetic yield of organic matter over the surface of the earth is at least \(10^{13}\) kg. The photosynthetic reaction is usually considered to consist of two stages, the reduction of \(H_2O\) with liberation of \(O_2\)

\[
H_2O \rightarrow 2 H + \frac{1}{2} O_2
\]

and the use of activated hydrogen to reduce \(CO_2\)

\[
2 CO_2 + 4 H \rightarrow 2 (CH_2O).
\]

It is known from studies with \(H_2O^{18}\), that all the \(O_2\) liberated does come from the water.
Exercise

A. Fill In the blanks with suitable words

1. The Quenching of fluorescence is due to from the excited atom to the particle with which it collides.

2. In the quenching of mercury fluorescence is most effective, followed by hydrogen and CO.

3. If tetramethylethylene is adding to the trans-stilbene; it must quench the fluorescence.

4. Photosensitization was first discovered by in 1922.

5. If a mixture of hydrogen, oxygen and mercury vapor is exposed to UV light, the vapor absorbs strongly at ____________.

6. Chlorophyll, acts as a, absorbing visible light and making it available for photosynthesis in the plant.

B. Write Short answers for following questions

1. Differentiate photochemical equilibrium or photo stationary and thermal equilibrium

2. What are the major types of Photographic emulsions?

3. What is the effect of photochemical reactions in liquid phase?

4. Write short note on the importance of photosensitization?

5. Briefly describe the quenching process in photochemical reactions.

C. Define the following terms

1. stern – volmer plot

2. geminate recombination

3. Photographic emulsions

4. Stoss Zweiter Art in photosensitization
CHAPTER 7
CHEMILUMINESCENCE

Luminescence occurring as a result of chemical reaction. Part of the energy of the reaction is taken up by exciting the electrons so that molecules of one of the products appear in excited states from which they decay by emission of light. Luminal, for example is a crystalline compound that emits blue light when oxidized with H$_2$O$_2$. Since the reaction may be proceeding at ordinary temperatures the light emitted is sometimes called “cold light” to contrast it with the “hot light” emitted by a flame or incandescent body. The chemiluminescence may be regarded as the reverse of a photochemical reaction which proceed by absorption of light. Some chemiluminescence processes are described here.

The reactions which can be carried out in the laboratory the most spectacular is the oxidation of alkaline aqueous solution of ortho-aminophthalic cyclic hydrazide. This substance is a pale yellow crystalline powder and has the formula.

\[
\text{NH}_2\text{CO.NH.CO.NH}
\]

When the hydrazide is dissolved in caustic soda and a little hydrogen peroxide is added and the liquid dropped from a dropping funnel into an alkaline solution of potassium ferricyanide as each drop enters the ferricyanide a bright greenish glow is produced. If sodium hypochlorite is substituted for the potassium ferricyanide the glow is bluish. The chemical changes are complex but the final product is ortho-amino-phthalic acid

\[
\text{NH}_2\text{COOH}
\]

A reaction in which a feeble glow is emitted is the precipitation of strontium sulphate. A solution of strontium chloride is made and dilute H$_2$SO$_4$ is added to it in a dark room.

When a stream of atomic hydrogen falls on a surface of liquid mercury a blue luminescence appears the spectrum consisting of the resonance line 2537 Å; and a bond system from 4500 to 3250 Å due to mercury hydride HgH. It does not appear that cold liquid mercury
must be used since the vapor gives no luminescence, nor does the liquid if its temperature is raised.

The combination of hydrogen atoms in the presence of sodium vapor results in the emission of the D – lines of the sodium spectrum the energy of the excited level is only 48 kcal g\(^{-1}\) atom, which is less than that given out in the formation of molecular hydrogen. The “glow” of active nitrogen belongs to the same type of reaction. When two nitrogen atoms combine a three-body collision is necessary and if a nitrogen molecule is involved it is raised to a high electronic level, on returning to the ground state the characteristic glow is emitted.

Alkali metal vapors react with halogens and with organic halides at low pressures, and as a result a luminescence consisting of the spectrum of the metal is produced. In order to account for the observations it is necessary to postulate a somewhat complex mechanism of three stages in the second of which i.e; between Na\(_2\) molecules and Cl atoms, sufficient energy is obtained by the NaCl molecule for it to excite a sodium atom on collision, thus

\[
\text{Na Cl}^* + \text{Na} \rightarrow \text{Na Cl} + \text{Na}^*
\]
on returning to its normal state the excited atom emits its characteristic spectrum. Similar luminescence occurs in the reaction between sodium or potassium vapor and HgCl\(_2\) vapor at very low pressures.

The most highly luminescent reaction that has yet been observed is the oxidation of the unsaturated silicon compound silical hydroxide, Si\(_2\)O\(_2\)H\(_2\) by means of permanganate. In this case the surface luminosity is equivalent to that of a white surface illuminated at a distance of 1.5 meters by a 32 candle – power lamp.

The greenish glow of slowly oxidizing phosphorous is apparently due to the formation of an oxide in an excited state. In conclusion reference may be made to the cold light produced by certain living organisms e.g fire – flies, glow – worms, certain bacteria and many deep sea – animals. The light emission from the fire – fly appears to be the most efficient as judged by eye because it has a maximum intensity at a wavelength of 5700 Å at which the eye is most sensitive. In fireflies, as enzyme in the abdomen works to produce bioluminescence. The glow of fireflies is due to the aerial oxidation of luciferon on (a protein) in the presence of enzyme luciferase. The light emitted by some micro – organisms in the course of metabolism, bioluminescence are other examples of chemiluminescence. In bioluminescence, the compound luciferin is oxidized with high efficiency by the enzyme luciferare. The phosphorescence observed in marshy areas is apparently due to a slow oxidation of rotting organic material. For example, the oxidation of 5-
aminophthalic cyclic hydrazide (Luminol) by $\text{H}_2\text{O}_2$ in alkaline solution, producing bright green light.

**PHOTOPHYSICAL PROCESSES: FLUORESCENCE AND PHOSPHORESCENCE**

Much of the photochemistry is in fact concerned with the phenomena of fluorescence and phosphorescence in systems that do not undergo any chemical change. Since all of the electrons are paired in the ground state of most molecules the result of the absorption of a quantum of radiation is to unpair two electrons and produce an excited electronic state that is either a singlet (opposite spin) or a triplet (same spin). The energy levels of the molecule then divide, much like the levels of the alkaline earth atoms, into a system of singlet levels and a system of triplet levels. At least some of these excited states are bound states that will have vibrational and rotational levels associated with them. A typical arrangement of the molecular levels is shown schematically in a Jablonski diagram (Fig. 7.1). The vertical axis measures the energy of the system, the horizontal axis simply spreads the figure for the sake of clarity.

The singlet and triplet electronic levels are labeled $S$ and $T$, respectively. Subscripts indicate the order of increasing energy the subscript $v$ indicates that a molecule has an excess vibrational energy absence of a subscript indicates that the vibrational energy of the molecule is in thermal equilibrium a zero subscript indicates that a molecule is in the lowest vibrational level. For clarity the vibrational and rotational levels are shown equally spaced. If the system is initially in the ground state, $S_0$, the only quanta that it can absorb are those which raise it to some level in another singlet state, $S_1$, or $S_2$ in the diagram. Because of the Frank – Condon requirement the molecule will most likely be in an excited vibrational state such as $S_1^v$ or $S_2^v$. Let us assume that the molecule is in the $S_2^v$ state and examine the various possibilities.

The thermal equilibration of the vibrational energy within the electronic level $S_2$ occurs rapidly, this is represented by the wavy arrow ending at $S_2$. The nonradiative transition from $S_2$ to $S_1^v$ is also rapid; this is represented by the wavy horizontal arrow and is called internal conversion (IC). Note that there is no change in energy in this process, whereas the equilibration of the vibrational energy entails a loss of energy and therefore, equires one or more collisions to carry off the excess energy. From the level of $S_1^v$ there is again a rapid equilibration of the vibrational energy via collision. In practice, this means that after equilibration the system will
most probably be in the ground vibrational level of \( S_1 \) since the vibrational level spacing is large enough to keep all but a few of the molecules from occupying the upper states.

Having reached the lowest level in \( S_1 \), the system has three paths available for return to the ground state, \( S_o \).

Fig. 7.1: Jablonski diagram. Excited states and Photophysical transitions between these states in a “typical” organic molecule. Radiative transitions between states are given by solid lines, radiationless process by wavy lines; IC = internal conversion, ISC = intersystem crossing. Vertical wavy lines are vibrational relaxation processes. Vibrational and rotational levels are shown approximately equally spaced for convenience in presentation.

**Path 1:**

Radiative transition with emission of a quantum of fluorescent radiation \( h \nu \). The fluorescent radiation has a lower frequency than that of the absorbed light which raised the system from \( S_o \) to \( S_2^\nu \). Since the transition \( S_1 \rightarrow S_o \) is permitted by the selection rules, it is very rapid. Since it drains the excited level very rapidly, it ceases almost immediately after the exciting radiation, which supplies population to the upper state is extinguished.

**Path 2:**

Non-radiative crossing to \( T_1^\nu \) followed by rapid vibrational equilibration to \( T_1 \). This is followed by a radiative transition \( T_1 \rightarrow S_o \). The radiation emitted is called phosphorescence. The non-radiative intersystem crossing (ISC) is much slower than the vibrational equilibrations, but competes with the fluorescent emission in the molecules that exhibit phosphorescence. The radiative transition \( T_1 S_o \) is usually very slow since the triplet-singlet transition is spin – forbidden by the selection rules. Consequently, the phosphorescence persists for some time after the exciting radiation is turned off.

**Path 3a:**

Non – radiative internal conversion to \( S_o^\nu \) and rapid thermilization of the vibrational energy to bring the system to \( S_o \).

**3 b:**

Non – radiative quenching of \( S_1 \) by collision. We can describe the system under steady illumination by writing the rate equation for each process.
<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>( S_o + h\nu )</td>
<td>( \rightarrow S_1 ) ( I_a )</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>( S_1 S_o + h\phi )</td>
<td>( \rightarrow ) ( A_{10}[S_1] )</td>
</tr>
<tr>
<td>Fluorescence quenching</td>
<td>( S_1 + M )</td>
<td>( \rightarrow S_o + M ) ( k_q^F[S_1][M] )</td>
</tr>
<tr>
<td>Internal conversion</td>
<td>( S_1 )</td>
<td>( \rightarrow S_o ) ( k_{ic}^F[S_1] )</td>
</tr>
<tr>
<td>Intersystem crossing</td>
<td>( S_1 T_1 )</td>
<td>( \rightarrow S_o + h\nu S ) ( k_{ic}^F[S_1] )</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>( T_1 )</td>
<td>( \rightarrow S_o + h\nu^z ) ( A_{TS}[T_1] )</td>
</tr>
<tr>
<td>Phosphorescence quenching</td>
<td>( T_1 + M )</td>
<td>( \rightarrow S_o + M ) ( k_q^F[T_1][M] )</td>
</tr>
<tr>
<td>Intersystem crossing</td>
<td>( T_1 )</td>
<td>( \rightarrow S_o ) ( k_{ISC}^F[T_1] )</td>
</tr>
</tbody>
</table>

The k’s are the rate constants for the various processes; the \( A_{10} \) and \( A_{TS} \) are the Einstein coefficients for spontaneous emission. In this mechanism, M is intended to represent any atom or molecule that may be present. Then \([M]\), the concentration of M, is proportional to the total concentration of all the species in solution; in the gas phase, \([M]\) is proportional to the total pressure.

The emitted intensity of fluorescence, \( I_{em}^F \) is given by

\[
I_{em}^F = A_{10}[S_1] \tag{7.9}
\]

If the system is under steady illumination, the \([S_1]\) and \([T_1]\) do not vary with time; the steady state conditions are

\[
\frac{d[S_1]}{dt} = 0 = I_a - A_{10}[S_1] - k_q^F[S_1][M] - k_{ic}^F[S_1] - k_{ISC}^F[S_1] \tag{7.10}
\]

And

\[
\frac{d[T_1]}{dt} = 0 = k_{ISC}^S[S_1] - A_{TS}[T_1] - k_q^P[T_1][M] - k_{ISC}^P[T_1] \tag{7.11}
\]

we define \( \tau_F \), the fluorescence lifetime and \( \tau_P \) the phosphorescence lifetime by

\[
\frac{1}{\tau_F} = A_{10} + k_{ic}^F + k_{ISC}^S + k_q^F[M] \tag{7.12}
\]

And
\[
\frac{1}{\tau_F} = A_{Ts} + k_{ISC}^T + k_q^F[M] \tag{7.13}
\]

These definitions reduce Eqs (7.10), (7.11) to

\[
\frac{d[S_1]}{dt} = 0 = I_a - \frac{S_1}{\tau_F} \tag{7.14}
\]

And

\[
\frac{d[T_1]}{dt} = 0 = k_{ISC}^s[S_1] - \frac{[T_1]}{\tau_p} \tag{7.15}
\]

solving these two equations for \([S_1]\) and \([T_1]\) yields

\[
[S_1] = \tau_F I_a; [T_1] = k_{ISC}^s \tau_F \tau_p I_a \tag{7.16}
\]

using this value of \([S_1]\) in the expression in Eq (7.9), we obtain for the fluorescence intensity,

\[
I_{em}^F = A_{10} \tau_F I_a \tag{7.17}
\]

and for the quantum yield,

\[
\Phi_F = \frac{I_{em}^F}{I_a} = A_{10} \tau_F \tag{7.18}
\]

If we invert Eq (7.17) and use the value in Eq (7.12) for \(T_F\) we find that

\[
\frac{1}{I_{em}^F} = \frac{1}{I_a} \left(1 + \frac{k_{IC}^s + k_{ISC}^s}{A_{10}}\right) + \frac{k_q^F[M]}{A_{10} I_a} \tag{7.19}
\]

A plot of \(1/I_{em}^F\) versus \([M]\), called a stern-volmer plot, should yield a straight line. From the measured value of \(I_a\) and a value of \(A_{10}\) we can obtain the quenching constant \(k_q^F\). The constant \(A_{10}\) can be calculated from the measurement of the molar absorption coefficient of the absorption band.

If the system does not exhibit phosphorescence this implies that \(k_{ISC}^s = 0\). Then the value of \(k_{IC}^s\) can be determined from the intercept of the stern – volmer plot if \(A_{10}\) is known.

If phosphorescence does occur, then
The value of \([T_1]\) is given by Eq(7.16) so that

\[
I_{em}^p = A_{TS} \left[ T_1 \right] \tag{7.20}
\]

The quantum yield for phosphorescence is

\[
\Phi = \frac{I_{em}^p}{I_a} = A_{TS} k_{ISC}^s \tau_F \tau_P \tag{7.21}
\]

Using Eq (7.18) we can write this in the form

\[
\Phi_p = \Phi_F \left[ \frac{A_{TS}}{A_{10}} \right] k_{ISC}^s \tau_P \tag{7.23}
\]

By inverting this equation and using the value in Eq (7.13) for \(T_p\), we have

\[
\frac{1}{\Phi_p} = \frac{1}{\Phi_F} \left[ \frac{A_{10}}{A_{TS}} \right] \left\{ A_{TS} + k_{ISC}^T + k_q^p [M] \right\} k_{ISC}^S \tag{7.24}
\]

If both \(\Phi_F\) and \(\Phi_P\) have been measured as a function of the total concentration, [M] a stern-volmer plot of \(\frac{1}{\Phi_p}\) versus [M] can yield the quenching cross – section for phosphorescence and the ratio,

\[
\frac{k_{ISC}^T}{k_{ISC}^S},
\]

If the Einstein coefficients are known.

**FLUORESCENCE AND PHOSPHORESCENCE:**

**The Fates of Electronically Excited States:** The energy of an electronically excited state may be lost in a variety of ways. A radiative decay process is a process in which a molecule discards its excitation energy as a photon. A more common fate is non – radiative decay, in which the excess energy is transferred into the vibration, rotation and translation of the surrounding molecules. This thermal degradation converts the excitation energy into thermal motion of the environment (i.e; to “heat”). An excited molecule can take part in a chemical reaction.

**Spin-orbit coupling:** The interaction of the spin and orbital magnetic moments is called spin – orbit coupling.
FLUORESCENCE

After a molecule has absorbed a photon and is raised to an activated state, it may emit part or all of this extra energy as radiation. If the emission takes place because of a transition to a state of like multiplicity the process is called fluorescence. Usually the emission follows less than $10^{-8}$ second after the absorption. If spin inversion is involved, so that the multiplicity changes the process takes longer and is called phosphorescence. The name fluorescence was adopted because fluorite, Ca F$_2$, exhibits this phenomenon in a striking way. Many organic compounds also show fluorescence, including chlorophyll and dyes such as eosin and fluorescein; a number of inorganic vapors also fluorescence like sodium, mercury and iodine. Phosphorescence is more likely to occur in solids, such as the sulfides of the alkaline earths. Fluorescence stops as soon as the incident radiation is cut off.

THEORY

G.B. Beccari, an Italian Physician, reported in 1757 that he had observed his hand glowing in a dark room shortly after exposure to intense sunlight. During the nineteenth and early twentieth century extensive studies were made of this afterglow, especially when induced by ultraviolet light. With the advent of modern atomic theory, fluorescence has become a valuable tool for investigating the nature of excited states. In most molecules the absorption of UV and visible radiation raises electrons to higher energy states, from a singlet ground state to a singlet excited state. There will usually be a triplet state somewhat below this excited singlet. In the electronic excitation one electron from an electron pair bond is excited to a higher. If the excited electron has a spin antiparallel to that of its mate, the state is a triplet.
A typical situation is shown in Fig. 7.1. The Fig shows the excitation of a molecule into a particular vibrational level in one of its higher electronic states. A common sequel to this event is for the molecule to drop to the v=0 level of the excited electronic state by a process of internal conversion in which surplus energy transferred to other degrees of freedom of the molecule without the emission of radiation. At this point, the molecule may return to the ground electronic state by the emission of radiation of lower frequency than was originally absorbed; this is the process of fluorescence. Certain dyestuffs are capable, by virtue of fluorescence, of absorbing invisible ultraviolet radiation and re-emitting visible frequencies of great brilliance. The vivid oranges and greens of fluorescence dyes are an everyday manifestation.

Fig. 7.1: The molecular energy levels concerned in photochemical processes are represented by a generalized Jablonski diagram. Deactivation processes for electronically excited molecules are shown.
of this effect: they absorb in the UV and blue, and fluorescence in the visible. The mechanism also suggests that the intensity of the fluorescence ought to depend on the ability of the solvent molecules to accept the electronic and vibrational quanta. It is found that a solvent composed of molecules with widely spaced vibrational levels (such as water) can in some cases accept the large quantum of electronic energy and so extinguish or “quench” the fluorescence. The fluorescence spectra of proteins have yielded valuable information about their structure. Extensive studies have been made of the fluorescence due to the presence of tryptophan and the evidence indicates that this ring differs widely in its physicochemical state depending on the particular protein in which it is present.

**Examples:**

(a). A solution of quinine sulphate on exposure to visible light, exhibits blue fluorescence.

(b). A solution of chlorophyll in ether shows blood red fluorescence.

The colour of fluorescence depends on the wavelength of light emitted.

**PHOSPHORESCENCE:**

Fig. 7.3: shows the sequence of events leading to phosphorescence. The first steps are the same as in fluorescence (Fig. 7.1) but the presence of a triplet excited state plays a decisive role. (The triplet states are states in which two electrons have parallel spins).

The singlet and triplet excited states share a common geometry at the point where their potential energy curves intersect Hence, if there is a mechanism for unparing two electron spins (and achieving the conversion of ↑ ↓ to ↑ ↑), the molecule may undergo intersystem crossing and become a triplet state. The singlet triplet transition may occur in the presence of spin – orbit coupling and the same is true in molecules. We can expect intersystem crossing to be important when a molecule contains a moderately heavy atom (such as S), because then the spin-orbit coupling is large.

If an excited molecule crosses into a triplet state, it continues to deposit energy into the surroundings and to step down the vibrational ladder. It is now stepping down the triplet’s ladder, and at the lowest vibrational energy level it is trapped because the triplet state is at a lower energy than the corresponding singlet. According to the nomenclature introduced by G.N. Lewis, a
radiative transition between two states of different multiplicity (usually triplet to singlet) is called phosphorescence. The origin of phosphorescence in a metastable state below the lowest excited singlet level was first suggested by Jablonski in 1935. Phosphorescence is more likely to occur in solids such as the sulfides of the alkaline earths. Phosphorescence occurs over periods that may extend into seconds. In fluorescence, the spontaneously emitted radiation ceases immediately after the exciting radiation is extinguished. In phosphorescence, the spontaneous emission may persist for long periods (even hours, but characteristically seconds or fractions of seconds). The mechanism of phosphorescence accounts for the observation that the excitation energy seems to get trapped in a slowly leaking reservoir.

It also suggests that phosphorescence should be most intense from solid samples: energy transfer is then less efficient and the intersystem crossing has time to occur as the singlet excited state steps slowly past the intersection point. The mechanism also suggests that the phosphorescence efficiency should depend on the presence of a moderately heavy atom (with strong spin–orbit coupling) which is in fact the case. The confirmation of the mechanism is the experimental observation (using the sensitive resonance techniques) that the sample is paramagnetic while the reservoir state, with its unpaired electron spins is populated.
Fig. 7.2: The sequence of steps leading to phosphorescence. The important step is the intersystem crossing the switch from singlet to triplet state brought about by spin – orbit coupling. The triplet state acts as a slowly radiating reservoir because the return to the ground state is spin-forbidden.

The various types of non – radiative and radiative transitions that can occur in molecules are often represented on a Jablonski diagram of the type shown in Fig. 7.3.

The substance which shows phosphorescence is called phosphorescent substance.

Examples:
(a). CaSO₄, BaSO₄ and Sr SO₄ exhibit phosphorescence.
(b). Fluorescein in boric acid shows phosphorescence in blue region at $\lambda = 5700$ Å.

Phosphorescence is mainly caused by UV-VIS light. It is generally shown by solids.
Figure 7.3. Jablonski diagram showing naphthalene absorption, fluorescence, and phosphorescence. The wavy lines indicate radiationless transitions; the closely spaced lines represent the vibrational levels.

Fig. 7.3: A Jablonski diagram (here, for naphthalene) is a simplified portrayal of the relative positions of the electronic energy levels of a molecule. Vibrational levels of states of a given electronic state lie above each other, but the relative horizontal locations of the columns bear no relation to the nuclear separations in the states. The ground vibrational states of each electronic state are correctly located vertically but the other vibrational states are shown only schematically.
1 - excitation
2 - vibronic relaxation
3 - fluorescence
4 - radiationless conversion
5 - inter system crossing
6 - triplet state relaxation
7 - phosphorescence
8 - relaxation to a singlet state
9 - relaxation to the ground state
10 - nonradiative energy transfer
CHAPTER 8

APPLICATIONS OF PHOTOCHEMISTRY IN ENVIRONMENTAL SCIENCES

Photochemical Process

Photochemical process uses UV radiations to excite a semiconductor by light. The oxidizing species either free holes or hydroxyl radicals (bound) are generated under these conditions. The semiconductor may be attached on the support or in fine suspended particles in the water. The most energetic photocatalysts for this purpose is the TiO$_2$ because of its low cost, good performance, high stability and no self-diffusion process (Andreozzi et al. 1999). The photocatalytic process starts by absorbing UV radiation that is equal or higher than the band gap energy onto the TiO$_2$ particles. This generates a photogeneration of electron pairs and holes in the semiconductor (Figure. 1). These excited electrons and holes can either recombine or can be used further in the oxidation and reduction process. The excited electrons and holes react with the adsorbed electron acceptor or donor species on the surface of semiconductor in these reactions (Bard, 1979).

Figure 9.1: Mechanism taking place on the surface of semiconductor (Kaneko and Okura, 2003)
An electrical field is created at the semiconductor/liquid junction of the solid side that separates the electrons pairs/energized holes thus allowing the electron and holes to move in separate direction (Heller, 1981). In photocatalytic degradation the first step initiates by hole trapping with the production of short-lived and very reactive hydroxyl radicals. The hydroxyl radicals are produced either in the highly hydroxylated semiconductor surface or by direct oxidation of the organic pollutant in Ultraviolet radiations. At the same time, the reduction of adsorbed oxygen species takes place, derived either from dissolved oxygen molecules in the aqueous system or by other electron acceptors available in the aqueous system (Turchi and Ollis, 1990; Puma et al. 2008). The heterogeneous photocatalytic oxidation mechanism is shown below;

\[
\text{TiO}_2 + hv \rightarrow \text{TiO}_2(h_{VB}^+ + e_{CB}^-) \tag{1}
\]

\[
\text{TiO}_2(h_{VB}^+) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \cdot\text{OH} + \text{H}^+ \tag{2}
\]

\[
\text{TiO}_2(h_{VB}^+)+ \text{OH}^- \rightarrow \text{TiO}_2 + \cdot\text{OH} \tag{3}
\]

\[
\text{TiO}_2(e_{CB}^-) + \text{O}_2 \rightarrow \cdot\text{O}_2^- + \text{TiO}_2 \tag{4}
\]

\[
\cdot\text{O}_2^- + \text{H}^+ \rightarrow \cdot\text{HO}_2 \tag{5}
\]

\[
\cdot\text{OH} + \text{Dye} \rightarrow \text{degraded products} \tag{7}
\]

\[
(h_{VB}^+) + \text{Dye} \rightarrow \text{oxidized products} \tag{8}
\]

\[
(e_{CB}^-) + \text{Dye} \rightarrow \text{reduced products} \tag{9}
\]

Various organic pollutants are attacked and oxidized by radicals formed according to the above mechanisms. Color and organic dyes removal by photocatalytic degradation is a promising and an efficient technique. The UV irradiation in titanium dioxide presence resulted in the decomposition of various organic compounds thus forming water, mineral acids or carbon dioxide (Kaur, 2007).

**Photocatalysts**

Research over the last three decades has not only confirmed the capability of sunlight for detoxification and disinfection but also has accelerated the natural process by the use of catalysts. The valence band (VB) oxidation potential must be higher than the material
under investigation for occurring oxidizing reactions. The valence and conductance band redox potential ranged from -1.5 and +4.0 volts opposed to normal hydrogen electrode for different semiconductors. Therefore, variety of species can be treated by Advanced Oxidation Process (AOP) by selecting different semiconductor photocatalysts. Different types of semiconductor materials appropriate for photocatalytic purposes are metal oxides and sulphides. Some of the important semiconductors that are using in photocatalytic reactions, with the properties of the band gap energy, CB and VB potentials, and the wavelength required for the activation of catalyst producing this gap are listed in Table 1, the radiation must be of an equal or lower wavelength than that calculated by that Planck’s equation (Eq. 10) (Kaur, 2007).

\[ \lambda = \frac{hc}{E_{bg}} \]  

(10)

where \( h \) = constant (Plank’s 6.626 x 10\(^{-34}\) J s), \( \lambda \) = wave length, \( c \) = the speed of light and \( E_{bg} \) = band-gap energy of semiconductor.

In variety of environmental applications, TiO\(_2\) is proved to be the most suitable semiconductors as compared to the listed semiconductors. Zinc oxide emerges also as an appropriate semiconductor but it cannot be used for practical applications due to its dissolution in acidic solutions. Other semiconductors (e.g. CdS) can form chemically activated surface-bond intermediates by absorbing larger portions of the solar radiations than TiO\(_2\), but unfortunately these catalysts can be degraded in heterogeneous photocatalysis during the repetitive cycles (Kaur, 2007).

Table 1: Band positions of some common semiconductor photocatalysts in aqueous solution (Kaur, 2007)

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Conductance band</th>
<th>Valance band</th>
<th>Band gap (eV)</th>
<th>Band gap wave length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>-0.1</td>
<td>+3.1</td>
<td>3.2</td>
<td>390</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>+0.3</td>
<td>+4.1</td>
<td>3.9</td>
<td>318</td>
</tr>
<tr>
<td>ZnO</td>
<td>-0.2</td>
<td>+3.0</td>
<td>3.2</td>
<td>390</td>
</tr>
</tbody>
</table>
Titanium dioxide as an ideal catalyst

Titanium dioxide is close to being an ideal photocatalysts in several aspects. It is the most efficient semiconductor/photocatalysts and frequently used in sun blocks or in vitamin tablets as a builder, pigment and cosmetic. It is chemically and biologically inert, do not corrode during photochemical reactions and is cheap as compare to other catalysts. Brookite, rutile and anatase are the crystalline forms of titanium dioxide. Among three the rutile and anatase are commonly used forms and the latter is being used mostly in treating wastewaters. However, the rutile and anatase band gap energies are about 3.0 eV and 3.2 eV respectively but the oxidation dynamic strength is comparable. Rutile is more stable than anatase thermodynamically, but at low temperature (<600 °C) the anatase formation is kinetically favored that can clarify its high surface density for active sites with its surface area for catalysis and adsorption. Moreover, TiO₂ is of unique importance as it can absorb UV radiation from sun. This is or the reason that titanium dioxide has a proper separation phenomenon among its different bands that can be exceeded via photons of solar energy (Kaur, 2007).

The conspicuous drawback of semiconductors is after excitation the photo-generated charge carriers depict a high rate of recombination. The electron-hole recombination declines the overall efficiency of the semiconductor by decreasing the quantum yield of the desired oxidation/reduction processes. The use of ultraviolet region of solar spectrum constitutes a subsequent problem because the earth receives only 4-6% of this excitation light. The said constraint is reduced by catalysts modification process, photosensitization and metal ions doping by various colored inorganic and organic compounds to cause a red shift in semiconductors light response (Kaur, 2007). Therefore, research on catalyst improvement has been done on the following points:

1. Physical and chemical modification of TiO₂ to improve the catalyst performance.
2. Dye sensitization to increase the useful wavelength range of the solar radiation.

The photo-sensitization mechanism of dye molecules by TiO$_2$ can be summarized as under:

\[
\text{Dye} + \text{hv} \rightarrow \text{dye}^* \quad (11)
\]
\[
\text{dye}^* + \text{TiO}_2 \rightarrow \text{TiO}_2(\text{e}^-) + \text{dye}^- \quad (12)
\]
\[
\text{TiO}_2(\text{e}^-)+ \text{O}_2 \rightarrow \text{O}_2^- + \text{TiO}_2 \quad (13)
\]
\[
\text{O}_2^- + \text{TiO}_2(\text{e}^-) + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{TiO}_2 \quad (14)
\]
\[
2\text{O}_2^- + 2\text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (15)
\]
\[
\text{H}_2\text{O}_2 + \text{TiO}_2(\text{e}^-) \rightarrow \text{HO}^- + \text{TiO}_2 + \cdot \text{OH} \quad (16)
\]
\[
\text{dye}^- + (\text{O}_2^-, \text{O}_2, \cdot \text{OH}) \rightarrow \text{peroxide or hydroxyl intermediate /degraded products} \quad (17)
\]

The oxidation potential of sensitizer is higher as compare to the conductance band of titanium dioxide, and under the irradiation of visible light the adsorbed dye follows the preliminary excitation. The electron is then transferred from the dye’s excited state to the titanium dioxide’s conduction band. If the regeneration step is eradicated carefully than oxidative degradation of the dye can possibly be initiated. Different variety of dye compounds have been studied as photosensitizers. Many recent reports showed the catalysts surface photo-excitation based decomposition is a significant method for treating dye containing wastewaters (Kaur, 2007).

**Photocatalytic oxidation**

The degradation and removal of organic contaminants by a photocatalytic oxidation process has been found as substitute or supplement method (Ollis et al. 1991; Muneer et al. 1997). Xia et al studied the activity of La$^{3+}$/S/TiO$_2$ co-doped photocatalysts on photo degradation of RB 19 under irradiation of visible light. The results showed that the S/La$^{3+}$/TiO$_2$photocatalysts showed highest absorption and activities in the visible range for degradation of RB 19 in sample (Xia et al. 2008). Decolorization of RB 19 is very efficient by advance
oxidation process under hydrogen peroxide/UV and increasing hydrogen peroxide concentration the rate of decolorization increases (Rezaee et al. 2008c).

Rezaee et al reported photochemical oxidation processes (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/UV-A, K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/UV-C) and chemical oxidation processes (dark/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) for RB 19 decolorization and found that UV-C/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} is much more effective as compared to (dark/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) and UV-A/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} processes (Rezaee et al. 2008a). Verma and Ghaly investigated the decolorization of Remazol Brilliant Blue dye in synthetic effluent by photo reactor, which consisted on; a UV lamp (low range) and a TiO\textsubscript{2} coated spiral coil. They tested the decolorization activity with separate techniques and then compared the results with combined techniques and concluded the result that this dye can better be degraded with combined techniques (Verma and Ghaly, 2008).

The photocatalytic discoloration of RB 19 was investigated in aqueous suspension of TiO\textsubscript{2} and ZnO (Lizama et al. 2002). The reactions were described in terms of pH amount of catalyst and the dye concentration it was reported that ZnO has greater degradation activity than TiO\textsubscript{2}. Lizama et al studied that the reactive dyes degradation (yellow 2, orange 16, red 2, and anthraquinone reactive blue 19) can best be obtained by the use of photo-assisted catalytic activity (Lizama et al. 2001).

**TiO\textsubscript{2} Doped with Metal and Nonmetal Species**

Titanium dioxide represents an effective photocatalysts for water and air purification and for self-cleaning surfaces. Additionally, it can be used as antibacterial agent because of strong oxidation activity and super hydrophilicity (Fujishima and Zhang et al. 2006). TiO\textsubscript{2} shows relatively high reactivity and chemical stability under ultraviolet light (\(\lambda<387\text{nm}\)), whose energy exceeds the band gap of 3.3 eV in the anatase crystalline phase. The development of photocatalysts exhibiting high reactivity under visible light (\(\lambda>400\text{ nm}\)) should allow the main part of the solar spectrum, even under poor illumination of interior lighting, to be used. Several approaches for TiO\textsubscript{2} modification have been proposed: metal-ion implanted TiO\textsubscript{2} (using transition metals: Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au,
Ag, Pt) (Anpo, 2000; Fuerte et al. 2001; Yamashita et al. 2001), reduced TiO$_2$ photocatalysts (Ihara et al. 2001; Takeuchi et al. 2000), non-metal doped TiO$_2$ (N, S, C, B, P, I, F) (Ohno et al. 2003; Liu et al. 2005; Yu et al. 2003), composites of TiO$_2$ with semiconductor having lower band gap energy (e.g. Cd-S particles (Hirai et al. 2001), sensitizing of TiO$_2$ with dyes (e.g. thionine) (Chatterjee and Mahata, 2001) and TiO$_2$ doped with up conversion luminescence agent (Wang et al. 2007; Zhou et al. 2006).

The visible light photo activity of metal-doped TiO$_2$ can be explained by a new energy level produced in the band gap of TiO$_2$ by the dispersion of metal nanoparticles in the TiO$_2$ matrix. As shown in Fig. (2) electron can be excited from the defect state to the TiO$_2$ conduction band by photon with energy equals $h\nu_2$. Additional benefit of transition metal doping is the improved trapping of electrons to inhibit electron-hole recombination during irradiation. Decrease of charge carriers recombination results in enhanced photoactivity.

![Figure 9.2. Mechanism of TiO$_2$ photocatalysis: $h\nu_1$: pure TiO$_2$; $h\nu_2$: metal-doped TiO$_2$ and $h\nu_3$: nonmetal-doped TiO$_2$](image)

There are three different main opinions regarding modification mechanism of TiO$_2$ doped with nonmetals. (1) Band gap narrowing; (2) Impurity energy levels; and (3) Oxygen vacancies.
1. Band gap narrowing: Asashi, et al. found N 2p state hybrids with O 2p states in anatase TiO₂ doped with nitrogen because their energies are very close, and thus the band gap of N-TiO₂ is narrowed and able to absorb visible light.

2. Impurity energy level: Irie, et al. stated that TiO₂ oxygen sites substituted by nitrogen atom form isolated impurity energy levels above the valence band. Irradiation with UV light excites electrons in both the VB and the impurity energy levels, but illumination with visible light only excites electrons in the impurity energy level.

3. Oxygen vacancies: Ihara, et al. concluded that oxygen-deficient sites formed in the grain boundaries are important to emerge vis-activity and nitrogen doped in part of oxygen-deficient sites are important as a blocker for reoxidation.

The current problem with doped TiO₂ may be the loss of photoactivity during recycling and long-term storage. It was assumed, that the efficiency of metal doped-TiO₂ under visible light strongly depended on the preparation method used. In same cases, such doped photocatalysts showed no activity under visible light and/or lower activity in the UV spectral range compared to the non-doped TiO₂ because of high carrier recombination rates through the metal ion levels. The main present problem with nonmetal-doped TiO₂ photocatalysts is that the photocatalytic activity under visible light is much lower than that under ultraviolet light. Therefore, development of new and optimization of existing photocatalysts exhibiting activity upon visible light with surface characteristics of improved performance and of the high chemical and physical stability are crucial for broader scale utilization of photocatalytic systems in commercial application. Such materials together with the development of technically applicable self-aligning photocatalytic coating systems adaptable to the major substrates (polymers, glass, ceramics or metals) will represent a ground breaking step change in this field particularly in the economic viability of a range of potential processes. Non-metal doping seems to be more promising than metal doped-TiO₂.

HETEROGENEOUS PHOTOCATALYSIS
Heterogeneous photocatalysis is a process of great potential for pollutant abatement and waste treatment. In order to improve the overall performance of the photo process, heterogeneous photocatalysis is being combined with physical or chemical operations, which affect the chemical kinetics and/or the overall efficiency. These combinations increase the photoprocess efficiency by decreasing the reaction time in respect to the separated operations or they decrease the cost in respect of heterogeneous Photocatalysis alone, generally in terms of light energy. Depending on the operation coupled with heterogeneous photocatalysis, two categories of combinations exist. When the coupling is with ultrasonic irradiation, photo-Fenton reaction, ozonation, or electrochemical treatment, the combination affects the photocatalytic mechanisms thus improving the efficiency of the photocatalytic process. When the coupling is with biological treatment, membrane reactor, membrane photoreactor, or physical adsorption, the combination does not affect the photocatalytic mechanisms but it improves the efficiency of the overall process. The choice of the coupling is related to the type of wastewater to be treated. A synergistic effect, giving rise to an improvement of the efficiency of the photocatalytic process, has been reported in the literature for many cases.

**Sonophotocatalytic reaction**

Heterogeneous photocatalysis and ultrasonic irradiation can cause degradation of organic pollutants in water by the same species, notably HO• radicals. However, distinct phenomena can also be involved; photocatalytic reactions may occur through direct electron transfer from the organic compounds to the semiconductor oxide and ultrasonic irradiation may selectively degrade less hydrophilic compounds through thermal degradation reactions (pyrolysis). The observed synergistic effect may be justified by different reasons. In fact, for the ultrasonic treatment the presence of solid particles in the aqueous system enhances the cavitation phenomenon as the microbubbles tend to break up into smaller ones thus increasing the total number of regions of high temperature and pressure. As a consequence, the number of hydroxyl radicals produced by the system
increases thus improving the oxidation capacity of the system. For the photocatalytic process, the acceleration of reactions is determined not only by chemical effects of ultrasound irradiation but also by mechanical effects caused by the ultrasonic waves, such as particle size reduction, increased mass transfer and surface cleaning, which hinder the blocking of the catalyst active sites by reaction intermediates (Vincenzo et al. 2006).

The integrated approach of ultrasound and photochemical is an established method for the treatment of wastewater (Augugliaro et al. 2006). The ultrasound usage for treating textile wastewater is reported in literature (Hua and Hoffmann, 1997; Suslick, 1999). Vajnhandl and Marechal reviewed the fundamentals of ultrasound and its applications in industrial processes, with the detailed dyeing procedures and the decolorization/decomposition of wastewaters (Vajnhandl and Marechal, 2005). Gogate and Pandit in their review highlighted the status of the hydrodynamic cavitation reactors with bubble dynamic analysis and also the optimum design illustrating the utilities of reactors (Gogate and Pandit, 2005). A comparative degradation of azo dyes at ultrasonic irradiation of 520 kHz and its combinations with ultraviolet light and/or ozone was investigated using a probe dye Acid Orange 7 (Guyer and Ince, 2004). It was observed that generally the degradation process was most quick under simultaneous operation of the three (UV/US/O₃) in the presence of a continuous flow of gas mixture (oxygen and argon).

The kinetic study on degradation of trihalomethanes (CHBrCl₂, CHCl₃, CHBr₂Cl, CHBr₃ and CHI₃) was conducted under 20 kHz ultrasonic frequencies (Shemer and Narkis, 2005). It was found that the most important parameter affecting the sonodegradation efficiency and kinetics was the vapor pressure. Okitsu et al reported the sonochemical degradation /decolorization of azo dyes e.g., Methyl Orange and RR 22. It was concluded that azo dye molecules were chiefly decomposed by ·OH radicals formed from the water sonolysis (Okitsu et al. 2005). The effect of sodium chloride, hydrogen peroxide, ultrasonic power and external gases was studied on the degradation of oxalic acid (Dukkanci and Gunduz, 2006). An optimal concentration of sodium chloride was found to improve the degradation of oxalic acid. On the other hand, the use of hydrogen
peroxide had negative effect on the degradation of oxalic acid. Mahamuni and Pandit studied a hybrid technique of ozonation coupled with cavitation for the degradation of phenol. He concluded that this hybrid technology leads to the formation of intermediates that can further be subjected to biodegradation (Mahamuni and Pandit, 2006). Zeng and James studied the audible frequency sonolytic ozonation for pentachlorophenol (PCP) degradation in water solution. The first-order rate constant of PCP degradation by ozonation combined with sonication was found to be 15 times more than that with bubbling ozone alone, while the rate constant with mechanical stirring was only four times faster (Zeng and James, 2006). Simona et al. found that the sonochemical decolorization/degradation of RB 5 using low and high ultrasonic frequencies i.e., 20 kHz and 279/817 kHz (high ultrasonic frequencies), without using any additional oxidant. It was concluded that ultrasound is capable for RB 5 color removal when used alone but the decomposition rate strongly depends on the operating parameters in use e.g., frequency, acoustic power, solution pH, transducer type, dye initial concentration. Nevertheless ultrasound alone is quite unsuccessful for the degradation of the dye (after 6 h of treatment only 50% degradation efficiency was achieved); by V. fischeri as test organisms negligible toxic degraded by products were detected under the conditions employed (Simona et al. 2007).

Velegraki et al. investigated the oxidation of Acid Orange 7 using sonophotocatalytic process with different effect i.e., ultrasonic frequency, reaction temperature and time on. It was found that under same operational parameters, ultrasonic irradiations resulted in better efficiency than photocatalysis. Furthermore, by observing reaction pathways it was found that the solutions irradiated sonochemically contained always low aliphatic intermediates whereas the solution irradiated photocatalytically, mostly consisted of aromatic intermediates (Velegraki et al. 2006). Adrian et al. investigated the treatment efficiency of 13 compounds containing model solution usually found in olive mill effluents, by means of sono-photocatalysis at 50 mgL⁻¹ concentration of each, over 0.75 gL⁻¹ Degussa TiO₂ suspensions. It was found that, photocatalytic
efficiency improved with increasing UVA power, whereas ultrasonic process when used as only method showed negligible degradation. In addition the process coupling as well as addition of extra oxidant resulted in considerable high level of degradation (Adrian et al 2007). Antonia and Martinez studied the sono-photocatalytic degradation of basic blue 9 dye using ultrasound with 20 kHz ultrasonic frequency, over a TiO₂ slurry employing an UV lamp (15 W, 352 nm). It was concluded from the results that the first order rate constants obtained with sono photocatalysis were twofold and tenfold than those attained under sonolysis and photocatalysis, respectively (Antonia and Martinez, 2008). Shuo et al prepared the carbon nanotubes (TiO₂/CNTs composite and investigated the sonophotocatalytic activity of TiO₂/CNTs nanoparticles. Their results showed a remarkable increase in the photocatalytic efficiency of TiO₂/CNTs when combined with ultrasonic technique, and the sono-photocatalysis process was found to follow first order kinetics (Shuo et al. (2009).

PHOTO-FENTON REACTION

The Fenton reaction is a dark process whose application for destroying toxic organic compounds began in 1960 (Vincenzo et al. 2006). In the absence of light, the most accepted mechanism of H₂O₂ decomposition by Fe²⁺ ions involves the production of HO• radicals. In the presence of UV-vis light, Fenton reaction rates are strongly increased. The positive effect of light on the degradation rate is due to the iron recycling caused by the photochemical reduction of ferric ions that concomitantly lead to additional HO• radical generation. The new generated Fe²⁺ ion reacts with H₂O₂ giving HO• radical and Fe³⁺ ion, and the cycle continues; in these conditions, iron behaves as a real catalyst. This type of homogeneous photoassisted reaction is referred to the photo-Fenton reaction; its main advantage is that the reaction occurs at radiation wavelengths up to 600 nm so that it may utilize a great part of the solar irradiation.

The combination of Fe(III), H₂O₂, TiO₂ and irradiation, i.e., photo-Fenton and photocatalysis, improves the destruction of some resistant pollutants. It has been reported
that ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and other oligocarboxylic acids are more rapidly mineralized in the presence of Fe(III)/H₂O₂ than when using TiO₂ alone (Baeza et al. 2003). Heterogeneous photocatalysis and photo-Fenton reaction were combined and the resulting process notably accelerated the degradation of the organic acids. In the case of EDTA, although photocatalytic degradation is rather fast, mineralization is difficult due to the formation of resistant intermediates; addition of oxidants like Fe(III) or H₂O₂ improves TOC removal. Oxalic acid does not give rise to intermediates alongside its degradation, TOC reduction paralleling the decrease of oxalic acid concentration. One important difference between EDTA and oxalic acid comes from the different quantum yields of the photolysis of the respective Fe(III)-complexes, more than one order of magnitude lower for Fe-EDTA. Therefore, for EDTA the degradation promoted by heterogeneous photocatalysis is important, the homogeneous process contributing only to a lesser extent. In contrast, in the oxalic acid system, TiO₂ would act as a screen or optical filter, reducing the efficiency of H₂O₂ photolysis.

Disinfection of drinking water by photocatalysis and photo-Fenton reaction was performed by Rincon and Pulgarin (Rincon and Pulgarin, 2006). Water contaminated with Escherichia coli was treated with the combined method by monitoring the bacterial culturability with time. The method is suitable for performing the bacterial inactivation, the rate being higher with respect to those of Photocatalysis and photo-Fenton reaction alone; however, the authors outline that the evaluation of the systems is very dependent on the relative concentrations of Fe³⁺, H₂O₂ and TiO₂.

**PHOTO-OZONATION REACTION**

Despite that photocatalysis has shown to be adequate for the destruction of a wide variety of compounds, in some cases the complete mineralization is slowly attained and the efficiency of the process, in terms of energy consumption, is advantageous only for very dilute effluents. Unlike photocatalysis, ozonation is capable of selectively destroying recalcitrant organics and it is more efficient for treating highly concentrated samples. In last times, ozonation has been increasingly used for drinking water treatment, because this
The method does not produce chlorinated compounds that can be originated in disinfection with chlorine or chlorine oxide. It is well known that the use of ozone allows a remarkable improvement of organoleptic properties, filtration characteristics and biodegradability of drinking water (Vincenzo et al. 2006).

The addition of light to the H$_2$O$_2$/O$_3$ process produces a net increase on the efficiency for decontamination of groundwater and for soil remediation. On this basis, the simultaneous application of ozonation and photocatalysis, hereafter indicated as photocatalytic ozonation, has potential use for the efficient treatment of contaminated waters in a wide range of concentrations. When O$_3$ is present in a photocatalytic suspension, in addition to the homogeneous pathways of direct ozonation, the role of O$_3$ as an electron trap must be considered. FTIR studies report different modes of ozone interaction with TiO$_2$ surface, such as: (i) physical adsorption; (ii) formation of weak hydrogen bonds with surface hydroxyl groups of the catalyst; and (iii) dissociative adsorption on strong surface Lewis acid sites leading to O$_3$ decomposition with formation of a free oxygen molecule and a surface oxygen atom that remains attached to the site (Bulanin et al. 1995; Vincenzo et al. 2006).

The favorable effect of ozone has been tested in the photocatalytic degradation of formic, acetic and propionic acids and monochloroacetic acid. The combined system proved to be the most effective; the degradation was accompanied by a continuous decrease of the dissolved organic carbon content, and aldehydes and carboxylic acids containing one carbon atom less than the starting material were formed as intermediates. Muller et al. used the photocatalytic ozonation for the treatment of waters polluted by 2,4-dichlorophenoxyacetic acid (2,4-D). The advantages of photocatalysis, giving a constant decline in total organic carbon content, and of ozonation, giving no buildup of high intermediate concentrations, were profited. Comparing ozonation, photocatalysis and the combination of both, they found that the combination approach reached the highest reaction rate (Muller et al. 1998; Vincenzo et al. 2006). Agustina et al. have carried out an exhaustive review of the most recent papers on the synergistic effect of photocatalysis and ozonation applied to wastewater treatment. This review focuses on the chemical effects of
ozone dosage, pH and crystal composition of photocatalyst on the degradation rate of different pollutants. The authors also give valuable information on the compounds degraded by various researchers, the detected intermediates, the mechanism, the kinetics and the economic aspects related to the application of photocatalytic ozonation to the treatment of industrial wastewaters (Agustina et al. 2005).

**PHOTO-ELECTROCHEMICAL REACTION**

The high degree of recombination between photo-generated electrons and holes is sometimes a major limiting factor controlling photocatalytic efficiency. The deposition of noble metals on TiO$_2$ films can strongly hinder the electron–hole recombination by attracting photogenerated electrons and so it would improve the performance of photocatalytic processes. However, if the accumulated negative charges are not consumed or not further transferred out of the metal particles, photogenerated holes may be attracted by negatively charged metal particles, which become recombination centres. It has been recently reported that an anodic bias applied to a TiO$_2$ film can not only spatially separate conduction band electrons but also drive away the photogenerated electrons accumulated on metal particles to another compartment of cell, reducing the electron–hole recombination and separating oxidation and reduction sites (Li at al. 2001).

A hybrid technology consisting in the combination of noble metal deposition with the application of an external electric field was developed by He et al.in order to improve the efficiency of photocatalytic degradation of formic acid on Ag-TiO$_2$ films. The combination of the Ag deposition and the application of anodic bias showed a beneficial effect not only in enhancing the formic acid oxidation rate but also the COD removal rate, which was higher than that of the pure photocatalytic process. The enhancement effect caused by the external electric field in the presence of Ag denotes that the deposited metal can not only trap the photogenerated electrons but also assist the external electric field to make them migrate from the TiO$_2$ film anode to the counter-electrode in another compartment of the cell. Upon close examination of the kinetic constants of each process, it was found that the rate constant of photoelectrocatalysis with Ag–TiO$_2$ is a simple sum
of those of photoelectrocatalysis on TiO$_2$ and photocatalysis on Ag–TiO$_2$. Even if the combined method does not show a synergistic effect but only an additive one, the method is very valuable when there is the need for degradation of organic pollutants recalcitrant to electrochemical or photocatalytic treatments. The main advantage of photoelectron catalysis is its great versatility joined to the simplicity of the reactors in terms of construction and management (particularly suitable for automation) (He et al. 2002).

However, application at large scale is limited by the difficulty to find materials with specific characteristics to make the process competitive. Moreover, the oxidation in the potential region of water stability can lead to electrode fouling due to the formation of polymeric materials. Ti/PbO$_2$, Ti/SnO$_2$, Ti/IrO$_2$, glassy carbon are generally used as the materials, but some of them decrease their activity due to surface fouling (glassy carbon) or limited service life (Ti/IrO$_2$).

**BIOLOGICAL AND PHOTOCATALYTIC METHOD**

The possibility to couple biological and photocatalytic methods has attracted the attention of many researchers in recent times. While photocatalysis is not specific (or almost not) for particular substrates, the biological method (which is the most common and cheapest process used for wastewater remediation) is not able to treat substances which are biorecalcitrant or bactericide. Substances used as herbicides (Metobromuron, isoproturon, etc.) or in the manufacture of dyes, such as 5- amino-6-methyl-2-benzimidazolone (AMBI) are biorecalcitrant molecules, while compounds, such as benzalkonium chloride are bactericides. The combination of biological method with heterogeneous photocatalysis can be used to reduce the bio-recalcitrance or the toxicity to bacteria to a level that permits the biological treatment. Therefore, the photocatalytic pretreatment is intended to modify the structure of the pollutants by transforming them into non-toxic and easily biodegradable intermediates. When the pretreatment is successful, the subsequent biological degradation is achieved in a shorter time and in a less-expensive way. For the coupled system, the photo treatment stage must be designed to obtain a solution biologically compatible after elimination of the initial biorecalcitrant compounds and their inhibitory intermediates. These requirements, and the information
concerning the toxicity and the biodegradability evolution of the photo treated solution, allow one to determine the optimal time to stop the photocatalytic treatment before feeding the treated water to the biological reactor. This time corresponds to the best compromise between the efficiency of the photo treatment and its cost. The shortest photo treatment time is desired to avoid long irradiation times and the consequent high electrical consumption. This is important because electricity represents about 60% of the total operational cost of photocatalytic reactors. However, if the fixed pretreatment time is too short, the intermediates remaining in solution could still be structurally similar to the initial biorecalcitrant compounds (Vincenzo et al. 2006).

In conclusion, the combination of heterogeneous photocatalysis with chemical, physical and biological operations appears to be the most promising tool for developing real applications of decontamination processes. However, by examining the literature on this topic, the authors noticed that almost the totality of experimental works have been carried out in artificial systems containing only one compound used as model molecule. It would be of a great importance to investigate real wastewater containing compounds of different chemical nature in order to elucidate the mutual effects of these compounds on their degradation rate.
Some Basic Concepts of Photochemistry

Q. No.01. What do you know about light absorption?
ANS: In physics, absorption of electromagnetic radiation is the way in which the energy of a photon is taken up by matter, typically the electrons of an atom. Thus, the electromagnetic energy is transformed into internal energy of the absorber, for example thermal energy. The reduction in intensity of a light wave propagating through a medium by absorption of a part of its photons is often called attenuation. Usually, the absorption of waves does not depend on their intensity (linear absorption), although in certain conditions (usually, in optics), the medium changes its transparency dependently on the intensity of waves going through, and saturable absorption (or nonlinear absorption) occurs.

Q. No.02. What do you know about quantifying light absorption?
Ans  Quantifying absorption
There are a number of ways to quantify how quickly and effectively radiation is absorbed in a certain medium, for example:

- Penetration depth and skin effect,
- Propagation constant, attenuation constant, phase constant, and complex wave number,
- Complex refractive index and extinction coefficient,
- Complex dielectric constant,
- Electrical resistivity and conductivity.
- Absorbance (also called "optical density") and optical depth (also called "optical thickness") are two related measures of the total light-blocking power of a certain medium with a certain thickness.
- Percentage of the incoming light which gets absorbed.

All these quantities measure, at least to some extent, how well a medium absorbs radiation. However, practitioners of different fields and techniques tend to conventionally use different quantities drawn from the list above.

Q. No. 03 How the Measurement of light absorption is carried out?
ANS: The absorbance of an object quantifies how much of the incident light is absorbed by it (instead of being reflected or refracted). This may be related to other properties of the object through the Beer–Lambert law.

Precise measurements of the absorbance at many wavelengths allow the identification of a substance via absorption spectroscopy, where a sample is illuminated from one side, and the intensity of the light that exits from the sample in every direction is measured. A few examples of absorption spectroscopy, in different parts of the spectrum, are ultraviolet–visible spectroscopy, infrared spectroscopy, and X-ray absorption spectroscopy.

Q. No. 04 What are the applications of light absorption?
ANS: Understanding and measuring the absorption of electromagnetic radiation has a variety of applications. Here are a few examples:

In meteorology and climatology, global and local temperatures depend in part on the absorption of radiation by atmospheric gases (such as in the greenhouse effect) and the ground.

- In medicine, X-rays are absorbed to different extents by different tissues (bone in particular), which is the basis for X-ray imaging. For example, see computation of radio wave attenuation in the atmosphere used in satellite link design.

- In chemistry and materials science, because different materials and molecules will absorb radiation to different extents at different frequencies, which allows for material identification.

- In optics, sunglasses, colored filters, dyes, and other such materials are designed specifically with respect to which visible wavelengths they absorb, and in what proportions.

- In biology, photosynthetic organisms require that light of the appropriate wavelengths be absorbed within the active area of chloroplasts, so that the light energy can be converted into chemical energy within sugars and other molecules.

Q. No. 05. What is Photosynthesis?
ANS: Photosynthesis is a process used by plants and other organisms to convert light energy, normally from the sun, into chemical energy that can be later released to fuel the organisms' activities. This chemical energy is stored in carbohydrate molecules, such as
sugars, which are synthesized from carbon dioxide and water – hence the name photosynthesis, from the Greek "light", and *synthesis*, "putting together". In most cases, oxygen is also released as a waste product. Most plants, most algae, and cyanobacteria perform photosynthesis, and such organisms are called photoautotrophs. Photosynthesis maintains atmospheric oxygen levels and supplies all of the organic compounds and most of the energy necessary for life on Earth.

The general equation for photosynthesis is therefore:

\[ 2n \text{CO}_2 + 2n \text{DH}_2 + \text{photons} \rightarrow 2(\text{CH}_2\text{O})_n + 2n \text{DO} \]

**Q. No. 06. What do you know about water photolysis?**

**ANS:** The NADPH is the main reducing agent in chloroplasts, providing a source of energetic electrons to other reactions. Its production leaves chlorophyll with a deficit of electrons (oxidized), which must be obtained from some other reducing agent. The oxidation of water is catalyzed in photosystem II by a redox-active structure that contains four manganese ions and a calcium ion; this oxygen-evolving complex binds two water molecules and stores the four oxidizing equivalents that are required to drive the water-oxidizing reaction. Photosystem II is the only known biological enzyme that carries out this oxidation of water. The hydrogen ions contribute to the transmembrane chemiosmotic potential that leads to ATP synthesis. Oxygen is a waste product of light-dependent reactions, but the majority of organisms on Earth use oxygen for cellular respiration, including photosynthetic organisms.

**Q. No. 07. What do you know about Solar cell?**

**ANS:** Solar cell (also called a photovoltaic cell) is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect. It is a form of photoelectric cell (in that its electrical characteristics—e.g. current, voltage, or resistance—vary when light is incident upon it) which, when exposed to light, can
generate and support an electric current without being attached to any external voltage source, but do require an external load for power consumption.

The operation of a photovoltaic (PV) cell requires 3 basic attributes:

- The absorption of light, generating either electron-hole pairs or excitons.
- The separation of charge carriers of opposite types.
- The separate extraction of those carriers to an external circuit.

**Q. No. 08. What is the Theory of solar cells?**

**ANS:** The solar cell works in three steps:

1. Photons in sunlight hit the solar panel and are absorbed by semiconducting materials, such as silicon.
2. Electrons (negatively charged) are excited from their current molecular/atomic orbital. Once excited the electron can either dissipate the energy, and return to its orbital or travel through the cell until it reaches an electrode. Current starts flowing through the material to cancel the potential and this electricity is captured. Due to the special composition of solar cells, the electrons are only allowed to move in a single direction.
3. An array of solar cells converts solar energy into a usable amount of direct current (DC) electricity.

**Q. No. 09. What are Light-absorbing dyes (DSSC) in solar cells?**

**ANS:** Dye-sensitized solar cells (DSSCs) are made of low-cost materials and do not need elaborate equipment to manufacture, so they can be made in a DIY fashion, possibly allowing players to produce more of this type of solar cell than others. In bulk it should be significantly less expensive than older solid-state cell designs. DSSC's can be engineered into flexible sheets, and although its conversion efficiency is less than the best
thin film cells, its price/performance ratio should be high enough to allow them to compete with fossil fuel electrical generation.

The circuit is completed by a redox couple in the electrolyte, which can be liquid or solid. This type of cell allows a more flexible use of materials, and is typically manufactured by screen printing or use of ultrasonic nozzles, with the potential for lower processing costs than those used for bulk solar cells. However, the dyes in these cells also suffer from degradation under heat and UV light, and the cell casing is difficult to seal due to the solvents used in assembly.

Q. No. 10. What is Quantum dot solar cells (QDSCs)?
ANS: Quantum dot solar cells (QDSCs) are based on the Gratzel cell, or dye-sensitized solar cell, architecture but employ low band gap semiconductor nanoparticles, fabricated with such small crystallite sizes that they form quantum dots (such as CdS, CdSe, Sb2S3, PbS, etc.), instead of organic or organometallic dyes as light absorbers. Quantum dots (QDs) have attracted much interest because of their unique properties. Their size quantization allows for the band gap to be tuned by simply changing particle size. They also have high extinction coefficients, and have shown the possibility of multiple exciton generation.

Q. No. 11. What do you know about light fluorescence?
ANS: Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It also occurs when molecules are excited to higher electronic states by energetic electron bombardment, such as occurs, for example, in the natural aurora, high-altitude nuclear explosions, and rocket-born electron gun experiments. It is a form of luminescence. In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation. However, when the absorbed electromagnetic radiation is intense, it is possible for one electron to absorb two photons; this two-photon absorption can lead to emission of radiation having a shorter
wavelength than the absorbed radiation. The emitted radiation may also be of the same wavelength as the absorbed radiation, termed "resonance fluorescence.

Q. No. 12 What do you know about Photochemistry?

ANS: Photochemistry, a sub-discipline of chemistry, is the study of chemical reactions that proceed with the absorption of light by atoms or molecules. Everyday examples include photosynthesis, the degradation of plastics and the formation of vitamin D with sunlight.

Q. No. 13 What do you know about Quantum yield?

ANS: The fluorescence quantum yield gives the efficiency of the fluorescence process. It is defined as the ratio of the number of photons emitted to the number of photons absorbed.

\[ \Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \]

The maximum fluorescence quantum yield is 1.0 (100%); each photon absorbed results in a photon emitted. Compounds with quantum yields of 0.10 are still considered quite fluorescent.

Q. No. 14 What is phosphorescence?

ANS: Phosphorescence is a specific type of photoluminescence related to fluorescence. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs. The slower time scales of the re-emission are associated with "forbidden" energy state transitions in quantum mechanics. As these transitions occur very slowly in certain materials, absorbed radiation may be re-emitted at a lower intensity for up to several hours after the original excitation.

Commonly seen examples of phosphorescent materials are the glow-in-the-dark toys, paint, and clock dials that glow for some time after being charged with a bright light such
as in any normal reading or room light. Typically the glowing then slowly fades out within minutes (or up to a few hours) in a dark room. The study of phosphorescent materials led to the discovery of radioactivity in 1896. Ironically, white phosphorus (from which phosphorescence takes its name) does not actually exhibit this property, but rather chemiluminescence.

Q. No. 15. What is the principles of photochemistry?
ANS: light is a type of electromagnetic radiation, a source of energy. The Grotthuss–Draper law (for chemists Theodor Grotthuss and John W. Draper) states that light must be absorbed by a chemical substance in order for a photochemical reaction to take place. For each photon of light absorbed by a chemical system, no more than one molecule is activated for a photochemical reaction, as defined by the quantum yield.

Chemical reactions occur only when a molecule is provided the necessary "activation energy". A simple example can be the combustion of gasoline (a hydrocarbon) into carbon dioxide and water. In this reaction, the activation energy is provided in the form of heat or a spark. In case of photochemical reactions light provides the activation energy. Simplistically, light is one mechanism for providing the activation energy required for many reactions. If laser light is employed, it is possible to selectively excite a molecule so as to produce a desired electronic and vibrational state. Equally, the emission from a particular state may be selectively monitored, providing a measure of the population of that state. If the chemical system is at low pressure, this enables scientists to observe the energy distribution of the products of a chemical reaction before the differences in energy have been smeared out and averaged by repeated collisions.

Q. No. 16. What are the applications of photochemistry?
ANS: Many important processes involve photochemistry. The premier example is photosynthesis, in which most plants use solar energy to convert carbon dioxide and water into glucose, disposing of oxygen as a side-product. Humans rely on photochemistry for the formation of vitamin D. In fireflies, an enzyme in the abdomen catalyzes a reaction that results in bioluminescence.
Photochemistry can also be highly destructive. Medicine bottles are often made with darkened glass to prevent the drugs from photodegradation. A pervasive reaction is the generation of singlet oxygen by photosensitized reactions of triplet oxygen. Typical photosensitizers include tetraphenylporphyrin and methylene blue. The resulting singlet oxygen is an aggressive oxidant, capable of converting C-H bonds into C-OH groups. In photodynamic therapy, light is used to destroy tumors by the action of singlet oxygen. Many polymerizations are started by photoinitiators, which decompose upon absorbing light to produce the free radicals for Radical polymerization.

Q. No. 17. What is photochemical reaction?

ANS: Photochemical reaction, a chemical reaction initiated by the absorption of energy in the form of light. The consequence of molecules’ absorbing light is the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules. These new chemical species can fall apart, change to new structures, combine with each other or other molecules, or transfer electrons, hydrogen atoms, protons, or their electronic excitation energy to other molecules. Excited states are stronger acids and stronger reductants than the original ground states.

Q. No. 18. What is absorption (of electromagnetic radiation)?

ANS: In a semiclassical fashion, this transfer of energy can be described as being due to an interaction of the electric field of the wave with an oscillating electric dipole moment set up in the material or molecular entity. This dipole moment is the result of the perturbation by the outside field, and its oscillation frequency \( \nu \) is given by the difference \( \Delta E \) of the energies of the lower and upper state in the absorbing material or \( M \) molecular entity, \( \Delta E = h \nu \). When the frequency of the oscillating dipole moment and the frequency of the field agree, a resonance occurs and energy can flow from the field into the material or molecule (an absorption occurs).

Q. No. 19. What is Beer–Lambert law (or Beer–Lambert–Bouguer law)?
ANS: The absorbance of a beam of collimated monochromatic radiation in a homogeneous isotropic medium is proportional to the absorption pathlength, $l$, and to the concentration, $c$, or (in the gas phase) to the pressure of the absorbing species. In some chemistry applications for liquids these relations are usually written as:

$$ T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\varepsilon lc} $$

Whereas in biology and physics, they are normally written

$$ T = \frac{I}{I_0} = e^{-\alpha' l} = e^{-\sigma l N} $$

where $I_0$ and $I$ are the intensity (power per unit area) of the incident light and the transmitted light, respectively; $\sigma$ is cross section of light absorption by a single particle and $N$ is the density (number per unit volume) of absorbing particles.

Q. No. 20. What is Photochemical smog?

ANS: A combination of fog and chemicals that come from automobile and factory emissions and is acted upon by the action of the sun. Nitrogen dioxide, in the presence of the sun and some hydrocarbons, is turned into nitric oxide and atomic oxygen. The atomic oxygen reacts with the oxygen molecules and other constituents of automobile exhaust fumes to form a variety of products including ozone. The ozone is harmful in itself and is also implicated in a highly complex series of continuing reactions. As long as there is ozone or nitrogen dioxide and sunlight present, other undesirable reactions will occur.

Photochemical smog was first described in the 1950s. It is the chemical reaction of sunlight, nitrogen oxides and volatile organic compounds in the atmosphere, which leaves airborne particles and ground-level ozone. This noxious mixture of air pollutants can include the following:

- Aldehydes
• Nitrogen oxides, such as nitrogen dioxide
• Peroxyacyl nitrates
• Tropospheric ozone
• Volatile organic compounds

Q. No. 21. What are the causes of Photochemical smog?
ANS: An erupting volcano can also emit high levels of sulphur dioxide along with a large quantity of particulate matter; two key components to the creation of smog. However, the smog created as a result of a volcanic eruption is often known as vog to distinguish it as a natural occurrence.

The radiocarbon content of some plant life has been linked to the distribution of smog in some areas. For example, the creosote bush in the Los Angeles area has been shown to have an effect on smog distribution that is more than fossil fuel combustion alone.

Q. No. 22. What is the location and production of ozone in Earth's atmosphere?
ANS: the highest levels of ozone in the atmosphere are in the stratosphere, in a region also known as the ozone layer between about 10 km and 50 km above the surface (or between about 6 and 31 miles). However, even in this "layer" the ozone concentrations are only two to eight parts per million, so most of the oxygen there remains of the dioxygen type.

Ozone in the stratosphere is mostly produced from short-wave ultraviolet rays (in the UVC band) but it can be also produced from x-rays reacting with oxygen:

\[
\begin{align*}
O_2 + h\nu & \rightarrow 2 \text{O} \quad k_1 \text{ (s}^{-1}\text{)} \\
O + O_2 + M & \rightarrow O_3 + M \quad k_2 \text{ (cm}^6 \text{molecule}^{-2} \text{s}^{-1}\text{)} \\
O_3 + h\nu & \rightarrow O + O_2 \quad k_3 \text{ (s}^{-1}\text{)} \\
O + O_3 & \rightarrow 2 \text{O}_2 \quad k_4 \text{ (cm}^3 \text{molecules}^{-1} \text{s}^{-1}\text{)} 
\end{align*}
\]

Where "M" denotes the third body that carries off the excess energy of the reaction. The thus produced ozone is destroyed by the reaction with atomic oxygen:
The latter reaction is catalysed by the presence of certain free radicals, of which the most important are hydroxyl (OH), nitric oxide (NO) and atomic chlorine (Cl) and bromine (Br). In recent decades the amount of ozone in the stratosphere has been declining mostly because of emissions of CFCs and similar chlorinated and brominated organic molecules, which have increased the concentration of ozone-depleting catalysts above the natural background.

**Q. No. 23. What is the Importance to surface-dwelling life on Earth?**

**ANS:** Ozone in the ozone layer filters out sunlight wavelengths from about 200 nm UV rays to 315 nm, with ozone peak absorption at about 250 nm.[22] This ozone UV absorption is important to life, since it extends the absorption of UV by ordinary oxygen and nitrogen in air (which absorb all wavelengths < 200 nm) through the lower UV-C (200–280 nm) and the entire UV-B band (280–315 nm). The small unabsorbed part that remains of UV-B after passage through ozone causes sunburn in humans, and direct DNA damage in living tissues in both plants and animals. Ozone's effect on mid-range UV-B rays is illustrated by its effect on UV-B at 290 nm, which has radiation intensity 350 million times as powerful at the top of the atmosphere as at the surface. Nevertheless, enough of UV-B radiation at similar frequency reaches the ground to cause some sunburn, and these same wavelengths are also among those responsible for the production of vitamin D in humans.

**Q. No. 24. What is Ozone cracking?**

**ANS:** Ozone gas attacks any polymer possessing olefinic or double bonds within its chain structure, such as natural rubber, nitrile rubber, and styrene-butadiene rubber. Products made using these polymers are especially susceptible to attack, which causes cracks to grow longer and deeper with time, the rate of crack growth depending on the load carried by the product and the concentration of ozone in the atmosphere. Such
materials can be protected by adding antiozonants, such as waxes, which bond to the surface to create a protective film or blend with the material and provide long term protection. Ozone cracking used to be a serious problem in car tires for example, but the problem is now seen only in very old tires. On the other hand, many critical products like gaskets and O-rings may be attacked by ozone produced within compressed air systems. Fuel lines are often made from reinforced rubber tubing and may also be susceptible to attack, especially within engine compartments where low levels of ozone are produced from electrical equipment. Storing rubber products in close proximity to DC electric motors can accelerate the rate at which ozone cracking occurs. The commutator of the motor creates sparks which in turn produce ozone.

Q. No. 25 .What is the chemistry of Photochemical Smog?

ANS: To begin the chemical process of photochemical smog development the following conditions must occur:

- Sunlight.
- The production of oxides of nitrogen (NOx).
- The production of volatile organic compounds (VOCs).
- Temperatures greater than 18 degrees Celsius.

If the above criteria are met, several reactions will occur producing the toxic chemical constituents of photochemical smog. The following discussion outlines the processes required for the formation of two most dominant toxic components: ozone (O3) and peroxycetyl nitrate (PAN). Note the symbol R represents a hydrocarbon (a molecule composed of carbon, hydrogen and other atoms) which is primarily created from volatile organic compounds.

Nitrogen dioxide can be formed by one of the following reactions. Notice that the nitrogen oxide (NO) acts to remove ozone (O3) from the atmosphere and this mechanism occurs naturally in an unpolluted atmosphere.
The atomic oxygen (O) formed in the above reaction then reacts with one of the abundant oxygen molecules (which makes up 20.94 % of the atmosphere) producing ozone (O3).

\[ O + O_2 \rightarrow O_3 \]

Nitrogen dioxide (NO2) can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as peroxyacetyl nitrates (PAN).

\[ NO_2 + R \rightarrow \text{products such as PAN} \]

It should be noted that ozone can be produced naturally in an unpolluted atmosphere. However, it is consumed by nitrogen oxide as illustrated in the first reaction. The introduction of volatile organic compounds results in an alternative pathway for the nitrogen oxide, still forming nitrogen dioxide but not consuming the ozone, and therefore ozone concentrations can be elevated to toxic levels.

Q. No. 26. What are the major sources of photochemical smog?
ANS: While nitrogen oxides and VOCs are produced biogenically (in nature), there are also major anthropogenic (man-made) emissions of both. Natural emissions tend to be
spread over large areas, reducing their effects, but man-made emissions tend to be
concentrated close to their source, such as a city.

- Biogenic sources

In nature, bushfires, lightning and the microbial processes that occur in soil generate
nitrogen oxides.
VOCs are produced from the evaporation of naturally-occurring compounds, such as
terpenes, which are the hydrocarbons in oils that make them burn. Eucalypts have also
been found to release significant amounts of these compounds.

- Anthropogenic sources

Nitrogen oxides are produced mainly from the combustion of fossil fuels, particularly in
power stations and motor vehicles. VOCs are formed from the incomplete combustion of
fossil fuels, from the evaporation of solvents and fuels, and from burning plant matter—
such as backyard burning and wood-burning stoves. In Adelaide in 2000, an estimated
66% of nitrogen oxides (NO and NO₂) came from motor vehicles, and a further 20% from
fuel combustion. Motor vehicles contributed 44% of VOC emissions, and area sources
including petrol and solvent evaporation contributed 33%.

Q. No. 27. How can we reduce the occurrence of photochemical smog?

ANS: The most effective way of reducing the amount of secondary pollutants created in
the air is to reduce emissions of both primary pollutants.

Reduction of nitrogen oxide

The main method of lowering the levels of nitrogen oxides is by a process called ‘catalytic
reduction’, which is used in industry and in motor vehicles. For example, a catalytic
converter fitted to a car’s exhaust system will convert much of the nitric oxide from the
engine exhaust gases to nitrogen and oxygen. In Australia, all motor vehicles built after 1985 must be fitted with catalytic converters.

Nitrogen is not in the actual fuels used in motor vehicles or power stations; it is introduced from the air when combustion occurs. Using less air in combustion can reduce emissions of nitrogen oxides.

Temperature also has an effect on emissions—the lower the temperature of combustion, the lower the production of nitrogen oxides. Temperatures can be lowered by using processes such as two-stage combustion and flue gas recirculation, water injection, or by modifying the design of the burner.

**Reduction of VOCs**

There are various ways to reduce VOC emissions from motor vehicles. These include the use of liquefied petroleum gas (LPG) or compressed natural gas (CNG) rather than petrol, decreasing distances vehicles travel by using other modes of transport, such as buses and bikes, and implementing various engine and emission controls now being developed by manufacturers. The other major contributor to VOC emissions, however, is not as simple to police because solvent evaporation occurs in many different places, from large factories to backyard sheds. Control strategies to reduce these emissions must be widely varied.

**Q. No. 28. What are the Impacts of Photochemical Oxidants (Ozone)?**

ANS: Photochemical oxidants are the products of reactions between NOx and a wide variety of volatile organic compounds (VOCs). The most well known 'oxidants' are ozone (O₃), peroxyacetyle nitrate (PAN) and hydrogen peroxide (H₂O₂). The main impact on the natural environment is mostly due to elevated O₃. Excessive concentrations of tropospheric O₃ have toxic effects on both plants and human health. Effects on vegetation include visible injury, early senescence of leaves, and reduction of crop yield. Experiments with open-top chambers in various parts of Europe (including the UK) show that exposure of plants to concentrations above 40 ppb for several weeks can reduce growth and the yield of sensitive crops species. However, it is difficult to translate
this kind of information into effects on crops growing in the field and on natural communities. The most comprehensive information is available for wheat, and the evidence indicates that yields are probably reduced in some parts of Britain in high ozone years. With regard to the effects on natural vegetation, it has proved difficult to determine whether there are important ecological effects under UK conditions and more technically-challenging research is needed.

REFERENCES


