

PHOTOCHEMISTRY

By

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Introduction

- Photochemistry is the study of the interaction of electromagnetic radiation with matter resulting into a physical change or into a chemical reaction .whose rates and mechanism studied after initiation by the radiant energy.
- One molecule is excited into an electronically excited state by absorption of a photon, it can undergo a number of different primary processes.
- Photochemical processes are those in which the excited species dissociates, isomerizes, rearranges, or react with another molecule.

Photochemistry

- Photophysical processes include radiative transitions in which the excited molecule emits light in the form of fluorescence or phosphorescence and returns to the ground state, and intramolecular non-radiative transitions in which some or all of the energy of the absorbed photon is ultimately converted to heat.
- The reaction which takes place by the absorption of light by the reacting substance are called as Photochemical reactions.

- The absorption of light radiations generally in visible and Ultraviolet region.
- The photochemical reaction is different from ordinary chemical reaction. The ordinary chemical reaction occurs by absorption of heat and can be replaced in the absence of light, such reaction is called as dark reaction or thermal reaction.

Difference between Photochemical and thermal reactions

Thermal Reaction

- Reaction involves absorption of heat.
- Reaction can take place in dark even.
- Reaction is markedly effected by temperature.
- Reaction involves decrease in free energy i.e. $\Delta G = -Ve$
- In these reaction the activation energy arises from the intermolecular collisions or it is supplied in the form of heat.
- $3H_2 + N_2 \quad \quad 2NH_3$

Photochemical Reaction

- Reaction involves absorption of light.
- Reaction can take place in the presence of light.
- Reaction has negligible effect of temperature.
- The free energy of Reaction increase or decrease i.e. $\Delta G = +Ve$ or $-Ve$.
- In these reaction the activation energy arises by absorption of photon of suitable energy.
- $H_2 + I_2 \quad \quad 2HI$

Laws Governing Absorption Of Light

- **Lambert's Law:** This law states that When beam of monochromatic is allowed to pass through homogeneous medium, decrease in the intensity of with the thickness of the absorbing medium is proportional to the intensity of incident light.

$$-dI/dx \propto I$$

here,-Ve sign indicates the decrease in intensity with thickness

$$-dI/dx = KI,$$

Where K is constant of proportionality called as absorption coefficient. It depends upon the nature of absorbing substance or medium.

$$-dI / I = K x$$

Integrating above equation with the limits at $x=0, I=I_0$ and at $x= x, I=I$

$$\int_{I_0}^I dI/I = \int_0^x K dx$$

Where I_0 = intensity of incident light.
I=intensity of transmitted light.
K= absorption co efficient.

Lambert's law

$$-\ln I/I_0 = Kx$$

$$I/I_0 = e^{-Kx}$$

$$I = I_0 e^{-Kx} \dots\dots\dots 1$$

Equation 1 can be written as,

$$2.303 \log I/I_0 = -Kx$$

$$\log I/I_0 = -Kx/2.303 \text{ or}$$

$$I = I_0 10^{-Kx/2.303} = I_0 10^{-K'x} \dots\dots\dots 2$$

Where, $K' = Kx/2.303$ is called extinction coefficient or absorptivity of the substance i.e. the absorption medium.

But $\log I/I_0$ is the absorbance or optical density i.e. A. Hence equation 2 becomes

$$A = K'x \dots\dots\dots 3$$

Equation 1, 2, and 3 represent the Lambert's law in different

Beer's Law

- This law can be stated as When beam of monochromatic light passes through the homogeneous solution, the decrease in intensity of light with the thickness of solution is directly proportional not only to the intensity of light but also to the concentration of solution.

Mathematically it can be represented as

$$-\frac{dI}{dx} \propto I * C$$

$$-\frac{dI}{dx} = \alpha I * C$$

Where α is the constant of proportionality and is called molar absorption coefficient, its value depends upon the nature of absorbing solute and the wavelength of light used and C is the molar concentration of solution under study

Beer's Law

■
$$-\frac{dI}{I} = \alpha C dx$$

Integrating the above equation with the limits at $x=0$ at $I=I_0$ And $x=x$ at $I=I$

-
$$\int_{I_0}^I \frac{dI}{I} = \int_0^x \alpha C dx$$

-
$$-\ln I/I_0 = \alpha C x$$

-
$$I/I_0 = e^{-\alpha C x} \text{ or}$$

-
$$I = I_0 e^{-\alpha C x} \dots\dots\dots 1$$

- Equation 1 can be written as,

-
$$-2.303 \log \frac{I}{I_0} = \alpha C x$$

Beer's Law



$$\log \frac{I}{I_0} = - \epsilon C x$$

$$\frac{I}{I_0} = 10^{-\epsilon C x}$$

$$I = I_0 10^{-\epsilon C x} \dots\dots\dots 2$$

Where $\epsilon = \frac{\alpha}{2.303}$ is called molar extinction coefficient or molar absorptivity. Since $A = \log \frac{I_0}{I}$ hence equation 2 becomes

$$A = \epsilon C x \dots\dots\dots 3$$

If concentration of solution is 1M and thickness of medium is 1cm, $A = \epsilon$. Hence molar extinction coefficient can be defined as the absorbance of solution containing 1M solution placed in a cell of thickness 1 cm.

Laws governing Photochemistry

- **Grotthus-Draper Law:** This law is also called first law of photochemistry

Only the light which is absorbed by a molecule can be effective in producing photochemical changes in the molecule. It means that the transmitted or reflected light does not cause any chemical change.

- **Stark-Einstein's Law (Second Law of Photochemistry):**

It states that for each atom or molecule of the reacting substance that take part in photochemical reaction absorbs one quantum of radiation(i.e. photon) to undergo reaction. $E=Nh\nu$. This energy is called one einstein.

Laws governing Photochemistry

- If ν is the frequency of absorbed radiation then the energy of quantum of radiation is given by $h\nu$ or hc/λ . This corresponds to the energy absorbed by one atom or molecule according to the Stark Einstein's law.
- One mole of substance contains N molecules where N is Avagadro number.
- Hence energy absorbed by one mole is given by $E=Nhc/\lambda$
- This energy absorbed by 1 mole of reacting molecules or energy possessed by 1 mole of photons is called One Einstein.

Units

□ In CGS Units

$$E = 2.86 / \lambda(\text{cm}) \text{ cal per mole}$$

or

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

□ In SI units

$$E = 0.1197 / \lambda(\text{m}) \text{ J mol}^{-1}$$

$$11.97 \times 10^{-5} / \lambda(\text{m}) \text{ KJ mol}^{-1}$$

Quantum Yield or quantum efficiency

- The number of molecules reacting per quantum of energy absorbed is called as quantum yield or quantum efficiency of the reaction. It is denoted by ϕ .
- It can also be defined as number of moles reacting per Einstein of energy absorbed.
- Quantum Efficiency $\phi =$
$$\frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta of light absorbed in the same time}}$$
- Or Quantum Efficiency $\phi =$
$$\frac{\text{No. of mole reacting in a given time}}{\text{No. of Einsteins absorbed in the same time}}$$

Quantum Yield

- Experimentally,
$$\Phi = \frac{\text{rate of chemical reaction}}{\text{quanta absorbed per second.}}$$
- If Stark- Einstein law is strictly obeyed, quantum yield of reaction should be equal to 1. However, for many reactions it is either greater or less than 1.
- For examples:
- In the photolysis of Cl₂ and H₂, Φ can be as high as 1 million.



Quantum Yield

- In the photolysis of Br_2 and H_2 , Φ_{HBr} is very low i.e about 0.01



- $\text{SO}_2 + \text{Cl}_2 \longrightarrow \text{SO}_2\text{Cl}_2 \quad \Phi = 1$
- $\text{CH}_3\text{COCH}_3 \longrightarrow \text{CO} + \text{C}_2\text{H}_6 \quad \Phi = 0.1$
- In order to explain these variations it was suggested that the photochemical reaction involve two distinct stages

Quantum Yield

1. Primary processes : In primary process, the quantum of energy is absorbed to form excited molecules. These processes are totally dependent on the absorption of quanta of energy from radiation. Hence law of photochemical equivalence can be applied to these processes.



2. Secondary processes : In secondary processes, these excited molecules may undergo various changes leading to high or low quantum yield. These processes have nothing to do with absorption of radiation

Quantum Yield

- In order to get a quantum yield of 1, following conditions have to be obeyed strictly.
- 1. all the molecules of reacting substance should be at the same energy level and all should be equally reactive.
- 2. The reactivity or the velocity of the reaction should be independent of temperature except that the change in temperature is effective in increasing the absorbing capacity of the system.
- 3. The product of absorption must become unstable with respect to original system.

□ Reasons for high quantum yields

- The atoms or free radicals produced in the primary process may start a series of chain reactions. In such cases, the quantum yield depends upon the extent of the chain reaction i.e. how far the chain reaction proceeds before the termination

For Ex. The high quantum yield of photochemical combination of H₂ and Cl₂ is due to chain reactions i.e.



The secondary process continuously repeats themselves till the chlorine atoms are deactivated by their combination to form chlorine molecules on the walls of the vessels.

Quantum Yield

- Hence, by the absorption of one quantum, only one molecule of chlorine dissociates and large number of HCl molecules are produced leading to high quantum yield.
- An intermediate product may be formed which acts as a catalyst making the further reaction feasible without absorption of radiation.
- The reaction take place may be exothermic. Hence heat evolved may activate other molecules thereby causing them to react without the absorption of additional quanta of radiation.
- Collision of the activated molecules with the other molecules may result in transfer of some of their energy so that more molecules may be activated.

Quantum Yield

- Reason for low quantum yields
- The excited molecules may get deactivated before they form products. This may happen due to the collision of excited molecules with nonexcited molecules or with the wall of container which may cause them to lose their energy and get deactivated.
- The primary process may get reversed.
- The fragments obtained by the dissociation, may recombine to form the original non-excited molecule.
- All absorbing molecules may not receive enough energy to enable them to react because part of absorbed energy may be lost in the form of fluorescence before they react

Quantum Yield

- Molecules with which activated molecules are to react may have energy below average so that even in spite of receiving energy from activated molecule, they may not reach the point of reaction.

Quantum Yield

□ Experimental determination of quantum yield

To determine the quantum yield of photochemical reaction two parameters are to be determined

1. Number of moles of substance that reacts in a given time.
2. Number of Einsteins of radiations absorbed by the same substance in same time.

Quantum Yield

- Experimental set up used for this purpose as shown

Quantum Yield

- Light source: The light source may be a sunlight, arc lamp, discharge tube, tungsten lamp etc. Mercury vapour lamp is used for Ultra violet radiation while tungsten lamp is used for visible region.
- Monochromator: The function of is to isolate desired wavelength .A color filter is sufficient for this purpose.
- Reaction cell : The reaction cell is generally made of glass or quartz with optically plane windows. For visible light the reaction cell and other part is made of glass while for ultraviolet light, all part is made of quartz because glass absorbs ultraviolet light.for solutions the reaction cell is provided with stirrer.

Quantum Yield

- Detector: It is used to determine the intensity of light coming from the reaction cell. The intensity is measured first for empty cell then with the reaction mixture. The difference between these two readings gives the amount of energy absorbed.
- Commonly used detectors are
 - i) Radiomicrometer
 - ii) Photoelectric cell
 - iii) Thermopile
 - iv) Chemical actinometer

Quantum Yield

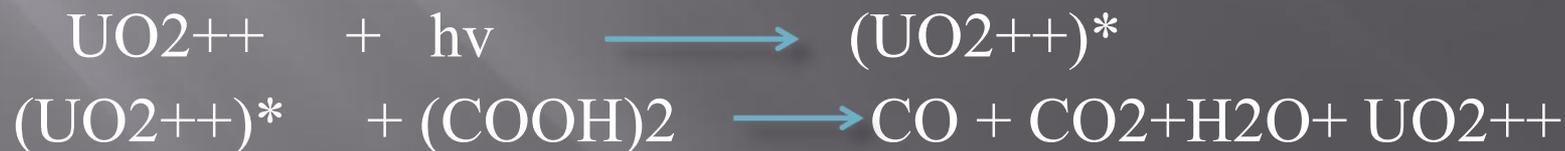
- Uranyl oxalate actinometer
- Chemical actinometer method though not very accurate but convenient method for measuring the number of einsteins absorbed.
- **Principle** :In this device a standard photochemical reaction is used to estimate energy of radiation absorbed.
- Uranyl oxalate actinometer is commonly used.
- Uranyl oxalate actinometer consist of a 0.05M oxalic acid mixed with 0.01M uranyl sulphate solution.
- Uranyl sulphate solution is used to sensitise the decomposition of oxalic acid on exposure on violet or UV light.

Quantum Yield

- The wavelength of the required light falls in the ranges of 2540 Å to 4350 Å.
- The extent of decomposition of oxalic acid is determined at the end of the experiment by titrating it against a standard KMnO_4 solution.
- It is assumed that the amount of decomposition is proportional to the product of intensity of light of a given wavelength and the time of exposure.

Quantum Yield

- The apparatus is first standardized with respect to radiations of different wavelengths. Hence it possible to calculate the amount of energy of light radiation of a given wavelength absorbed in the case of photochemical reaction.
- The measurements are made before and after passing the light through the reaction cell.
- The decomposition of oxalic acid take place as follows, where the uranyl ion $(\text{UO}_2)^{++}$ obtained from uranyl sulphate behaves as photosensitizer.



Quantum Yield

- Procedure:
 1. First reaction cell is kept empty and the light is allowed to pass through it. If the reaction mixture is solution then filled the reaction cell with pure solvent. The intensity is determined.
 2. The cell is then filled with reaction mixture. The light is allowed to pass through it for a known time. The intensity of light after passing through the reaction mixture is measured. The difference in two intensity readings will give the amount of energy absorbed by the reaction system.

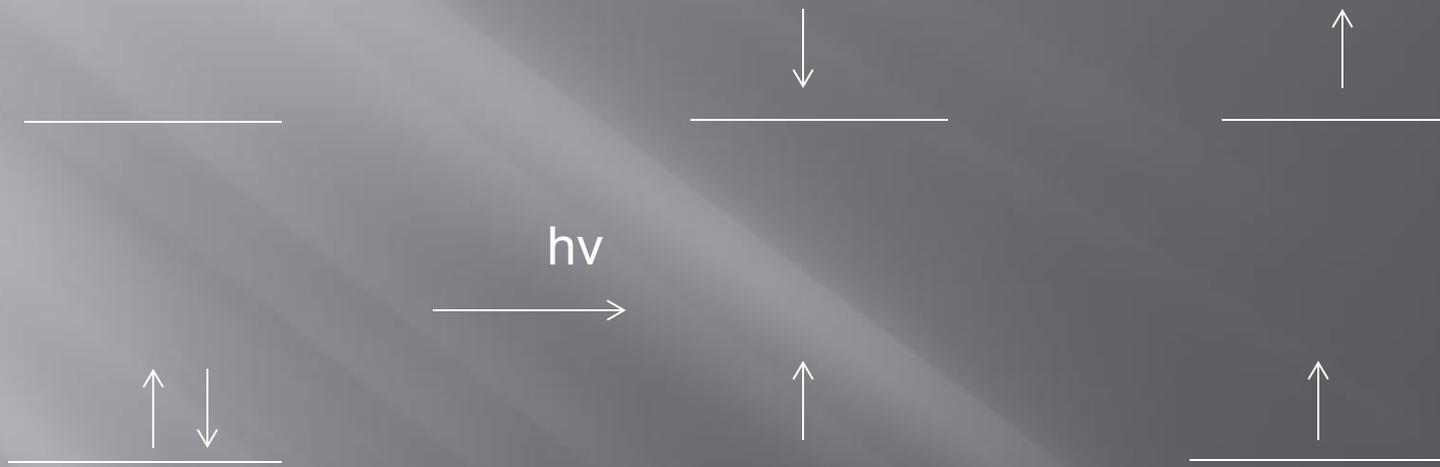
Quantum Yield

1. The number of moles reacting in the same time can be determined by suitable analytical technique, by finding the initial and the final concentrations of the reaction mixture.
2. From the values of number of moles reacted and number of einsteins absorbed, the quantum yield can be calculated.

Spin states of molecules

- In the ground states , all the electrons in a molecule are paired up and so the total spin of molecule is $S=0$
- The multiplicity (M) is $2S+1$.
- For ground state $S=0$ so $M=2*0+1=1$ and it is called as singlet ground state represented as S_0 .
- When electron excites to higher energy level, it may retain its spin or may change the spin.
- If its spin is same as that of in ground state, the total spin remains $S=0$ and multiplicity $M=1$. It is called as singlet excited state represented as S_1 .
- .

- If electron changes its spin, the total spin becomes $S=1$ and multiplicity $M=3$. It is called as triplet excited state represented by T_1
- The energy of triplet state is lower than the singlet state. Hence triplet state is more stable than singlet state.
- The first, second, third singlet and triplet excited states are represented as S_1, S_2, S_3
 T_1, T_2, T_3 etc. respectively



$$S = 1/2 - 1/2 = 0$$

Singlet ground state
state

$$\text{Multiplicity} = 2S + 1 = 1$$

$$\text{Multiplicity} = 2(1) + 1 = 3$$

$$S = 1/2 - 1/2 = 0$$

Singlet excited state

$$\text{Multiplicity} = 2S + 1 = 1$$

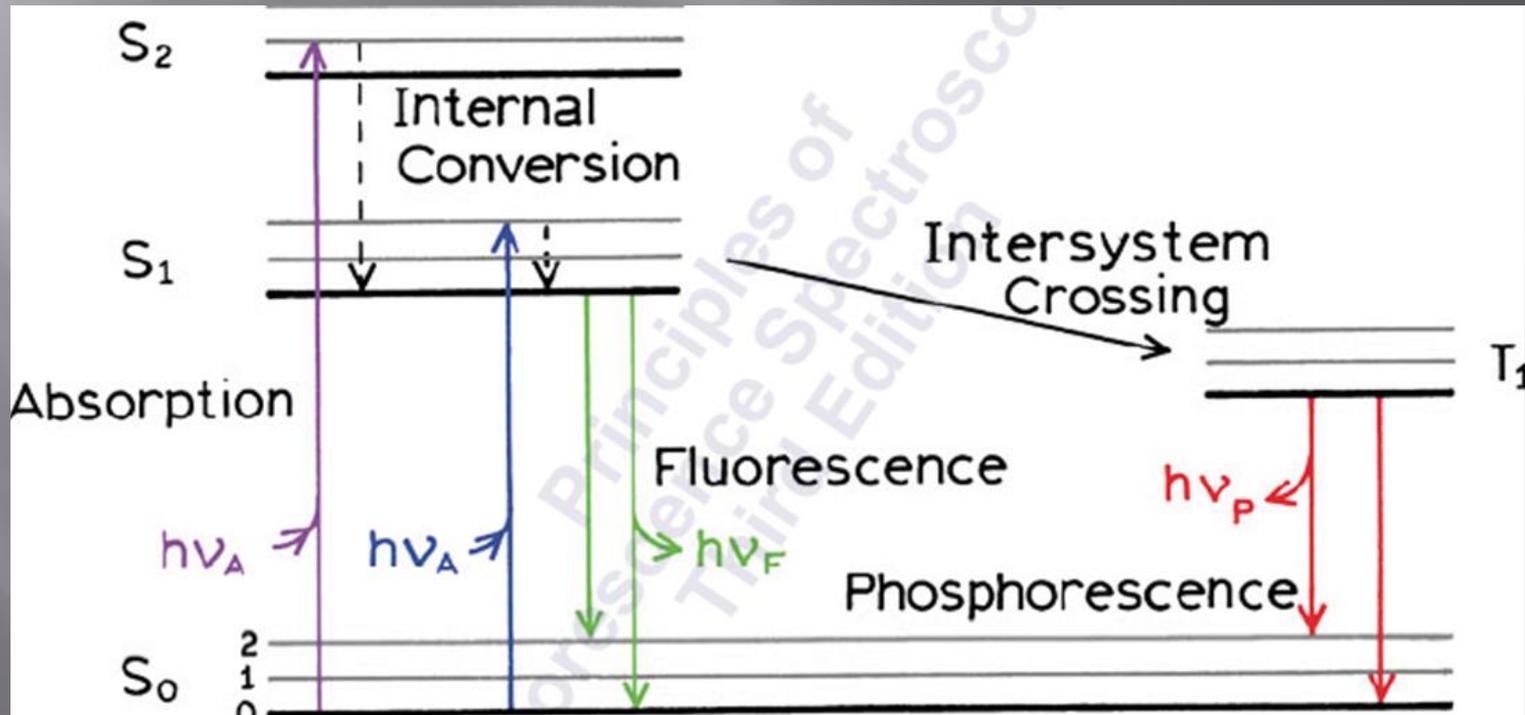
$$S = 1/2 + 1/2 = 1$$

Triplet excited

$$\text{Multiplicity} = 2(1) + 1 = 3$$

Jablonski Diagram

- Allowed singlet states Forbidden triplet states due to spin conversion



- As we seen, light absorbed by the system is used up in bringing up a photochemical reaction. But absorbed light may not necessarily bring about a photochemical reaction but gives other phenomena also. The various phenomenon shown by excited molecule are represented by Jablonski diagram. After excitation, the molecule returns back to ground state through various mechanisms as

□ **Non-radiative transitions:**

The transitions which do not lead to emission of light radiation are called as non-radiative transitions. They are of two types

i) Internal conversion(IC)

ii) Inter system crossing(ISC)

- **i) Internal conversion(IC):** If the molecule loses some of its energy in the form of heat and higher singlet state to lower singlet state(S₃ TO S₂ or S₂ TO S₁).it is called as internal conversion (IC).This process occurs in less than 10⁻¹¹ seconds.Since the energy is released in the form of heat,it is a non radiative or radiationless transition.

- **ii) Inter system crossing(ISC):** If energy is released in the form of heat and the molecule changes its spin state or spin multiplicity, the process is called as inter system crossing(ISC).In this case, molecule comes from S2 to T2, S3 to T3 etc. These transitions are spectroscopic ally forbidden and so occur at relatively slow rates.

□ **Radioative transitions:**

The transitions which lead to emission of light radiation are called as radiative transitions. These transitions are also of two types-

- a. If a molecule comes to ground state from first excited singlet state (S_1 to S_0), it leads to emission of radiation called as fluorescence. This transition is spectroscopically allowed and so occurs in about 10^{-8} seconds.
- b. If molecule comes to ground state from first excited tripletted state (T_1 to S_0), it leads to emission of radiation called as phosphorescence.

This transition is spectroscopically forbidden. Since the transition involves inversion of spin, it takes relatively longer time of the order of 10^{-3} seconds.

Both fluorescence as well as phosphorescence occur at lower frequency compared to excitation frequency because some energy is lost in the form of heat in non radiative transitions.

- Chemical reactions: In some cases, none of the above transition takes place after excitation. However, the molecule undergoes chemical reaction called as photochemical reaction. Since the singlet state returns quickly back to ground state, the probability of photochemical reaction is more in triplet state. Hence most of the photochemical reactions occur through triplet excited state.

□ **Fluorescence:**

When a beam of radiation is incident on certain substances, they emit visible radiation instantaneously, the phenomenon is known as fluorescence. It is observed due to molecular transition from first singlet excited state to ground state. This phenomenon shows following properties-

- This phenomenon is instantaneous and starts immediately after the absorption of light.
- Different substances fluoresce light of different wavelength.
- Extent of fluorescence depends upon the nature of solvent and presence of certain anions in the solution.
- It is exhibited by liquid as well as solid.
- As soon as the incident radiation is cut off, fluorescence is stopped.

Examples:

- A solution of chlorophyll shows a red colour fluorescence when illuminated in presence of oxygen.
- Teeth, hair, skin etc show fluorescence with blue light.
- Fluorescein shows intense green fluorescence in dilute alkali solution.

- Application of fluorescence
- The difference in the fluorescence caused by UV rays in different types of inks enable to detect forgotten documents
- Ring worm may be detected in fluorescence caused by UV radiation
- Fluorescence of phosphorous is being used in fluorescence lamps
- Use of this phenomenon may be made to detect presence of invisible radiation like UV rays

Phosphorescence

- When beam of light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This phenomenon are called as Phosphorescence.
- The substances exhibiting the phenomenon are called as phosphorescent substances.

- This phenomenon occurs when transition takes place from first excited triplet state(T_1) to ground state(S_0). This phenomenon has following properties:
 1. The phenomenon is caused chiefly by the ultraviolet and violet radiations.
 2. The phenomenon is mainly shown by solids.
 3. The magnetic and dielectric properties of phosphorescent substances are different before and after illumination. This is due to change in spin of electron.

4. The time for which light is emitted from the phosphorescent substances depends upon the nature of the substances and sometimes on the temperature changes.

5. Phosphorescence continues even after the incident radiation is cut off.

Examples:

- Sulphides of zinc, alkali and alkaline earth metals exhibit the phenomenon
- Many dyes when fixed by suitable method show phosphorescence
- Minerals, ruby, emerald show phosphorescence

□ **Applications of phosphorescence:**

- Luminous paints contain about 2-5% alkali chlorides and trace of heavy metal sulphide , such a mixture is generally used for painting, watch dials, electric switches, road signs etc.

Chemiluminescence

- Certain chemical reactions results in the formation of products which are in electroconically excited state. When these excited molecules return to ground state, they emit extra energy in the form of visible light radiations. The phenomenon of emission of visible light in a chemical reaction is known as chemiluminescence.
- When alkali metal vapours react with halogens or with mercuric halides, chemiluminescenc occurs which consist of the spectrum of alkali metal.

- Consider reaction of metallic sodium with chlorine. Sodium metal contains monoatomic and diatomic molecules. The mechanism is as follows:



- Sodium vapour lamps and mercury vapour lamps used as street lights are common examples of chemiluminescence.

Photosensitization(Energy transfer process)

- There are many substances which do not react directly when exposed to light . However if some third substance is added, the photochemical reaction starts. The third substance thus added itself does not undergo any chemical change. It merely absorbs the light energy and then transfers it on to one of the reactants . Such a substance which when added to a reaction mixture helps to start a photochemical reaction but itself does not undergo any chemical change is called a photosensitizer and the process is called ***photosensitization***. Thus ,photosensitizer simply acts as a carrier of energy

Photosensitization



In this reaction chlorophyll act as photosensitizer

- Hydrogen molecules do not dissociates when exposed to UV light . However when hydrogen gas is mixed with mercury vapor and then exposed to UV light, hydrogen molecules dissociate to give hydrogen atoms
- Oxalic acid undergoes decomposition in the of uranyl sulphate which remains unchanged at the end of reaction. Uranyl ions act as photosensitizer in the reaction.