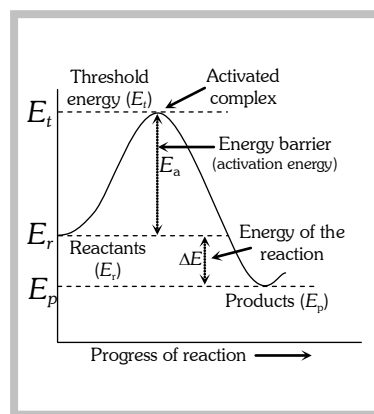
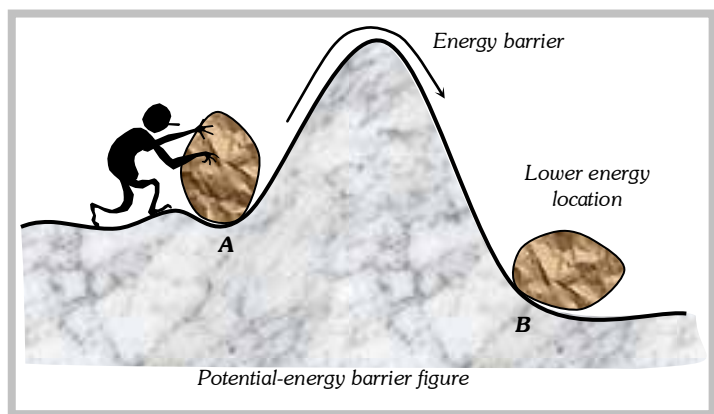


## Chemical Kinetics Part 2



**Note :** ✱ The activation energy is found to increase with the lowering of temperature i.e., at lower temperatures the activation energy tends to increase.

### (2) Transition state theory

(i) According to transition state theory the activated complex is supposed to be in equilibrium with the reactant molecules.

(ii) Once the transition state is formed it can either return to the initial reactants or proceeds to form the products.

(iii) Assuming that once formed the transition state proceeds to products we can say that rate is proportional to concentration of transition state. Mathematically,  $\text{Rate} \propto \text{Transition state}$ ; **Rate = Constant  $\times$  Transition state**

(iv) The activation energy for the forward reaction, ( $E_a^f$ ) and the activation energy for the reverse reaction ( $E_a^r$ ) are related to the enthalpy ( $\Delta H$ ) of the reaction by the equation  $\Delta H = E_a^f - E_a^r$ .

(a) For endothermic reactions,  $\Delta H > 0$ , so that  $E_a^r < E_a^f$

(b) For exothermic reaction,  $\Delta H < 0$ , so that  $E_a^r > E_a^f$ .

**Note :** ✱ Exothermic reaction requires less activation energy than the endothermic reaction. Therefore an exothermic reaction proceeds at a faster rate than the endothermic reaction.

✱ Kinetic stability of fuels : Combustion of fuels is highly exothermic reaction yet these can be safely stored in contact with oxygen or air. The stability of fuels is due to high activation energy of these combustion reactions.

✱  $E_a$  cannot be zero (if suppose  $E_a = 0$  then according to Arrhenius equation  $k = A$  i.e., every collision between molecules leads to be chemical reaction. This is not true.)

### Dependence of reaction rate on temperature.

A general approximate rule or the effect of temperature on reaction rates is that the rate of a reaction becomes almost double for every  $10^\circ\text{C}$  rise in temperature. This is also called temperature coefficient.

**Temperature coefficient :** Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by (generally  $25^\circ\text{C}$  and  $35^\circ\text{C}$ ) 10.

$$\boxed{\text{Temperature coefficient} = \frac{k \text{ at } (t + 10^\circ\text{C})}{k \text{ at } t^\circ\text{C}} = \frac{k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}}} \quad \text{Or} \quad \boxed{\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}}$$

The temperature coefficient for most of the reactions lies between 2 and 3 i.e. the rate of reaction increase by a factor of 2 to 3, for every  $10^\circ\text{C}$  rise in temperature.

## Chemical Kinetics Part 2

### Arrhenius equation and Calculation of activation energy.

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$$k = Ae^{-E_a/RT} \quad \dots(i)$$

The equation is called **Arrhenius equation** in which constant  $A$  is known as **frequency factor**. This factor is related to number of binary molecular collision per second per litre.  $E_a$  is the activation energy.  $T$  is the absolute temperature and  $R$  is the gas constant. Both  $A$  and  $E_a$  are collectively known as **Arrhenius parameters**. Taking logarithm equation (i) may be written as,

$$\log k = \log A - \frac{E_a}{2.303RT} \quad \dots(ii)$$

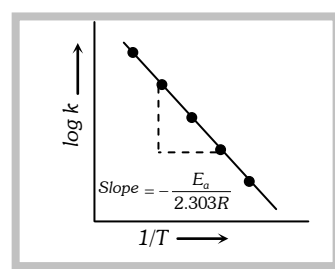
The value of activation energy ( $E_a$ ) increases, the value of  $k$  decreases and therefore, the reaction rate decreases. When  $\log k$  plotted against  $\frac{1}{T}$ , we get a straight line. The intercept of this line is equal to  $\log A$  and slope equal to  $-\frac{E_a}{2.303R}$ . Therefore

$$E_a = -2.303R \times \text{slope}.$$

Rate constants for the reaction at two different temperatures  $T_1$  and  $T_2$ ,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots(iii)$$

where  $k_1$  and  $k_2$  are rate constant at temperatures  $T_1$  and  $T_2$  respectively ( $T_2 > T_1$ ).



**Note :** ✱ Generally rate of reaction increases with increase in temperature but remember for the reaction

$2NO + O_2 \rightarrow 2NO_2$ ; the rate decreases slightly with increase in temperature because it has small negative temperature coefficient.

✱ When  $E_a = 0$ , the rate of reaction becomes independent of temperature ( $E_a =$  activation energy)

**Example : 17** In the Arrhenius equation for a certain reaction, the values of  $A$  and  $E_a$  are  $4 \times 10^{13} \text{ sec}^{-1}$  and  $9.86 \text{ kJ mol}^{-1}$  respectively. If the reaction is of first order, at what temperature will its half life period be 10 minute

[IIT 1990]

- (a) 311.34 K                      (b) 31.134 K                      (c) 411.34 K                      (d) 41.134 K

**Solution :** (a) According to Arrhenius equation,  $k = Ae^{-E_a/RT}$  or  $\log \frac{k}{A} = -\frac{E_a}{RT} \times \frac{1}{2.303}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \times 60} = 1.155 \times 10^{-3}$$

$$\therefore \log \frac{1.155 \times 10^{-3}}{4 \times 10^{13}} = -\frac{98.6 \times 10^3}{8.314 \times T \times 2.303} \quad \text{or} \quad -16.54 = -\frac{98600}{8.314 \times 2.303 T}$$

$$\text{or } T = \frac{98600}{8.314 \times 2.303 \times 16.54} = 311.34 \text{ K.}$$

**Example : 18** A first order reaction is 50% completed in 30 minutes at  $27^\circ\text{C}$  and in 10 minutes at  $47^\circ\text{C}$ . Calculate the activation energy of the reaction.

## Chemical Kinetics Part 2

- (a)  $46.8 \text{ kJ mol}^{-1}$       (b)  $43.8 \text{ kJ mol}^{-1}$       (c)  $50.8 \text{ kJ mol}^{-1}$       (d)  $60.8 \text{ kJ mol}^{-1}$

**Solution :** (b) Let us first calculate  $k_1$  and  $k_2$  at temperatures  $27^\circ\text{C}$  and  $47^\circ\text{C}$ . We know that  $t_{1/2} = \frac{0.693}{k}$  or  $k = \frac{0.693}{t_{1/2}}$

$$\text{At } 27^\circ\text{C}, t_{1/2} = 30 \text{ min}; k_1 = \frac{0.693}{30} = 0.0231$$

$$\text{At } 47^\circ\text{C}, t_{1/2} = 10 \text{ min}; k_2 = \frac{0.693}{10} = 0.0693$$

$$\text{Now, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]; \log \frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{300} - \frac{1}{320} \right]$$

$$\log 3 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{20}{300 \times 320} \right] \Rightarrow 0.4771 = \frac{E_a \times 20}{2.303 \times 8.314 \times 300 \times 320}$$

$$\text{or } E_a = \frac{0.4771 \times 2.303 \times 8.314 \times 300 \times 320}{20} = 43848 \text{ J mol}^{-1} \text{ or } 43.8 \text{ kJ mol}^{-1}.$$

**Example : 19** The rate of reaction becomes 2 times for every  $10^\circ\text{C}$  rise in temperature. How the rate of reaction will increase when temperature is increased from  $30^\circ\text{C}$  to  $80^\circ\text{C}$

- (a) 16      (b) 32      (c) 64      (d) 128

**Solution:** (b)  $\frac{k_t + 10}{k_t} = \frac{r_t + 10}{r_t} = 2.$

For an increase of temperature to  $50^\circ\text{C}$ , i.e., 5 times, the rate increases by  $2^5$  times, i.e., 32 times.

**Example : 20** The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at  $25^\circ\text{C}$  are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant as  $T \rightarrow \infty$  is

[IIT 1996]

- (a)  $2.0 \times 10^{18} \text{ s}^{-1}$       (b)  $6.0 \times 10^{14} \text{ s}^{-1}$       (c) Infinity      (d)  $3.6 \times 10^{30} \text{ s}^{-1}$

**Solution:** (b)  $k = Ae^{-E_a/RT}$ ; At  $T \rightarrow \infty$  i.e.,  $\frac{1}{T} \rightarrow 0$ ;  $k = A = 6 \times 10^{14} \text{ sec}^{-1}$

**Example : 21** The activation energy of a reaction is  $9 \text{ kcal / mole}$ . The increase in the rate constant when its temperature is raised from 295 to 300 K is approximately

[Pb. CET 1988]

- (a) 10%      (b) 50%      (c) 100%      (d) 28.8%

**Solution:** (d)  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] = \frac{9000}{2.303 \times 2} \left[ \frac{300 - 295}{295 \times 300} \right] = 0.1103$

Hence  $\frac{k_2}{k_1} = 1.288$  or  $k_2 = 1.288 k_1$  i.e., increase = 28.8%.

### Mechanism of the reaction.

- The study of reaction pathway or mechanism of a reaction is very important aspect of kinetics of reaction.
- In some reactions, intermediates formed which accumulate during the early period of the reaction, reach to the maximum concentration and then react and give the final products.
- The necessary condition for a mechanism is that it must lead to the correct law.

#### (1) Reaction involving first order consecutive reactions

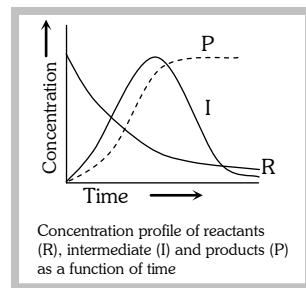
## Chemical Kinetics Part 2

(i) In such reactions, the reactions form a stable intermediate compound before they are finally converted into the products.

(ii) For example, reactants ( $R$ ) are first converted to intermediate ( $I$ ) which is then converted to product ( $P$ ) as  $R \xrightarrow{k_1} I \xrightarrow{k_2} P$ ; Therefore, the reaction takes place in two steps, both of which are first order i.e.,



This means that  $I$  is produced by step I and consumed by step II. In these reactions, each stage will have its own rate and rate constant the reactant concentration will always decrease and product concentration will always increase as shown in fig.



(2) **Reaction involving slow step** : When a reaction occurs by a sequence of steps and one of the step is slow, then the rate determining step is the slow step. For example in the reaction

$R \xrightarrow{k_1} I$ ;  $I \xrightarrow{k_2} P$ , if  $k_1 \ll k_2$  then  $I$  is converted into products as soon as it is formed, we can say that

$$-\frac{d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

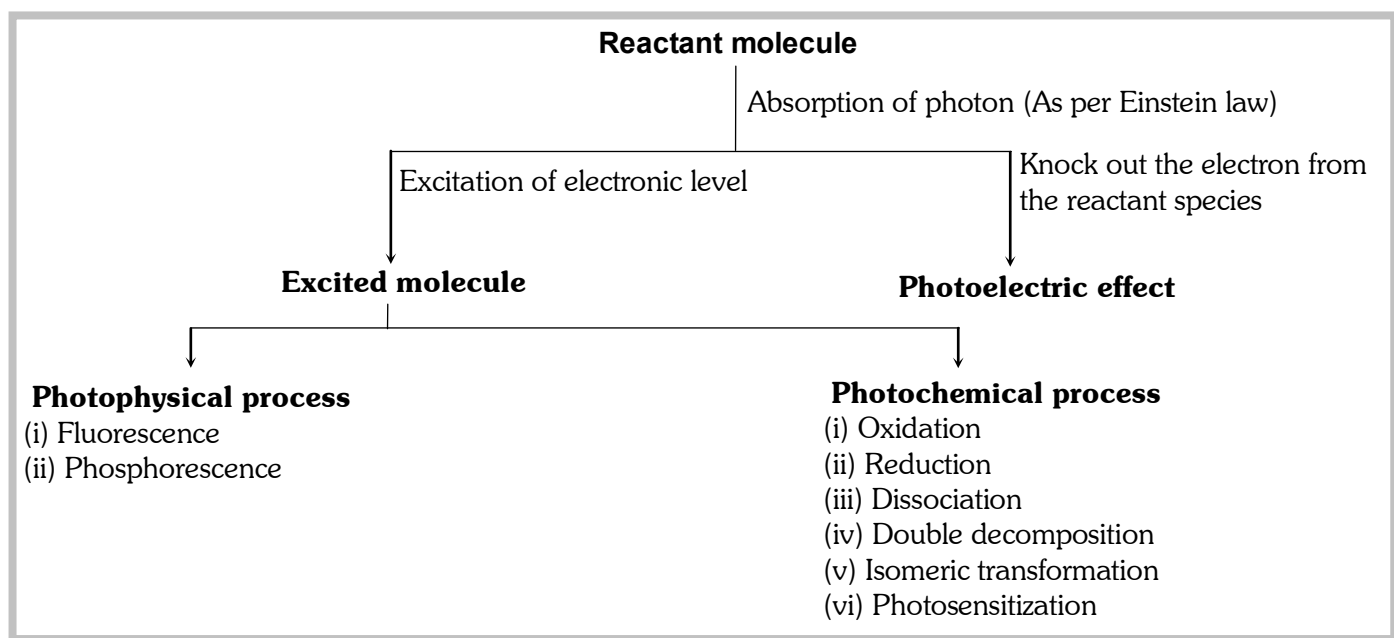
(3) **Parallel reactions** : In such type of reactions the reactants are more reactive, which may have different orders of the reactions taking place simultaneously. For example, in a system containing  $NO_2$  and  $SO_2$ ,  $NO_2$  is consumed in the following two reactions,  $2NO_2 \xrightarrow{k_1} N_2O_4$ ;  $NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$

The rate of disappearance of  $NO_2$  will be sum of the rates of the two reactions i.e.,

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 + k_2[NO_2][SO_2]$$

### Photochemical reactions:

Absorption of radiant energy by reactant molecules brings in photophysical as well as photochemical changes. According to **Einstein's law** of photochemical equivalence, the basic principle of photo processes, each reactant molecule is capable of absorbing only one photon of radiant energy. The absorption of photon by a reactant molecule may lead to any of the photo process.



## Chemical Kinetics Part 2

The chemical reactions, which are initiated as a result of absorption of light, are known as **photochemical reactions**. In such cases, the absorbed energy is sufficient to activate the reactant molecules to cross the energy barrier existing between the reactants and products or in other words, energy associated with each photon supplies activation energy to reactant molecule required for the change.

### (1) Characteristics of photochemical reactions

(i) Each molecule taking part in a photo process absorbs only one photon of radiant energy thereby increasing its energy level by  $h\nu$  or  $\frac{hc}{\lambda}$

(ii) Photochemical reactions do not occur in **dark**.

(iii) Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon. For example, reactions needing more energy are carried out in presence of UV light (lower  $\lambda$ , more E/Photon). A reaction-taking place in UV light may not occur on exposure to yellow light (lower  $\lambda$  and lesser E/Photon)

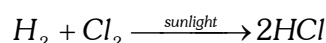
(iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.

(v) The  $\Delta G$  values for light initiated reactions may or may not be **negative**.

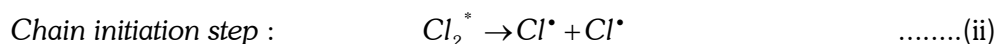
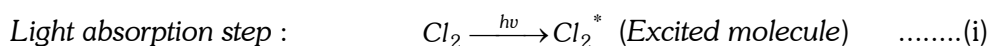
(vi) The temperature does not have marked effect on the rate of light initiated reactions.

### (2) Mechanism of some photochemical reactions

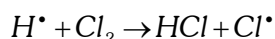
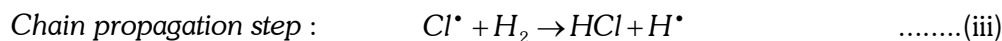
(i) **Photochemical combination of  $H_2$  and  $Cl_2$** : A mixture of  $H_2$  and  $Cl_2$  on exposure to light give rise to the formation of  $HCl$ , showing a chain reaction and thereby producing  $10^6$  to  $10^8$  molecules of  $HCl$  per photon absorbed.



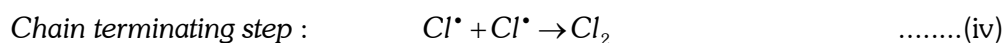
The mechanism leading to very high yield of  $HCl$  as a result of chemical change can be as follows. Chlorine molecules absorb radiant energy to form an excited molecule which decomposes to chlorine free radicals ( $Cl$ ) to give chain initiation step.



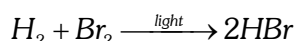
The chlorine free radical then combines with  $H_2$  molecule to form  $HCl$  and  $H^\bullet$  free radical. The  $H^\bullet$  free radical so formed again combines with another  $Cl_2$  molecule to give  $HCl$  and  $Cl^\bullet$  free radical back resulting into chain propagation step.



The combination of two  $Cl^\bullet$  free radicals leads to chain terminating step.

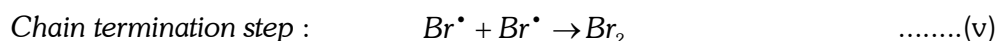
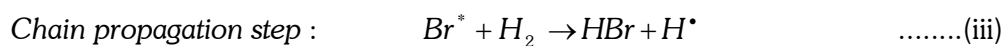
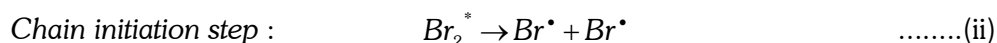
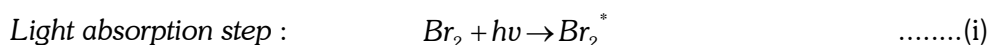


(ii) **Photochemical combination of  $H_2$  and  $Br_2$** : The combination of  $H_2$  and  $Br_2$  to form  $HBr$  in presence of light is also an example of chain reaction like photochemical combination of  $H_2$  and  $Cl_2$ . Here two  $Br_2$  molecules absorb photon, however, inspite of chain reaction only one molecule of  $HBr$  is formed for each 100 photon absorbed by 100 molecules of  $Br_2$ . The mechanism of reaction is given below.



## Chemical Kinetics Part 2

### Mechanism :



The lower values of  $HBr$  formation per photon of light absorbed has been attributed to the fact that step (III) is highly endothermic and thus before step (III) can take place most of the bromine free radicals recombine as per step (V) to give  $Br_2$  molecule and thus providing less feasibility for step (IV) i.e. steps regenerating free radicals. Also the decomposition of  $HBr$  increases with increase in temperature.

(3) **Quantum yield** (or quantum efficiency) : The quantum efficiency or yield ( $\phi$ ) of a photochemical reaction may be expressed as,  $\phi = \frac{\text{No. of molecules reacted or product formed}}{\text{No. of photon absorbed}}$

(4) **Application of photochemistry** : Photochemistry has significant role in our daily life. Some of the photochemical reactions commonly known as cited below,

- |   |  |
|---|--|
| (i) Photosynthesis in plants                              | (ii) Photography                         |
| (iii) The formation and destruction of ozone layer        | (iv) Photoetching in electronic industry |
| (v) Many polymerization reactions.                        | (vi) Modern printing technology          |
| (vii) Free radical combinations to obtain many compounds. |  |

(5) **Damaging effect of photochemistry** : As already discussed, the destruction of ozone layer by chloro-fluorocarbon is due to photochemical decomposition of these compounds. The fading away of colours in coloured fabrics is due to the photochemical decomposition of colouring material (i.e. dyes) used in printing technology.

**Note** : \* Generally ultraviolet or visible radiation's are used for carrying out such type of reactions because their photons possess energies approximately of the order of 420 kJ per mol which is comparable to mole of the bond energy. Thus UV radiation energy is capable of breaking the bonds. On the other hand IR radiation's are generally not used because their photons possess energy of the order of 60 kJ per mole which is quite less for breaking the bonds.

\*Destruction of ozone layer : The formation and dissociation of ozone keeps a balance of ozone and oxygen in the ozone layer. However the diffusion of chloro-fluorocarbon such as  $CFCl_3$  and  $CF_2Cl_2$  into the ozone layer are destroying the ozone.  $Cl_2 + hv \rightarrow CF_2 \dot{Cl} + \dot{Cl}$ ;  $\dot{Cl} + O_3 \rightarrow \dot{ClO} + O_2$ ;  $\dot{ClO} + O_3 \rightarrow \dot{Cl} + 2O_2$ . Chloro-fluorocarbons are used as aerosol repellents and as refrigerants.

Hence, ozone layer which acts as an umbrella for earth is being continuously destroying by the harmful UV radiation's coming from the sun.

## Chemical Kinetics Part 2

### Study of fast reactions.

Rates of chemical reactions differ from very slow to very fast. The rates of moderate speed reactions lying in between these two extreme reactions. However, rates of some instantaneous reactions are so fast that they occur within  $10^{-12}$  second or in even less time. For example,

- **Neutralization** reactions have half life of  $10^{-10}$  sec ;  $H^+_{(aq.)} + OH^-_{(aq.)} \rightarrow H_2O_{(l)}$
- **Photosynthesis** has half life of  $10^{-12}$  sec ;  $6CO_2 + 6H_2O \xrightarrow[h\nu]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$
- **Some precipitation** reactions have very short half life;  $AgNO_3 + KCl \rightarrow AgCl \downarrow + KNO_3$
- **Isomerisation** of retinal in vision has half life of  $10^{-12}$  sec

Rates of such reactions cannot be studied by ordinary methods because change in concentration cannot be measured during this short interval of time. However, modern techniques such as flow methods, relaxation methods, flash photolysis, laser technique and spectrophotometric methods are used to study such fast reactions.

(1) **Photosynthesis in plants** : Plants obtain their food for growth by the combination of  $CO_2$  and  $H_2O$  in presence of chlorophyll and light (a fast reaction) which leads to the preparation of carbohydrate and this phenomenon is known as **photosynthesis**. The studies on photosynthesis involve flash photolysis technique. The following mechanism has been proposed for photosynthesis. First step of the reaction mechanism involves the excitation of chlorophyll molecule by absorbing photon of red light. The excited chlorophyll molecule transfers its energy in the form of an electron to nearby reactant molecule A within  $10^{-12}$  second. The reactant molecule which accepts this energy is known as **electron acceptor**.



The electron acceptor (A) transfer this electron to another electron acceptor molecule (B).  $A^- + B \rightarrow A + B^- + E$

The process leads to release of energy which is used for the series of reaction to yield the synthesis of energy rich molecule of carbohydrates from  $CO_2$  and water.  $6CO_2 + 6H_2O \xrightarrow{\text{Energy}} C_6H_{12}O_6 + 6O_2$

(2) **Isomerisation of retinal in vision** : The mechanism involves two steps

(i) The retinal molecule (a light sensitive molecule present in the retina of eye) gets excited on exposure to light and undergoes geometrical isomerization and the energy absorbed is stored as chemical energy. The process takes place within  $10^{-12}$  sec.

(ii) As soon as the first step gets completed, the retinal is converted back into its original form within  $10^{-12}$  sec and the energy released is used to send signals to the brain which ultimately causes the sensation of vision.

### Differences between Photochemical and Thermochemical reactions

Photochemical reactions	Thermochemical reactions
These reactions are initiated by light radiation.	These reactions are initiated by heat energy.
They cannot occur in dark.	They do occur in dark.
Temperature does not have any significant effect on the rates of such reactions and temperature coefficient is low.	The temperature does have a marked effect on the rates of these reactions and temperature coefficient is generally high.
<b>The value of <math>\Delta G</math> may be +ve or - ve.</b>	<b><math>\Delta G</math> is - ve for such reactions.</b>



## Chemical Kinetics Part 2

### Important tips

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- **Chemiluminescence** : It is the emission of light in chemical reaction at ordinary temperature e.g., the light emitted by **glow worms** (fire flies) is due to the oxidation of a protein **Luciferin** present in them.
  - **Fluorescence and Phosphorescence** : There are some substances which when exposed to light or radiation, absorb light and immediately start re-emitting the energy. The glow continues as long as the source of light is there. Such substances are called fluorescent substances and the phenomenon as fluorescence e.g., **fluorite** ( $\text{CaF}_2$ ), fluorescein dye etc.  
  
On the other hand, there are some substances which continue to glow for some time even after the source of light is cut off. Such substances are called phosphorescent substances and the phenomenon as phosphorescence e.g., **Zinc sulphide** and sulphides of other alkaline earth metals.
  - **Bioluminescence** : Certain living organisms emit light and show the phenomenon of chemiluminescence. It is known as Bioluminescence e.g., light emission in fire flies.
  - Example of fourth order reaction,  $4\text{KClO}_3 \rightleftharpoons 3\text{KClO}_4 + \text{KCl}$
  - **Grothus-Draper law** : When light falls on a substance, a part of light is absorbed, a part is reflected and a part is transmitted. Only that part of light which is absorbed causes a particular reaction to occur.
  - **Stark's Einstein law of photochemical equivalence** : According to this law, every atom or molecule taking part in a photochemical reaction absorbs only one quantum of radiation. ( $E = h\nu$ ). The energy absorbed by one mole of reacting molecules is known as one Einstein.
  - Free energy ( $\Delta G$ ) for thermochemical reactions is always negative but remember,  $\Delta G$  for photochemical reactions may not always be negative. It is because a part of the light energy absorbed by the reactants is converted into free energy of the products. In the following photochemical reactions for which  $\Delta G$  is positive and still they are spontaneous  
(a) Ozonisation of oxygen (b) Synthesis of carbohydrates (c) Decomposition of  $\text{HCl}$  to  $\text{H}_2$  and  $\text{Cl}_2$
  - There are some substances which when added to a reaction mixture helps to start the photochemical reaction but do not undergo any chemical change are called photosensitizer and this process is called photosensitization. A photosensitizer simply acts as a carrier of energy. For example (i) Dissociation of  $\text{H}_2$  in the presence of mercury vapours. (ii) Photosynthesis in presence of chlorophyll.
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