

B.Sc. (Honours) Part-III
Paper-VA

Topic: Photochemistry-Basic Concepts
UG

Subject-Chemistry

Dr. Laxman Singh
Asst. Professor
Department of Chemistry
R.R.S. College (PPU)
(Mokama, Patna)

Chemistry: forming or breaking of chemical bonds and charge transfer within or between molecules. Photochemical reactions are processes during which the energy required for their *activation* (AU^\pm) or their development (AGr) is provided by an electromagnetic radiation. Activation energies of the order of $AU^\pm = 100 \text{ kJ}\cdot\text{mol}^{-1}$ and bond energies of the order of $AG = 200\text{-}400 \text{ kJ}\cdot\text{mol}^{-1}$ imply absorption of photons that should individually carry an equivalent amount of energy.

Ordinary reactions occur by absorption of heat energy from outside. The reacting molecules are energised and molecular collisions become effective. These bring about the reaction. The reactions which are caused by heat and in absence of light are called **thermal or dark reactions**.

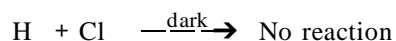
On the other hand, some reactions proceed by absorption of light radiations. These belong to the visible and ultraviolet regions of the electromagnetic spectrum (2000 to 8000 Å). The reactant molecules absorb photons of light and get excited. These excited molecules then produce the reactions.

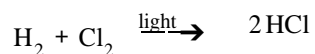
A reaction which takes place by absorption of the visible and ultraviolet radiations is called a photochemical reaction.

The branch of chemistry which deals with the study of photochemical reactions is called **photochemistry**.

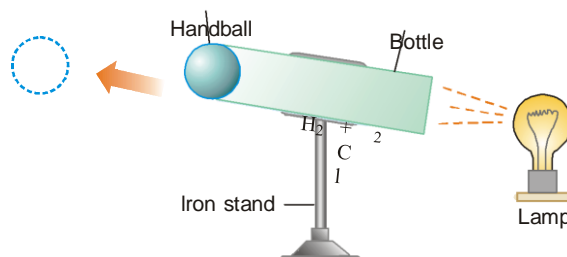
Demonstration of a Photochemical reaction

A mixture of hydrogen and chlorine remains unchanged with lapse of time. But when exposed to light, the reaction occurs with a loud explosion.





A bottle is filled with equimolar amounts of hydrogen and chlorine (Fig. 30.1). It is tightly stoppered with a handball. When the lamp is turned on, a beam of light falls on the mixture through the bottom of the bottle. The reaction occurs with an explosion. The ball is expelled with high velocity so that it strikes the opposite wall of the lecture theatre.



The 'HCl-cannon' experiment.

DIFFERENCE BETWEEN PHOTOCHEMICAL AND THERMOCHEMICAL REACTIONS

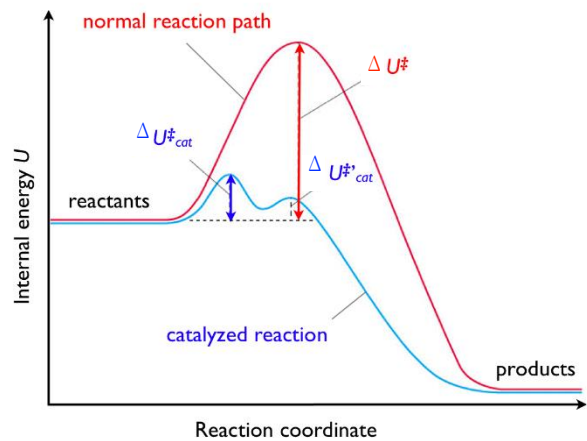
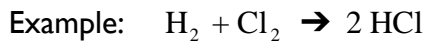
Photochemical Reactions	Thermochemical Reactions
<ol style="list-style-type: none"> 1. These involve absorption of light radiations. 2. The presence of light is the primary requirement for reactions to take place. 3. Temperature has a very little effect on the rate of photochemical reactions. 4. AG for photochemical spontaneous reactions may be +ve or -ve. 5. Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction. 	<ol style="list-style-type: none"> 1. These reactions involve absorption or evolution of heat. 2. These reactions can take place in dark as well as in light. 3. Temperature has a significant effect on the rate of a thermochemical reaction. 4. AG for a thermochemical reaction is always negative. 5. Thermochemical activation is not selective in nature

Types of photochemical reactions

a) $\Delta G_r < 0$ (exergonic reaction, spontaneous)

Light enable for overcoming the activation barrier or to lower it by acting as a catalyst.

Such reactions are called "photocatalytic"

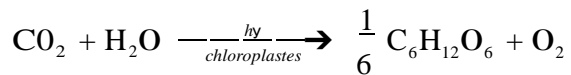


b) $\Delta G_r > 0$ (endergonic, non spontaneous)

Energy required by the reaction is brought by light. Light energy is (partially) converted into chemical energy.

Example:

Natural photosynthesis



$$\Delta G = 496 \text{ kJ} \cdot \text{mol}^{-1}$$

Functions associated with light

a) Light as a reactant

- synthesis of B

- reaction inhibition (photo-stabilization of A)

b) Light as an energy vector

- endergonic formation of B

- energy storage

c) Light as information vector

- optical absorption profile (photography, information storage)

- charge density profile (xerography)

- 3D material profile (photolithography)