## PHOTOSENSITIZED REACTIONS

In many photochemical reactions the reactant molecule does not absorb the radiation required for the reaction. Hence the reaction is not possible. In such cases the reaction may still occur if a foreign species such as mercury vapour is present. The mercury atom absorbs the incident radiation and subsequently transfers its energy to the reactant molecule which is activated. Thus the reaction occurs. A species which can both absorb and transfer radiant energy for activation of the reactant molecule, is called a **photosensitizer.** The reaction so caused is called a **photosensitized reaction.**

The role of mercury vapour is that of a go-between. The mercury atom absorbs the incident radiation and is excited. The excited atom collides with a reactant molecule (A) and transfer to it the excitation energy. This energy is enough to activate the molecule (A). The mercury atom returns to the original unactivated state.

$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + A \longrightarrow A^* + Hg$$

### Examples of Photosensitized reactions

(*a*) **Reaction between $H_2$ and $O_2$.** This reaction is photosensitized by mercury vapour. The product is hydrogen peroxide, $H_2O_2$.

$$Hg + h\nu \longrightarrow Hg^* \qquad \text{Primary absorption}$$

$$Hg + H_2 \longrightarrow 2H + Hg \qquad \text{Energy transfer}$$

$$\left.\begin{array}{l} H + O_2 \longrightarrow HO_2 \\ HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \end{array}\right\} \text{Reaction}$$

Hydrogen peroxide may decompose to form water, $H_2O$.

(*b*) **Reaction between $H_2$ and CO.** Mercury vapour is used as photosensitizer. The product is formaldehyde, HCHO.

$$Hg + h\nu \longrightarrow Hg^* \qquad \text{Primary absorption}$$

$$Hg + H_2 \longrightarrow 2H + Hg \qquad \text{Energy transfer}$$

$$H + CO \longrightarrow HCO$$

$$\left.\begin{array}{l} HCO + H_2 \longrightarrow HCHO + H \\ 2HCO \longrightarrow HCHO + CO \end{array}\right\} \text{Reaction}$$

Some glyoxal, CHO-CHO, is also formed by dimerization of formyl radicals, HCO.

## PHOTOPHYSICAL PROCESSES

If the absorbed radiation is not used to cause a chemical change, it is re-emitted as light of longer wavelength. The three such photophysical processes which can occur are :

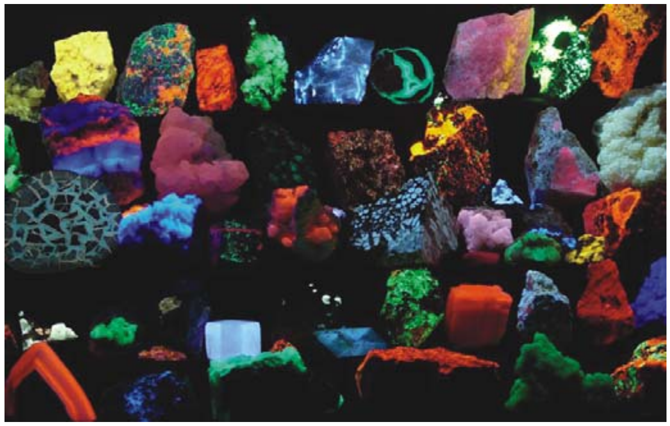
(*a*) Fluorescence (*b*) Phosphorescence (*c*) Chemiluminescence

### Fluorescence

**Certain molecules (or atoms) when exposed to light radiation of short wavelength (high frequency), emit light of longer wavelength.** The process is called **fluorescence** and the substance that exhibits fluorescence is called florescent substance. Florescence stops as soon as the incident radiation is cut off.

**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.



■ **Figure 30.7**
**Fluorescent minerals, shown under ultraviolet light.**


■ **Figure 30.8**
**Tonic water is clear under normal light, but vividly fluorescent under ultraviolet light, due to the presence of the quinine used as a flavoring.**

■ **Figure 30.9**
**A solution of chlorophyll in ether solution shows blood red fluorescence.**

**Explanation.** When a molecule absorbs high energy radiation, it is excited to higher energy states. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits light of longer frequency. The colour of fluorescence depends on the wavelength of light emitted.

## Phosphorescence

**When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off, the process is called phosphorescence.** The substance which shows phosphorescence is called **phosphorescent substance.**

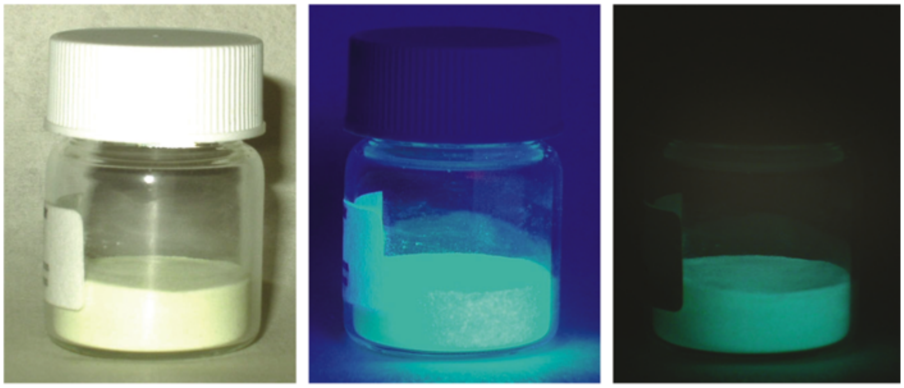
Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by solids.

**Examples.** (*a*) Sulphates of calcium, barium and strontium exhibit phosphorescence.

(*b*) Fluorescein in boric acid shows phosphorescence in the blue region at 5700 Å wavelength.

**Explanation.** As in fluorescence, a molecule absorbs light radiation and gets excited. While returning to the ground state, it emits light energy of longer wavelength. In doing so the excited molecule passes from one series of electronic states to another and gets trapped. This shows the emission of light which persists even after the removal of light source. Thus **phosphorescence could be designated as delayed fluorescence.**

$$A + h\nu \longrightarrow A^* \xrightarrow{\text{slow}} h\nu'$$



■ **Figure 30.10**
**Phosphorescent powder under visible light, ultraviolet light, and total darkness**

### Chemiluminescence

Some chemical reactions are accompanied by the emission of visible light at ordinary temperature. **The emission of light as a result of chemical action is called chemiluminescence.** The reaction is referred to as **a chemiluminescent reaction.** Such a reaction is the reverse of a photochemical reaction which proceeds by absorption of light. The light emitted in a chemiluminescent reaction is also called **'cold light'** because it is produced at ordinary temperature.

■ **Figure 30.11**
**Chemiluminescence of fireflies and luminol.**

**Examples.** (*a*) The glow of fireflies due to the aerial oxidation of *luciferin* (a protein) in the presence of enzyme *luciferase*.

(*b*) The oxidation of 5-*aminophthalic* cyclic hydrazide (*luminol*) by hydrogen peroxide in alkaline solution, producing bright green light.

**Explanation.** In a chemiluminescent reaction, the energy released in the reaction makes the product molecule electronically excited. The excited molecule then gives up its excess energy as visible light while reverting to ground state.

## EXAMINATION QUESTIONS

**1.** Define or explain the following terms :

(*a*) Photochemical reaction
(*b*) Lambert law
(*c*) Lambert-Beer law
(*d*) Grothus-Draper law
(*e*) Stark Einstein law
(*f*) Quantum yield
(*g*) Quantum Efficiency
(*h*) Energy of photons
(*i*) Einstein

**2.** (*a*) Distinguish between photochemical and thermal reactions.

(*b*) Derive the Lambert-Beer law.

(*c*) A radiation of 2530 Å incident on HI results in the decomposition of $1.85 \times 10^{-2}$ mole per 1000 cal. of radiant energy. Calculate the quantum efficiency.

( $h = 6.62 \times 10^{-27}$; $N = 6.023 \times 10^{23}$; $c = 3 \times 10^{10}$ cm/sec.)

**Answer.** 2.09

**3.** (*a*) What is meant by quantum energy and Einstein energy? State Einstein law of photochemical equivalence.

(*b*) In the photochemical reaction B $\rightarrow$ C, $1.00 \times 10^{-5}$ mole of C is formed as a result of the absorption of $6.00 \times 10^{7}$ ergs at 3600 Å. Calculate the Quantum yield.

**Answer.** (*b*) 0.553

**4.** (*a*) How would you explain very high and very low quantum efficiencies of some photochemical reactions.

(*b*) For the photochemical reaction A $\rightarrow$ B, $1.0 \times 10^{-5}$ moles of B were formed on absorption of $6.0 \times 10^{7}$ ergs at 3600 Å. Calculate the quantum efficiency of the reaction.

($N = 6.02 \times 10^{23}$; $h = 6.0 \times 10^{-27}$ erg/sec)

(*c*) What is an actinometer? Describe how a uranyl oxalate actinometer may be used.

**Answer.** (*b*) 90.92%

**5.** Calculate the values of frequency, quantum energy and einstein for 500 nm radiation.

$c = 3.0 \times 10^{10}$ cm/sec; $N = 6.02 \times 10^{23}$; $h = 6.62 \times 10^{-27}$ erg sec.

**Answer.**$6 \times 10^{8}$; $39.72 \times 10^{-19}$ ergs; $57 \times 10^{2}$ kcal/mole$^{-1}$

**6.** (*a*) Explain briefly fluorescence and chemiluminescence.

(*b*) In a photochemical combination of $H_2$ and $Cl_2$ a quantum yield of $1 \times 10^{6}$ is obtained with a wavelength of 4800 Å. How many moles of HCl would be produced under these conditions per calories of radiation energy absorbed?

**Answer.** (*b*) 16.78 moles

**7.** A beam of monochromatic light was passed through a 1.5 m long cell filled with a solution of concentration *c* and 12 percent of the incident intensity was absorbed. What must be the length of another cell which is filled with a solution of concentration 1.5 *c* and which absorbs 48 percent of incident intensity?

**Answer.** 51.15 cm

**8.** (*a*) State and explain Einstein's law of photochemical equivalence.

(*b*) A certain system absorbs $3.0 \times 10^{16}$ quantum of light per second on irradiation for 10 minutes. 0.002 mole of the reactant was found to have reacted. Calculate the quantum efficiency of the process. ($N = 6.023 \times 10^{23}$).

**Answer.** (*b*) 66.92

**9.** A certain system absorbs $8.81 \times 10^{8}$ ergs of radiation of the wavelength 2540 Å in a certain time. It is observed that $1.12 \times 10^{-4}$ moles of the irradiated substance has reacted in the same time. What is the quantum efficiency of the process?