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30 Photochemistry

CHAPTER

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PHOTOCHEMICAL REACTIONS

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 absorbs 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.

$$H_2 + Cl_2 \xrightarrow{\text{dark}} \text{No reaction}$$

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2\,HCl$$

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.

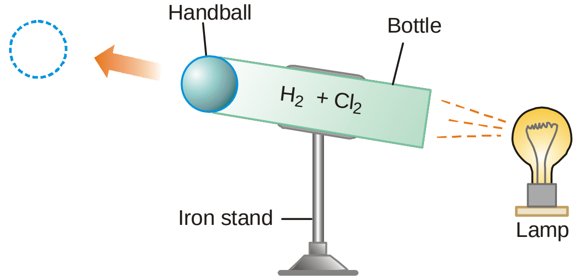


Figure 30.1
The 'HCl-cannon' experiment.

DIFFERENCE BETWEEN PHOTOCHEMICAL AND THERMOCHEMICAL REACTIONS

Photochemical Reactions	Thermochemical Reactions
1. These involve absorption of light radiations.	1. These reactions involve absorption or evolution of heat.
2. The presence of light is the primary requirement for reactions to take place.	2. These reactions can take place in dark as well as in light.
3. Temperature has a very little effect on the rate of photochemical reactions.	3. Temperature has a significant effect on the rate of a thermochemical reaction.
4. ΔG for photochemical spontaneous reactions may be +ve or –ve.	4. ΔG for a thermochemical reaction is always negative.
5. Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction.	5. Thermochemical activation is not selective in nature.

LIGHT ABSORPTION

When light is passed through a medium, a part of it is absorbed. It is this absorbed portion of light which causes photochemical reactions. Let a beam of monochromatic light pass through a thickness dx of the medium. The intensity of radiation reduces from I and $I\text{-}dI$.

The intensity of radiation can be defined as the number of photons that pass across a unit area in unit time.

Let us denote the number of incident photons by N and the number absorbed in thickness dx by dN. The fraction of photons absorbed is then dN/N which is proportional to thickness dx. That is,

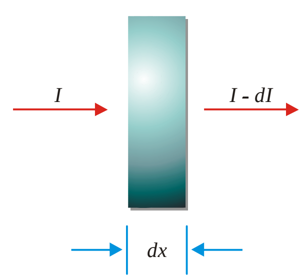


Figure 30.2
As a beam of intensity I passes through a medium of thickness dx, the intensity of the beam is reduced to I - dI.

$$\frac{dN}{N} = b\ dx = -\frac{dI}{I}$$

where b is proportionality constant called **absorption coefficient.**

Let us set $I = I_0$ at $x = 0$ and integrate. This gives

$$I = I_0\,(-\,bx)$$

or
$$\text{In}\left(\frac{I}{I_0}\right) = -\,bx \qquad ...(1)$$

Lambert first derived equation (1) and it is known as **Lambert Law.** Beer extended this relation to solutions of compounds in transparent solvents. The equation (1) then takes the form (2).

$$\text{In}\left(\frac{I}{I_0}\right) = -\in C\,x \qquad ...(2)$$

where C = molar concentration; $\in$ is a constant characteristic of the solute called the *molar absorption coefficient.* The relation (2) is known as the **Lambert-Beer Law.** This law forms the basis of spectrophotometric methods of chemical analysis.

DETERMINATION OF ABSORBED INTENSITY

A photochemical reaction occurs by the absorption of photons of light by the molecules. Therefore, it is essential to determine the absorbed intensity of light for a study of the rate of reaction.

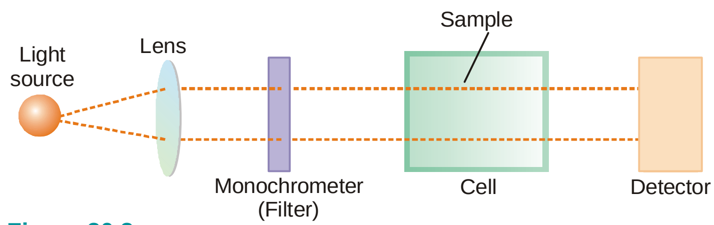


Figure 30.3
Schematic diagram of the apparatus used for measurement of light intensity.

An experimental arrangement for the purpose is illustrated in Fig. 30.3.

Light beam from a suitable source (tungsten filament or mercury vapour lamp) is rendered parallel by the lens. The beam then passes through a 'filter' or monochrometer which yields light of one wavelength only. The monochromatic light enters the reaction cell made of quartz. The part of light that is not absorbed strikes the *detector.* Thus the intensity of light is measured first with the empty cell and then the cell filled with the reaction sample. The first reading gives the incident intensity, I_0, and the second gives the transmitted intensity, I. The difference, $I_0 - I = I_a$, is the absorbed intensity.

The detector generally used for the measurement of intensity of transmitted light is :

(*a*) a thermopile (*b*) photoelectric cell (*c*) a chemical actinometer.

Thermopile

It is made of a series of thermocouples in which unlike metals such as bismuth and silver are joined together. One end of the couple is blackened with lamp black and the other end is left as such. When the radiation strikes the black end it absorbs energy and is heated up. The temperature difference between the two ends causes a current to flow in the circuit as indicated by the galvanometer. **The current is proportional to intensity of radiation.** The thermopile is previously calibrated against a standard source of light.

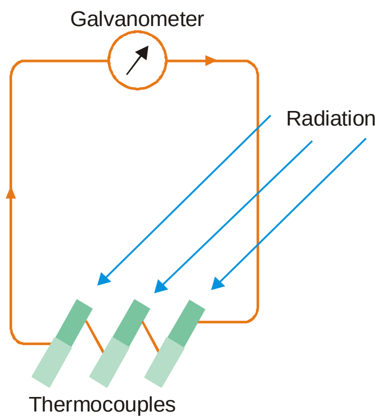


Figure 30.4
A thermopile.

Photoelectric Cell

A photoelectric cell (Fig. 30.5) can be conveniently used for measuring intensity of light. The light striking the active metal electrode (cesium, sodium or potassium) causes the emission of electrons. A current flows through the circuit which can be measured with an ammeter. The intensity of light is proportional to the current.

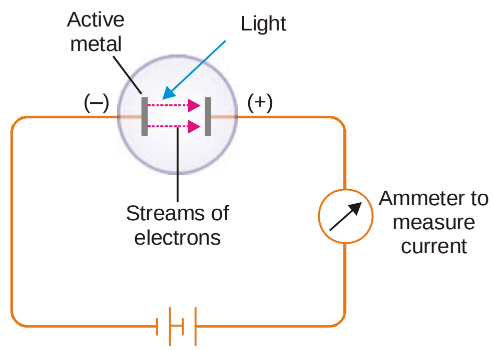


Figure 30.5
A photoelectric cell (illustration).

Chemical Actinometer

A chemical actinometer uses a chemical reaction whose rate can be determined easily. One such simple device is **Uranyl oxalate actinometer.** It contains 0.05 M oxalic acid and 0.01 M uranyl sulphate in water. When it is exposed to radiation, oxalic acid is decomposed to CO_2, CO and H_2O.

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + \underset{\text{oxalic acid}}{\begin{array}{c}\text{COOH}\\ |\\ \text{COOH}\end{array}} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The concentration of oxalic acid that remains can be found by titration with standard $KMnO_4$ solution. The used up concentration of oxalic acid is a measure of the intensity of radiation.

LAWS OF PHOTOCHEMISTRY

There are two basic laws governing photochemical reactions :

(*a*) The Grothus-Draper law

(*b*) The Stark-Einstein law of Photochemical Equivalence

Grothus–Draper Law

When light falls on a cell containing a reaction mixture, some light is absorbed and the remaining light is transmitted. Obviously, it is the absorbed component of light that is capable of producing the reaction. The transmitted light is ineffective chemically. Early in the 19th century, Grothus and Draper studied a number of photochemical reactions and enunciated a generalisation. This is known as **Grothus-Draper law** and may be stated as follows : **It is only the absorbed light radiations that are effective in producing a chemical reaction.** However, it does not mean that the absorption of radiation must necessarily be followed by a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy remains unused. It may be re-emitted as heat or light.

The Grothus-Draper law is so simple and self-evident. But it is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and the molecules undergoing change.

Stark-Einstein Law of Photochemical Equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of *Quantum theory of light.* They noted that each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction. Stark and Einstein thus proposed a basic law of photochemistry which is named after them. The **Stark-Einstein law of photochemical equivalence** may be stated as :

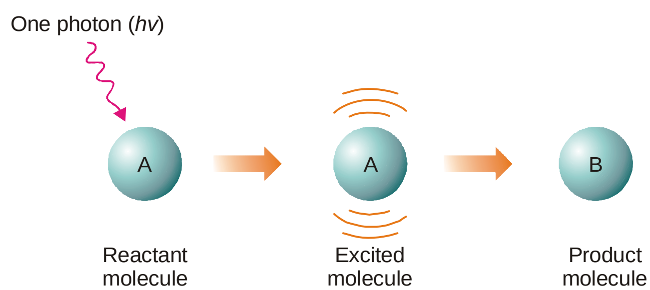


Figure 30.6
Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule.

In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products.

The law of photochemical equivalence is illustrated in Fig. 30.6 where a molecule ‘A’ absorbs a photon of radiation and gets activated. The activated molecule (A*) then decomposes to yield B. We could say the same thing in equational form as :

$$\mathrm{A} + h\nu \longrightarrow \mathrm{A}^*$$

$$\mathrm{A}^* \longrightarrow \mathrm{B}$$

$$\text{overall} \quad \mathrm{A} + h\nu \longrightarrow \mathrm{B}$$

In practice, we use molar quantities. That is, one mole of A absorbs one mole of photons or one einstein of energy, E. The value of E can be calculated by using the expression given below:

$$E = \frac{2.859}{\lambda} \times 10^5 \ \text{kcal mol}^{-1}$$

Primary and Secondary reactions

The overall photochemical reaction may consist of :

(*a*) a primary reaction

(*b*) secondary reactions

A primary reaction proceeds by absorption of radiation.

A secondary reaction is a thermal reaction which occurs subsequent to the primary reaction.

For example, the decomposition of HBr occurs as follows :

$$\begin{array}{llll} HBr + h\nu & \longrightarrow & H + Br & \text{Primary reaction} \\ HBr + H & \longrightarrow & H_2 + Br & \text{Secondary reaction} \\ Br + Br & \longrightarrow & Br_2 & \text{Secondary reaction} \\ \hline 2HBr + h\nu & \longrightarrow & H_2 + Br_2 & \text{Overall reaction} \end{array}$$

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

Quantum yield (or Quantum efficiency)

It has been shown that not always a photochemical reaction obeys the Einstein law. The number of molecules reacted or decomposed is often found to be markedly different from the number of quanta or photons of radiation absorbed in a given time.

The number of molecules reacted or formed per photon of light absorbed is termed Quantum yield. It is denoted by ϕ so that

$$\phi = \frac{\text{No. of molecules reacted or formed}}{\text{No. of photons absorbed}}$$

For a reaction that obeys strictly the Einstein law, one molecule decomposes per photon, the quantum yield $\phi = 1$. When two or more molecules are decomposed per photon, $\phi > 1$ and the reaction has a **high quantum yield.** If the number of molecules decomposed is less than one per photon, the reaction has a **low quantum yield.**

Cause of high quantum yield

When one photon decomposes or forms more than one molecule, the quantum yield $\phi > 1$ and is said to be high. The chief reasons for high quantum yield are :

(*a*) **Reactions subsequent to the Primary reaction.** One photon absorbed in a primary reaction dissociates one molecule of the reactant. But the excited atoms that result may start a subsequent secondary reaction in which a further molecule is decomposed

$$\begin{array}{llll} AB + h\nu & \longrightarrow & A + B & \text{Primary} \\ AB + A & \longrightarrow & A_2 + B & \text{Secondary} \end{array}$$

Obviously, one photon of radiation has decomposed two molecules, one in the primary reaction and one in the secondary reaction. Hence the quantum yield of the overall reaction is 2.

(*b*) **A reaction chain forms many molecules per photon.** When there are two or more reactants, a molecule of one of them absorbs a photon and dissociates (primary reaction). The excited atom that is produced starts a secondary reaction chain.

$$\begin{array}{lllll} A_2 + h\nu & \longrightarrow & 2A & ...(1) & \text{Primary} \\ A + B_2 & \longrightarrow & AB + B & ...(2) & \text{Secondary} \\ B + A_2 & \longrightarrow & AB + A & ...(3) & \text{Reaction chain} \end{array}$$

It is noteworthy that A consumed in (2) is regenerated in (3). This reaction chain continues to form two molecules each time. Thus the number of AB molecules formed in the overall reaction per photon is very large. Or that the quantum yield is extremely high.

Examples of high quantum yield

The above reasons of high quantum yield are illustrated by citing examples as below :

(*i*) **Decomposition of HI.** The decomposition of hydrogen iodide is brought about by the absorption of light of less than 4000 Å. In the primary reaction, a molecule of hydrogen iodide absorbs a photon and dissociates to produce H and I. This is followed by secondary steps as shown below :

$$HI + h\nu \longrightarrow H + I \quad ...(1) \quad \text{Primary}$$
$$\left.\begin{array}{ll} H + HI \longrightarrow H_2 + I & ...(2) \\ I + I \longrightarrow I_2 & ...(3) \end{array}\right\} \text{Secondary}$$
$$\overline{2HI + h\nu \longrightarrow H_2 + I_2} \quad \text{Overall reaction}$$

In the overall reaction, two molecules of hydrogen iodide are decomposed for one photon ($h\nu$) of light absorbed. Thus the quantum yield is 2.

(*ii*) **Hydrogen-Chlorine reaction.** This is a well known example of a **photochemical chain reaction.** A mixture of hydrogen and chlorine is exposed to light of wavelength less than 4000 Å. The hydrogen and chlorine react rapidly to form hydrogen chloride. In the primary step, a molecule of chlorine absorbs a photon and dissociates into two Cl atoms. This is followed by the secondary reactions stated below :

$$Cl_2 + h\nu \longrightarrow 2Cl \quad ...(1) \quad \text{Primary reaction}$$
$$\left.\begin{array}{ll} Cl + H_2 \longrightarrow HCl + H & ...(2) \\ H + Cl_2 \longrightarrow HCl + Cl & ...(3) \end{array}\right\} \text{Secondary reactions}$$

The Cl atom used in step (2) is regenerated in step (3). Thus the steps (2) and (3) constitute a self-propagating chain reaction. This produces two molecules of HCl in each cycle. Thus one photon of light absorbed in step (1) forms a large number of HCl molecules by repetition of the reaction sequence (2) and (3). The chain reaction terminates when the Cl atoms recombine at the walls of the vessel where they lose their excess energy.

$$2Cl \xrightarrow{\text{walls}} Cl_2$$

The number of HCl molecules formed for a photon of light is very high. The quantum yield of the reaction varies from 10^4 to 10^6.

Causes of low quantum yield

The chief reasons of low quantum yield are :

(*a*) **Deactivation of reacting molecules.** The excited molecules in the primary process may be deactivated before they get opportunity to react. This is caused by collisions with some inert molecules or by fluorescence.

$$A + h\nu \longrightarrow A^* \quad \textit{Activation}$$
$$A^* \longrightarrow A + h\nu' \quad \textit{Fluorescence}$$

(*b*) **Occurrence of reverse of primary reaction.** Here the primary reaction generally yields a polymer. The product then undergoes a thermal reaction giving back the reactant molecules.

$$2A \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} A_2$$

The reverse thermal reaction proceeds till the equilibrium state is reached.

(*c*) **Recombination of dissociated fragments.** In a primary process the reactant molecules may dissociate to give smaller fragments. These fragments can recombine to give back the reactant.

$$(AB) + h\nu \longrightarrow A + B$$

$$A + B \longrightarrow (AB)$$

Thus the secondary reactions involving the fragments to form the product will not occur. This will greatly lower the yield.

The yield of particular photochemical reaction may be lower than expected for more than one reason cited above.

Examples of low quantum yield

The examples listed below will illustrate the above causes of low quantum yield:

(*i*) **Dimerization of Anthracene.** When anthracene, $C_{14}H_{10}$, dissolved in benzene is exposed to ultraviolet light, it is converted to dianthracene, $C_{28}H_{20}$.

$$2C_{14}H_{10} + h\nu \longrightarrow C_{28}H_{20}$$

Obviously, the quantum yield should be 2 but it is actually found to be 0.5. The low quantum yield is explained as the reaction is accompanied by fluorescence which deactivates the excited anthracene molecules. Furthermore, the above reaction is reversible.

$$2C_{14}H_{10} \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} C_{28}H_{20}$$

The transformation of the product back to the reactant occurs till a state of equilibrium is reached. This further lowers the quantum yield.

(*ii*) **Combination of H_2 and Br_2.** When a mixture of hydrogen and bromine is exposed to light, hydrogen bromide is formed. The reaction occurs by the following possible steps.

$$Br_2 + h\nu \longrightarrow 2Br \quad ...(1) \quad \text{Primary reaction}$$

$$Br + H_2 \longrightarrow HBr + H \quad ...(2)$$

$$\left.\begin{array}{ll} H + Br_2 \longrightarrow HBr + Br & ...(3) \\ H + HBr \longrightarrow H_2 + Br & ...(4) \\ Br + Br \longrightarrow Br & ...(5) \end{array}\right\} \text{Secondary reactions}$$

The reaction (2) is extremely slow. The reactions (3), (4) and (5), depend directly or indirectly on (2) and so are very slow. Therefore most of the Br atoms produced in the primary process recombine to give back Br_2 molecules. Thus the HBr molecules obtained per quantum is extremely small. The quantum yield of the reaction is found to be 0.01 at ordinary temperature.

CALCULATION OF QUANTUM YIELD

By definition, the quantum yield, ϕ, of a photochemical reaction is expressed as :

$$\phi = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of photons of radiation energy absorbed}}$$

or

$$\phi = \frac{\text{Number of moles decomposed or formed}}{\text{Number of moles of radiation energy absorbed}}$$

Thus we can calculate quantum yield from :

(*a*) The amount of the reactant decomposed in a given time and

(*b*) The amount of radiation energy absorbed in the same time

The radiation energy is absorbed by a chemical system as photons. Therefore we should know the energy associated with a photon or a mole of photons.

The energy of photons; einstein

We know that the energy of a photon (or quantum), $\in$, is given by the equation.

$$\in = h\nu = \frac{hc}{\lambda} \qquad ...(1)$$

where h = Planck's constant (6.624×10^{-27} erg-sec)

ν = frequency of radiation

λ = wavelength of radiation

c = velocity of light (3×10^{10} cm sec^{-1})

If λ is given in cm, the energy is expressed in ergs.

The energy, *E*, of an Avogadro number (*N*) of photons is referred to as one einstein. That is,

$$E = \frac{Nhc}{\lambda} \qquad ...(2)$$

Substituting the values of N (= 6.02×10^{23}), h and c, in (2), we have

$$E = \frac{1.196 \times 10^{8}}{\lambda} \text{ erg mol}^{-1}$$

If λ is expressed in Å units (1Å = 10^{-8} cm),

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1} \qquad ...(3)$$

Since 1 cal = 4.184×10^{7} erg, energy in calories would be

$$E = \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^{7}} \qquad ...(4)$$

$$= \frac{2.859}{\lambda} \times 10^{8} \text{ cal mol}^{-1}$$

or

$$E = \frac{2.859}{\lambda} \times 10^{5} \text{ kcal mol}^{-1} \qquad ...(5)$$

It is evident from (3) that the numerical value of einstein varies inversely as the wavelength of radiation. **The higher the wavelength, the smaller will be the energy per einstein.**

SOLVED PROBLEM 1. Calculate the energy associated with (*a*) one photon; (*b*) one einstein of radiation of wavelength 8000 Å. $h = 6.62 \times 10^{-27}$ erg-sec; $c = 3 \times 10^{10}$ cm sec^{-1}.

SOLUTION

(*a*) Energy of a photon

$$= \frac{hc}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{8000 \times 10^{-8}}$$

$$= \frac{6.62 \times 3}{8.0} \times 10^{-12} \text{ erg} = 2.4825 \times 10^{-12} \text{ erg}$$

(*b*) Energy per einstein

$$= \frac{Nhc}{\lambda} = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{8000 \times 10^{-8}}$$

$$= \frac{6.02 \times 6.62 \times 3}{8.0} \times 10^{11} \text{ erg} = \mathbf{1.4945 \times 10^{12}} \textbf{ erg}$$

SOLVED PROBLEM 2. When a substance *A* was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time *A* absorbed 2.0×10^{6} photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Number of molecules of *A* reacting = $0.002 \times N = 0.002 \times 6.02 \times 10^{23}$

Number of photons absorbed per second = 2.0×10^6

Number of photons absorbed in 20 minutes and 4 seconds = $2.0 \times 10^6 \times 1204$

Quantum yield $\phi = \dfrac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$

$$= \frac{0.002 \times 6.02 \times 10^{23}}{2.0 \times 10^6 \times 1204} = \mathbf{5.00 \times 10^{11}}$$

SOLVED PROBLEM 3. When irradiated with light of 5000 Å wavelength, 1×10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if its quantum efficiency is 10.00. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Quantum efficiency of the reaction = 10.00

No. of moles decomposed $= 1 \times 10^{-4}$

No. of molecules decomposed $= 1 \times 10^{-4} \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{19}$

we know that,

$$\phi = \frac{\text{No. of molecules decomposed}}{\text{No. of photons absorbed}}$$

$$= \frac{6.02 \times 10^{19}}{\text{No. of photons absorbed}}$$

No. of photons absorbed $= \dfrac{6.02 \times 10^{19}}{10} = \mathbf{6.02 \times 10^{18}}$

SOLVED PROBLEM 4. When propionaldehyde is irradiated with light of λ = 3020 Å, it is decomposed to form carbon monoxide.

$$CH_3CH_2CHO + h\nu \longrightarrow CH_3CH_3 + CO$$

The quantum yield for the reaction is 0.54. The light energy absorbed is 15000 erg mol in a given time. Find the amount of carbon monoxide formed in moles in the same time.

SOLUTION

From expression (3), we have

$$\text{one einstein } (E) = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}$$

$$\text{when } \lambda = 3020 \text{ Å, one einstein} = \frac{1.196 \times 10^{16}}{3020} \text{ erg mol}$$

$$\text{or} \quad 15000 \text{ erg mol of energy} = \frac{15000 \times 3020}{1.196 \times 10^{16}} = 3.78 \times 10^{-9} \text{ einstein}$$

But $\phi = \dfrac{\text{No. of moles of CO formed}}{\text{No. of einsteins absorbed}} = 0.54$

Hence the amount of CO formed = $0.54 \times 3.78 \times 10^{-9}$ = $\mathbf{2.04 \times 10^{-9}}$ **moles**

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.

$$Hg + h\nu \longrightarrow Hg^* \quad \text{Primary absorption}$$
$$Hg + H_2 \longrightarrow 2H + Hg \quad \text{Energy transfer}$$
$$\left.\begin{array}{l} H + O_2 \longrightarrow HO_2 \\ HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \end{array}\right\} \text{Reaction}$$

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.

$$Hg + h\nu \longrightarrow Hg^* \quad \text{Primary absorption}$$
$$Hg + H_2 \longrightarrow 2H + Hg \quad \text{Energy transfer}$$
$$H + CO \longrightarrow HCO$$
$$\left.\begin{array}{l} HCO + H_2 \longrightarrow HCHO + H \\ 2HCO \longrightarrow HCHO + CO \end{array}\right\} \text{Reaction}$$

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 :

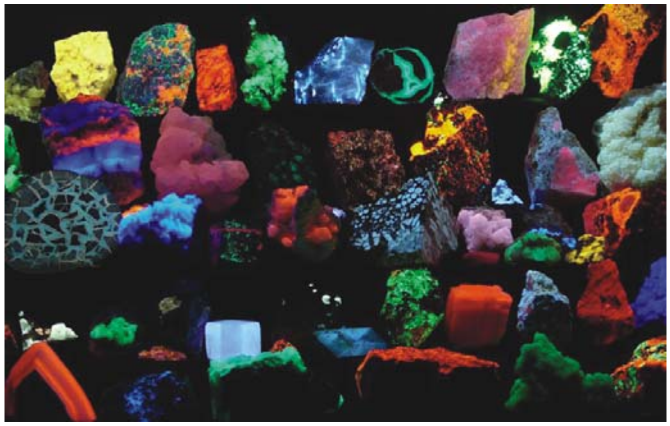
(*a*) Fluorescence (*b*) Phosphorescence (*c*) Chemiluminescence

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.**

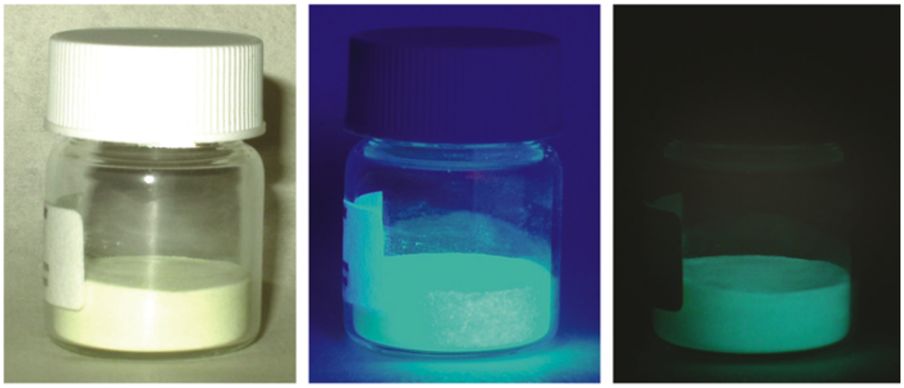
Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by solids.

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 1.85×10^{-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, 1.00×10^{-5} mole of C is formed as a result of the absorption of 6.00×10^{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, 1.0×10^{-5} moles of B were formed on absorption of 6.0×10^{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.

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

Answer.6×10^{8}; 39.72×10^{-19} ergs; 57×10^{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 1×10^{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 3.0×10^{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 8.81×10^{8} ergs of radiation of the wavelength 2540 Å in a certain time. It is observed that 1.12×10^{-4} moles of the irradiated substance has reacted in the same time. What is the quantum efficiency of the process?

$N = 6.023 \times 10^{23}$; $h = 6.625 \times 10^{-27}$ erg sec; $c = 2.998 \times 10^{10}$ cm/sec.

Answer. 0.5977

10. Radiation of wavelength 2500 Å was passed through a cell containing 10 ml of a solution which was 0.05 molar in oxalic acid and 0.01 molar in uranyl sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

Answer. 0.598

11. (*a*) 10% incident light is transmitted after passing through 2 cm thick glass. If glass is 1 cm thick, then how much light is absorbed of the same wavelength ?

(*b*) The quantum efficiency for the hydrogen chlorine reaction is very high, why?

(*c*) Explain extinction coefficient and molar absorption coefficient.

Answer. 68.38%

12. Give an account of :

(*a*) Beer's-Lambert Law

(*b*) Einstein Stark Law of photochemical equivalence (*Jiwaji BSc, 2000*)

13. (*a*) State Beer-Lambert law and mention its uses.

(*b*) Write a note on photodimerisation of anthracene. (*Madurai BSc, 2000*)

14. (*a*) Explain - Phosphorescence.

(*b*) Define quantum yield. How can it be experimentally determined? (*Jamia Millia BSc, 2001*)

15. State Stark-Einstein law of photochemical equivalence. (*Guru Nanak Dev BSc, 2002*)

16. (*a*) Distinguish between fluorescence and phosphorescence. Draw energy level diagrams to explain these processes and discuss them briefly.

(*b*) Briefly discuss flash photolysis. (*Panjab BSc, 2002*)

17. (*a*) State and explain the law of photochemistry. What do you mean by quantum yield? How is it determined experimentally?

(*b*) What do you mean by one Einstein of energy? How is it related to wavelength?

(*Panjab BSc, 2002*)

18. (*a*) Name and state the basic laws of photochemistry. Give the numerical value of one Einstein in different units in terms of wavelength in cm and Å.

(*b*) A system is irradiated for 20 minutes and is found to absorb 4×10^{18} quantum per second. If the amount decomposed is 3×10^{-3} mole and $N = 6.023 \times 10^{23}$, calculate the quantum efficiency of the reaction.

Answer. 0.376 (*Punjabi BSc, 2002*)

19. Calculate :

(*i*) Wave number and

(*ii*) Wave length of the radiation with frequency of 4×10^{14} sec^{-1}.

(Given velocity of light = 3×10^{8} m sec^{-1})

Answer. 0.75×10^{-6} m; 1.33×10^{6} m^{-1} (*Nagpur BSc, 2002*)

20. Discuss the photochemistry of following reactions:

(*i*) Photolysis of HBr

(*ii*) Photolysis of Acetone (*Panjab BSc, 2002*)

21. (*a*) Define quantum yield.

(*b*) What are the reasons for abnormal quantum yield.

(*c*) Explain fluorescence and phosphorescence. (*Andhra BSc, 2002*)

22. (*a*) Explain Lambert-Beer Law while discussing physical significance of extinction coefficient and molar extinction coefficient.

(*b*) What does the quantum efficiency or quantum yield signify? (*Panjab BSc, 2003*)

23. (*a*) Derive the mathematical expression of Beer-Lambert Law.

(*b*) Write the mathematical expression for quantum efficiency.

(*c*) Write a short note on 'Chemiluminescence'. (*Arunachal BSc, 2003*)

24. (*a*) What are photochemical reactions? Explain the photochemical decomposition of HI.

(*b*) Write a short note on Stark-Einstein Law of photochemical equivalence.

(*Purvanchal BSc, 2003*)

25. (*a*) What are the primary and secondary photochemical reactions?

(*b*) How do you apply Lambert-Beer Law to determine unknown concentrations in solution?

(*Sambalpur BSc, 2003*)

26. Discuss the following :

(*a*) Quantum yield (*b*) Fluorescence

(*c*) Chemiluminescence (*Arunachal BSc, 2003*)

27. The optical density of 0.001 M solution of A in a cell of 0.1 cm path length is 0.162. Calculate its extinction coefficient.

Answer. 1620 mol^{-1} cm^{-1} (*Sambalpur BSc, 2003*)

28. A certain substance in a cell of length '*l*' absorbs 10% of incident light. What %age of light will be absorbed in cell which is five times as long?

Answer. 41% (*Delhi BSc, 2003*)

29. A 0.001 M aqueous solution of a certain substance absorbs 10% of the incident light in a Lambert-Beer law cell of path length 1 cm. Calculate the concentration required for the absorption of the incident light.

Answer. 0.0218 mol lit^{-1} (*HS Gaur BSc, 2003*)

30. A certain system absorbs 3×10^8 quanta of light per second. On irradation for 400 s, 0.001 mole of the reactant was found to have reacted. Calculate the quantum yield for the process. (Avogadro's number = 6.023×10^{23} mol^{-1})

Answer. 50.19×10^8 (*Marathwada BSc, 2004*)

31. A certain system absorbs 2×10^{16} quanta of light per second. On irradiation for 10 minutes, 0.001 mole of the reactant was found to have reacted. Calculate the quantum yield for the process. (Avogadro's number = 6.024×10^{23})

Answer. 50.2 (*Mumbai BSc, 2004*)

32. State and explain the law of photochemical equivalence and calculate the value of 1 einstein for light having λ = 2000 Å.

Answer. 142.9 kcal (*Meerut BSc, 2004*)

33. Calculate the energy of a photon corresponding to wave length 360 nm. Given :

velocity of light = 3×10^8 m sec^{-1}; $h = 6.62 \times 10^{-34}$ J sec^{-1}.

Answer. 5.525×10^{-19} J (*Delhi BSc, 2005*)

34. Calculate percentage of light transmitted through 5 mm length of a liquid of absorption coefficient 2.5.

Answer. 28.65% (*Bundelkhand BSc, 2005*)

35. What percentage of light will be transmitted through two cells put together in the path of light, if their individual transmissions are 60% and 30%.

Answer. 18% (*Kalyani BSc, 2006*)

36. A 2 mm thick plate of a material transmits 70% of the incident light. Calculate the percentage of light transmitted if the thickness of the plate is 0.5 mm.

Answer. 91.47 (*Mysore BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. A photochemical reaction takes place by the absorption of
   (*a*) visible and ultraviolet radiations (*b*) Infrared radiations
   (*c*) heat energy (*d*) none of these
   Answer. (*a*)
2. Photochemistry deals with the study of
   (*a*) photons
   (*b*) photos
   (*c*) reactions which proceed with absorptions of UV light
   (*d*) reactions which proceed with absorption of IR light
   Answer. (*c*)
3. The wavelength of ultraviolet and visible regions of electromagnetic spectrum is
   (*a*) less than 2000 Å (*b*) more than 8000 Å
   (*c*) 2000° to 8000 Å (*d*) none of these
   Answer. (*c*)
4. Which of the following statements about the photochemical reactions is true ?
   (*a*) the presence of light is the primary requirement for reactions to take place
   (*b*) temperature has a very little effect on the rate of photochemical reactions
   (*c*) ΔG for photochemical spontaneous reactions may +ve or –ve
   (*d*) all of the above
   Answer. (*d*)
5. Photochemical activation is highly selective. This statement is
   (*a*) true (*b*) false
   (*c*) sometimes true (*d*) none of these
   Answer. (*a*)
6. The number of photons that pass through a unit area in a unit time is called
   (*a*) amplitude of light (*b*) frequency of light
   (*c*) intensity of light (*d*) wavelength of light
   Answer. (*c*)
7. The absorption coefficient is given by
   (*a*) $b = \frac{-dI}{I} \times \frac{1}{dx}$ (*b*) $b = \frac{-dI}{I} \times \frac{dN}{N}$
   (*c*) $b = \frac{dI}{I} \times \frac{1}{dx}$ (*d*) $b = \frac{dI}{I} \times \frac{dn}{N}$
   Answer. (*a*)
8. The equation for the Lambert's law is
   (*a*) $l\,n\left(\frac{I_o}{I}\right) = -b\,x$ (*b*) $l\,n\left(\frac{I}{I_o}\right) = -b\,x$
   (*c*) $l\,n\left(\frac{I}{I_o}\right) = -\in C\,x$ (*d*) $l\,n\left(\frac{I}{I_o}\right) = \in C\,x$
   Answer. (*b*)
9. "It is only the absorbed light radiations that are effective in producing a chemical reaction." This is the statement of
   (*a*) Lambert law (*b*) Lambert-Beer law

(*c*) Grothus-Draper law (*d*) Stark-Einstein law

Answer. (*c*)

10. "In a photochemical reaction each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products." This is the statement of

(*a*) Lambert-Beer's law (*b*) Grothus-Draper law

(*c*) Stark-Einstein law (*d*) Lambert's law

Answer. (*c*)

11. One einstein of energy is

(*a*) $E = \frac{2.859}{\lambda} \times 10^5 \text{ ca mol}^{-1}$ (*b*) $E = \frac{2.859}{\lambda} \times 10^5 \text{ kcal mol}^{-1}$

(*c*) $E = \frac{2.859}{\lambda} \times 10^5 \text{ J mol}^{-1}$ (*d*) $E = \frac{2.859}{\lambda} \times 10^5 \text{ kJ mol}^{-1}$

Answer. (*b*)

12. Which of the following statements is true?

(*a*) it is the secondary reaction in which absorption of radiation takes place

(*b*) it is the primary reaction in which absorption of radiation takes place

(*c*) the absorption of radiation takes place in both – the primary and secondary reactions

(*d*) none of the above

Answer. (*b*)

13. The number of molecules reacted or formed per photon of light absorbed is called

(*a*) yield of the reaction (*b*) quantum efficiency

(*c*) quantum yield (*d*) quantum productivity

Answer. (*c*)

14. For a reaction that obeys Einstein law,

(*a*) $\phi = 1$ (*b*) $\phi > 1$

(*c*) $\phi < 1$ (*d*) $\phi = \alpha$

Answer. (*a*)

15. In some photochemical reactions low quantum yield is obtained. It is due to

(*a*) deactivation of reacting molecules (*b*) occurrence of reverse primary reaction

(*c*) recombination of dissociated fragments (*d*) all of these

Answer. (*d*)

16. The quantum yield, ϕ, of a photochemical reaction is expressed as

(*a*) $\phi = \frac{\text{no. of molecules decomposed or formed}}{\text{no. of photons of radiation energy absorbed}}$

(*b*) $\phi = \frac{\text{no. of molecules activated}}{\text{no. of photons of radiation energy absorbed}}$

(*c*) $\phi = \frac{\text{no. of molecules of reactants}}{\text{no. of photons of radiation energy absorbed}}$

(*d*) none of the above

Answer. (*a*)

17. The energy associated with a photon is given by the equation

(*a*) $\in = h \times \lambda$ (*b*) $\in = h \times v$

(*c*) $\in = h \times c$ (*d*) $\in = h \times c^2$

Answer. (*b*)

18. One einstein is the energy associated with

(*a*) one molecule (*b*) one photon

(*c*) Avogadro number of photons (*d*) Faraday number of photons

Answer. (*c*)

19. One einstein is given by (N is Avogadro's number)

(*a*) $E = \frac{Nhc^2}{\lambda}$ (*b*) $E = \frac{Nhc}{\lambda^2}$

(*c*) $E = \frac{Nhc}{\lambda}$ (*d*) $E = \frac{Nh}{c\lambda}$

Answer. (*c*)

20. The energy per einstein depends upon the wavelength of photon. The higher the wavelength, the _______ will be the energy per einstein.

(*a*) higher (*b*) smaller

(*c*) zero (*d*) infinity

Answer. (*b*)

21. The ratio of energy per einstein and that of a photon is

(*a*) equivalent number (*b*) Einstein number

(*b*) Lambert's number (*d*) Avogadro's number

Answer. (*d*)

22. A species which can both absorb and transfer radiant energy for activation of the reactant molecule is called

(*a*) radioactive substance (*b*) an ioniser

(*c*) a photochemical substance (*d*) a photosensitizer

Answer. (*d*)

23. The substances that when exposed to light radiations of short wavelength emit light of longer wavelength are called

(*a*) photosensitized substances (*b*) phosphorescent substances

(*c*) fluorescent substances (*d*) none of these

Answer. (*c*)

24. _______ stops as soon as the incident radiation is cut off

(*a*) fluorescence (*b*) phosphorescence

(*d*) chemiluminescence (*d*) none of these

Answer. (*a*)

25. Sulphates of calcium, barium and strontium exhibit

(*a*) chemiluminescence (*b*) fluorescence

(*c*) phosphorescence (*d*) none of these

Answer. (*c*)

26. The emission of light as a result of chemical action is called _______

(*a*) phosphorescence (*b*) fluorescence

(*c*) chemiluminescence (*d*) none of these

Answer. (*c*)

27. The light emitted in a chemiluminescent reaction is also called

(*a*) cold light (*b*) hot light

(*c*) bright light (*d*) none of these

Answer. (*a*)

28. The glow of fireflies is due to the aerial oxidation of luciferin. It is an example of

(*a*) fluorescence (*b*) phosphorescence

(*c*) chemiluminescence (*d*) none of these

Answer. (*c*)

29. A solution of quinine sulphate on exposure to visible light exhibits

(*a*) fluorescence (*b*) phosphorescence
(*c*) chemiluminescence (*d*) none of these
Answer. (*a*)

30. The reactions which are caused by heat and in absence of light are called
(*a*) photochemical reactions (*b*) catalytic reactions
(*c*) exothermic reactions (*d*) thermal or dark reactions
Answer. (*d*)

31. A glass of certain thickness is found to have a transmission of 70% of light. If the thickness of glass is reduced, the transmission of light would
(*a*) decrease (*b*) increase
(*c*) remains the same (*d*) reduce to zero
Answer. (*a*)

32. A substance in a cell length (*l*) absorbs 20% of incident light. If the cell length is changed to 5*l*, the fraction of incident light that will be absorbed is
(*a*) also increased (*b*) decreased
(*c*) unchanged (*d*) none of these
Answer. (*a*)

33. "Only the fraction of incident light that is absorbed by the substance can bring about a chemical change". is
(*a*) First law of photochemistry (*b*) Second law of photochemistry
(*c*) Third law of photochemistry (*d*) none of these
Answer. (*a*)

34. The energy of an einstein of radiation of wavelength 400 nm is _______ than that of radiation of 300 nm
(*a*) lesser (*b*) greater
(*c*) equal to (*d*) none of these
Answer. (*a*)

35. Photochemical decomposition of a substance is called
(*a*) thermal dissociation (*b*) thermolysis
(*c*) photolysis (*d*) none of the above
Answer. (*c*)

36. Out of the photons corresponding to light of wavelengths 200 nm, 400nm, 600nm and 800 nm, the one with highest energy will be
(*a*) photon of light with 200 nm wavelength (*b*) photon of light with 400 nm wavelength
(*c*) photon of light with 600 nm wavelength (*d*) photon of light with 800 nm wavelength
Answer. (*a*)

37. The substances which initiate a photochemical reaction but itself does not undergo any chemical change is called
(*a*) catalysis (*b*) fluorescent
(*c*) sensitizer (*d*) none of these
Answer. (*c*)

38. Organic dyes like eosin, chlorophyll, ultrarine etc. show _______ in the visible or UV region
(*a*) fluorescence (*b*) phosphorescence
(*c*) chemiluminescence (*d*) none of these
Answer. (*a*)

39. In photochemical reactions, the absorption of light takes place in
(*a*) primary processes only (*b*) secondary processes only
(*c*) either primary or secondary process (*d*) both primary and secondary processes
Answer. (*a*)

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