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Paper: C-14T (Photochemistry)
Topic: Lambert-Beer's law: Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients; Laws of photochemistry, Stark Einstein Law of photochemical equivalence quantum yield, Actinometry, examples of low and high quantum yields

Comments: Read as much as you can. The highlighted and the quoted portions are must read.

Reference: Physical Chemistry (Vol, 5, page 234)
K.L.Kapoor

3 Photochemistry

3.1 INTRODUCTION

Many reactions can be initiated by the absorption of radiation lying in the visible and ultraviolet regions (roughly from 800 nm to 200 nm). These reactions are called photochemical reactions. The science of photochemistry deals with the study of the effect of radiant energy on chemical reactions and with rates and mechanisms by which photochemical reactions proceed. The energy carried by the above mentioned region of radiation is sufficient to cause an electronic excitation in the molecule and thereby makes it more reactive which may result in a chemical reaction. Thus with the help of absorption of radiations, many reactions of different types, e.g. synthesis, decomposition, polymerization, isomeric change, oxidation and reduction, can be carried out.

Before we discuss the kinetics of photochemical reactions, a few definitions are in order.

3.2 TWO BASIC LAWS OF PHOTOCHEMISTRY

To all photochemical reactions, two basic laws hold good. These are:

The Grothuss-Draper Law

This law states that

(*Only those radiations which are absorbed by the reacting system are effective in producing chemical change.*)

This law can be easily accounted for as the molecules acquire energy for reaction by absorbing photons.

It should be clearly understood that though the law states that a photochemical reaction must have resulted because of the absorption of light, the reverse of this is not always true, i.e. the system on absorbing light may or may not result into a chemical reaction. In many cases, the absorbed light is converted into the kinetic energy of the absorbing molecules and thereby only heat effects are produced. In many cases, the absorbed light is re-emitted as fluorescence or phosphorescence.

The amount of light absorbed by a system is given by Lambert-Beer's law, a brief description of which is given in the next section.

Law of Photochemical Equivalence

The second law of photochemistry is the law of photochemical equivalence proposed by Stark and Einstein. According to this law, we have

(*Each light absorbing molecule in a photochemical reaction absorbs only one quantum of light which causes the activation.*)

If ν is the frequency of the absorbed light, its energy as given by the Planck's relation is

$$\Delta E = h\nu$$

Hence, energy absorbed per mol of the substance is

$$\Delta E = N_A h\nu$$

and is conventionally known as one *Einstein of energy.*

3.3 LAMBERT-BEER'S LAW

Statement of Lambert Law

The amount of light absorbed by a pure substance follows Lambert's law which states that:

Equal fractions of the incident radiation are absorbed by successive layers of equal thickness of the light absorbing substance.

Mathematically,

$$-\frac{dI}{I} \propto (dl) \quad \text{i.e.} \quad -\frac{dI}{I} = k(dl) \tag{3.3.1}$$

where the constant k is known as *absorption coefficient* and is characteristic of the given material and the wavelength of the radiation. It has the unit of length^{-1}.

Alternative Definition

Alternatively, Lambert's law may be written as:

$$-\frac{dI}{dl} = kI$$

that is, the rate of decrease of intensity with thickness of the medium (i.e. $-dI/dl$) *is proportional to the intensity of the radiation.*

Integration Form of Lambert Law

Equation (3.3.1) on integration yields

$$-\int_{I_0}^{I} \frac{dI}{I} = k\int_{0}^{l} dl$$

i.e.

$$\ln\left(\frac{I}{I_0}\right) = -kl \tag{3.3.2}$$

or

$$I = I_0 e^{-kl} \tag{3.3.3}$$

Equation (3.3.2) may be written as

$$\log\left(\frac{I}{I_0}\right) = -\frac{k}{2.303}\, l = -al$$

or

$$\frac{I}{I_0} = 10^{-al} \tag{3.3.4}$$

The constant a which is equal to $k/2.303$ is known as absorption coefficient (formely as absorptivity or extinction coefficient). It has the unit of length^{-1}.

Extension of the Lambert Law to Solutions

The absorption of light by solutions of known concentration c is given by Beer's law, according to which, we have

$$-\frac{\mathrm{d}I}{I} \propto c$$

Combining the above equation with Eq. (3.3.1), we get

$$-\frac{\mathrm{d}I}{I} \propto (\mathrm{d}l)\,(c)$$

or
$$-\frac{\mathrm{d}I}{I} = k(\mathrm{d}l)\,(c) \tag{3.3.5}$$

Equation (3.3.5) is known as Lambert-Beer's law which on integration gives

$$\ln\frac{I}{I_0} = -\,klc \tag{3.3.6a}$$

or
$$I = I_0(10)^{-\varepsilon lc} \tag{3.3.6b}$$

where $\varepsilon = k/2.303$ and has the unit of (concentration) (length)$^{-1}$. It is knows as molar absorption coefficient (formerly as the *molar extinction coefficient* or *molar absorptivity*):

Beer's law is applicable for dilute solutions, deviations are observed for concentrated solutions. There is no exception of Lambert's law.

Absorbance of a Solution

The absolute value of the exponent in Eq. (3.3.6b) is defined as the *absorbance A* or (formerly as extinction or *optical density*).

$$A = \varepsilon lc \tag{3.3.7}$$

$A = \log\frac{I_0}{I} = \log\left(\frac{1}{T}\right)$
$= \varepsilon cl.$

The terms absorptivity (for absorption coefficient) and molar absorptivity (for molar absorption coefficient) are to be avoided as these terms have been recommended for the absorptance per unit length. Also the terms extinction (for absorbance), extinction coefficient (for absorption coefficient) and molar extinction coefficient (for molar absorption coefficient) are to be avoided as the term extinction is now reserved for diffusion of radiation rather than absorption.

The ratio I/I_0 is called the *transmittance*. The amount of light absorbed is given by

$$I_0 - I = I_0 - I_0\,10^{-\varepsilon lc} = I_0\,(1 - 10^{-\varepsilon lc}) \tag{3.3.8}$$

Absorption of a Solution Containing more than one Absorbing Substance

For a solution containing more than one light absorbing substance, Lambert-Beer's law takes the form

$$-\frac{\mathrm{d}I}{I} = (\mathrm{d}l)\left(\textstyle\sum_i k_i c_i\right) \tag{3.3.9}$$

On integration the above expression yields

$$I = I_0 \exp\left(-l\left(\textstyle\sum_i k_i c_i\right)\right) \tag{3.3.10a}$$

or
$$I = I_0\,10^{-l(\sum_i \varepsilon_i c_i)} \tag{3.3.10b}$$

The absorbance of the solution in this case is given by

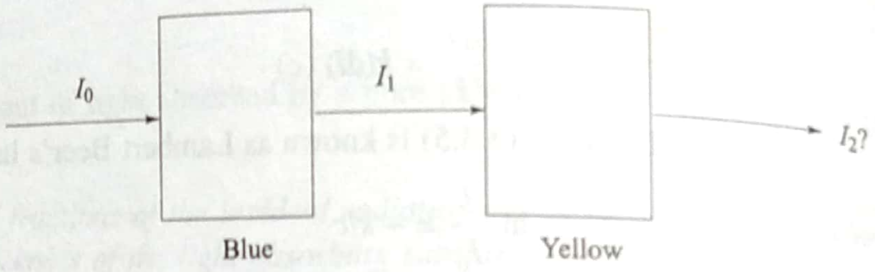
$$A = l(\textstyle\sum_i \varepsilon_i c_i) = \sum_i \varepsilon_i c_i \, l = \sum_i A_i \tag{3.3.11}$$

where A_i is the absorbance of the ith constituent.

Equation (3.3.11) indicates that the absorbance is additive, i.e. the absorbance of a solution is equal to the sum of absorbances of its constituents.

Example 3.3.1 At 460 nm a blue filter transmits 72.7% of the light and a yellow filter 40.7% of the light. What is the transmittance at the same wavelength of two filters in combination?

Solution We have



It is given that

$$\frac{I_1}{I_0} = 0.722 \quad \text{and} \quad \frac{I_2}{I_1} = 0.407$$

Hence, $$\frac{I_2}{I_0} = \frac{I_2}{I_1} \times \frac{I_1}{I_0} = 0.727 \times 0.407 = 0.296$$

Example 3.3.2 In a given absorption cell transmittance of 0.1 mol dm^{-3} of A is 0.75 and that of 0.1 mol dm^{-3} of B is 0.55 at a given wavelength. Calculate the transmittance of a solution that is simultaneous 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B.

Solution The absorbance of 0.1 mol dm^{-3} in A is

$$A_A = \varepsilon l c = -\log \frac{I}{I_0} = -\log (0.75) = 0.124\,9$$

Similarly, for 0.1 mol dm^{-3} in B is

$$A_B = \varepsilon l c = \log \frac{I}{I_0} = -\log (0.55) = 0.259\,6$$

Now, the absorbance of the solution which is simultaneously 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B is

Absorbance of mixture additive.

$$A = A_A + A_B = 0.124\,9 + 0.259\,6 = 0.384\,5$$

Since $A = -\log \left(\frac{I}{I_0}\right)$

therefore

$$\frac{I}{I_0} = \text{antilog}\,(-A) = \text{antilog}\,(-0.384\,5) = \text{antilog}\,(\bar{1}.6165) = 0.412\,5$$

(**Note:** Since absorbance is additive, transmittance will be multiplicative. Hence, $I/I_0 = 0.55 \times 0.75 = 0.4125$.)

If l increases. A increased.

$I = I_0 10^{-\epsilon c l} \Rightarrow \log I/I_0 = -\epsilon c l \Rightarrow \log \frac{I_0}{I} = A = \epsilon c l$

Example 3.3.3 A certain substance in a cell of length l absorbs 10 per cent of the incident light. What fraction of the incident light will be absorbed in a cell five times as long?

Solution We have

$$\log \left(\frac{I}{I_0}\right)_1 = -\varepsilon c l, \qquad \text{where} \quad \left(\frac{I}{I_0}\right)_1 = 0.9$$

$$\log \left(\frac{I}{I_0}\right)_2 = \varepsilon c(5l)$$

Hence,
$$\frac{\log (I/I_0)_2}{\log (I/I_0)_1} = 5$$

or
$$\log (I/I_0)_2 = 5 \times \log (I/I_0)_1 = 5 \times \log (0.9) = 5 \times \bar{1}.954\,2 = \bar{1}.771$$

Thus
$$I/I_0 = 0.590\,2$$

Hence, light absorbed is 40.98 per cent.

Example 3.3.4 In a cell of a certain length and at a pressure of 100 mmHg, gaseous acetone transmits 25.1 per cent of the incident radiation of wavelength 265 nm. Assuming Beer's law to apply, calculate the pressure at which 98 per cent of the incident radiation will be absorbed by acetone in the same cell at the same temperature.

Solution For gaseous system, c in the Lambert-Beer's law may be replaced by p. Thus, we have

$$\log \left(\frac{I}{I_0}\right) = -\varepsilon l p$$

Since at 100 mmHg transmittance is 0.251, we have

$$\log (0.251) = -\varepsilon l(100 \text{ mmHg})$$

or
$$(\varepsilon l) = -\frac{\log (0.251)}{100 \text{ mmHg}} = 0.006\,003 \text{ mmHg}^{-1}$$

For 98 per cent absorption or 2 per cent transmittance, we have

$$\log (0.02) = -(\varepsilon l)p = -(0.006\,003 \text{ mmHg}^{-1})p$$

or
$$p = -\frac{\log (0.02)}{0.006\,003 \text{ mmHg}^{-1}} = 283.0 \text{ mmHg}$$

Example 3.3.5 In an experiment to determine the concentrations of the two substances A and B in a certain solution spectrophotometrically, the following data were obtained.

Solution	[A] mol dm^{-3}	[B] mol dm^{-3}	*Per cent Transmittance at* 400 nm	*Per cent Transmittance at* 500 nm
1	0.001	0	10	60
2	0	0.005	80	20
3	unknown	unknown	40	50

Determine the concentrations of A and B in solution 3.

Solution The relation between absorbance and transmittance is

$$A = \varepsilon l c = -\log\left(\frac{I}{I_0}\right)$$

For solution 1, we have

$$A_A \text{ at } 400 \text{ nm} = \varepsilon_A l c_A = -\log\ (10/100) = 1$$

$$A_A \text{ at } 500 \text{ nm} = \varepsilon_A l c_A = -\log\ (60/100) = 0.22$$

Since $c_A = 0.001$ mol dm^{-3}, we have

$$(\varepsilon_A l)_{400\text{ nm}} = \frac{1}{0.001 \text{ mol dm}^{-3}} = 1000 \text{ mol}^{-1} \text{ dm}^3$$

$$(\varepsilon_A l)_{500\text{ nm}} = \frac{0.22}{0.001 \text{ mol dm}^{-3}} = 220 \text{ mol}^{-1} \text{ dm}^3$$

For solution 2, we have

$$A_B \text{ at } 400 \text{ nm} = \varepsilon_B l c_B = -\log\ (80/100) = 0.097$$

$$A_B \text{ at } 500 \text{ nm} = \varepsilon_B l c_B = -\log\ (20/100) = 0.699$$

Since $c_B = 0.005$ mol dm^{-3}, we have

$$(\varepsilon_B l)_{400\text{ nm}} = \frac{0.097}{0.005 \text{ mol dm}^{-3}} = 19.4 \text{ mol}^{-1} \text{ dm}^3$$

$$(\varepsilon_B l)_{500\text{ nm}} = \frac{0.669}{0.005 \text{ mol dm}^{-3}} = 139.8 \text{ mol}^{-1} \text{ dm}^3$$

For solution 3, we have

$$\text{At 400 nm:} \quad (\varepsilon_A l)_{400\text{ nm}}\, c_A + (\varepsilon_B l)_{400\text{ nm}}\, c_B = -\log\ (40/100) = 0.398$$

$$\text{At 500 nm:} \quad (\varepsilon_A l)_{500\text{ nm}}\, c_A + (\varepsilon_B l)_{500\text{ nm}}\, c_B = -\log\ (50/100) = 0.301$$

Substituting the values, we have

$$(1000 \text{ mol}^{-1} \text{ dm}^3)\, c_A + (19.4 \text{ mol}^{-1} \text{ dm}^3)\, c_B = 0.398$$

$$(220 \text{ mol}^{-1} \text{ dm}^3)\, c_A + (139.8 \text{ mol}^{-1} \text{ dm}^3)\, c_B = 0.301$$

Solving for c_A and c_B, we get

$$c_A = 0.000\ 368 \text{ mol dm}^{-3} \quad \text{and} \quad c_B = 0.001\ 57 \text{ mol dm}^{-3}$$

√3.4 PRIMARY AND SECONDARY PROCESSES

Photochemical reactions can be classified as primary and secondary processes.

Primary Process

The primary process of the reaction is the light absorbing process which follows the law of photochemical equivalence. As stated earlier, the photon absorbed by a molecule causes the electronic excitation. The electronic transitions follow the Franck-Condon rule, according to which, the time required for the electronic excitation is so small that the internuclear distance remains unchanged during the excitation.

Based on the relationship between the lower and the upper electronic levels, four types of primary processes are possible. A brief discussion on these four processes is in order.[†]

Type I In this case, the vibrational energy of the molecule in the upper electronic state exceeds the maximum value, which leads to the dissociation of molecule in its first oscillation. The electronic spectrum consists of a series of discrete vibration-rotation bands converging to a limit and followed by a region of continuous absorption.

Type II In this case, the molecule is simply excited to the upper electronic state. The electronic spectrum consists of a series of bands with no continuous region.

Type III The molecule is again dissociated as the upper level represents an unstable state. The electronic spectrum is continuous throughout.

Type IV In this case, stable and unstable upper levels overlap each other. Transition occurs from the lower level to the stable upper level. During the course of vibration, the molecule is switched over to the unstable one at the point where two levels cross each other; and the molecule then dissociates. This behaviour is referred to as *predissociation*. The electronic spectrum consists of a banded region. In the predissociation region, the rotational lines are absent and the vibrational bands have diffuse appearance.

Secondary Processes

The products of primary process may involve in subsequent thermal reactions. These processes are known as secondary processes. The secondary process may involve only one step or more than one step. Sometimes, the secondary processes represent the chain reaction.

For example, the photochemical decomposition of HI involves the following processes:

Primary process $\mathrm{HI} \xrightarrow{h\nu} \mathrm{H} + \mathrm{I}$

Secondary Processes $\mathrm{H} + \mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I}$

$\mathrm{I} + \mathrm{I} \longrightarrow \mathrm{I_2}$

3.5 QUANTUM EFFICIENCY

Definition

An important parameter of a photochemical reaction is the quantum efficiency or quantum yield which is defined as the number of light absorbing molecules reacted per photon of light absorbed, i.e.

$$\boxed{\Phi = \frac{\text{Number of molecules reacted}}{\text{Number of photons absorbed}}}$$

In terms of amount of substance reacted, we have

$$\Phi = \frac{\text{Amount of the substance reacted}}{\text{Amount of photons absorbed}}$$

According to the law of photochemical equivalence, the quantum efficiency will always be equal to one. But reactions of low and high quantum yields (as low as 0.04 and as high as 10^5) are known.

For a primary process, the quantum yield is always one, it is the secondary processes which alter the overall quantum yield of the reaction. Therefore, the determination of quantum yield helps understanding the nature of secondary processes.

Determination of Number of Photons Absorbed

The number of photons absorbed are counted either with a *thermopile* or a *chemical actinometer*.

The **thermopile** is made up of a large number of junctions of two dissimilar metals. The radiation falling on it is converted into thermal energy. The increase in temperature is a measure of the intensity of radiation. The instrument is calibrated with standard lamps.

A **chemical actinometer** depends on the use of a photochemical reaction of known quantum yield. A common reaction used in actinometers is the decomposition of oxalic acid, sensitized by uranyl ion. The uranyl ion UO_2^{2+} absorbs light in the wavelength region from 250 nm to 440 nm. The excited UO_2^{2+} transfers the absorbed energy to the oxalic acid which is decomposed. The reactions are

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

$$(UO_2^{2+})^* + (COOH)_2 \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The amount of oxalic acid decomposed can be determined by titrating undecomposed oxalic acid against $KMnO_4$ solution. The quantum efficiency of the above reaction is 0.57. Hence, knowing the amount of oxalic acid decomposed, the amount of photons absorbed can be determined.

The radiation used for the photochemical reaction must be monochromatic. These are usually obtained by using discharge tubes which give atomic line spectra; the line of desired wavelength is isolated by means of a filter or by passage through a prism in a spectrograph. A device of this kind is called a monochromator.

Experimental set up of Photochemical Reactions

A schematic diagram of the apparatus used for the study of a photochemical reaction is shown in Fig. 3.5.1, where A represents a light source emitting radiation of suitable intensity in the desired spectral range, B is the lens, C is the monochromator or filter, D photochemical cell which contains the reaction mixture, and E is the recorder where its intensity is measured.

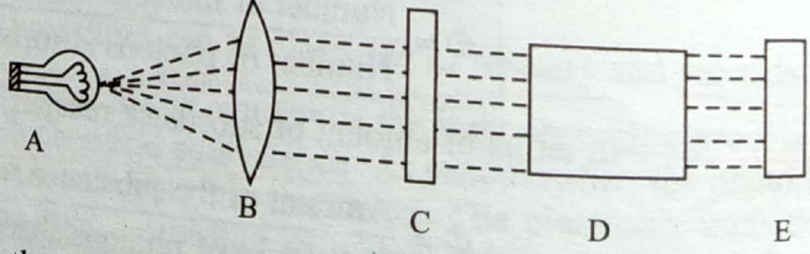


Fig. 3.5.1 Experimental set up to study photochemical reactions

First of all, the cell filled with the solvent is exposed to the radiation and the reading is recorded. This gives the total energy incident upon the system in a given interval of time. Next the cell is filled with the reacting mixture and is exposed to the radiation over the same interval of time and the reading is recorded. This gives the total energy transmitted. The difference between the two readings gives the total energy absorbed by the reacting mixture in the given interval of time.

Reasons of Low and High Quantum Efficiency

The quantum efficiency of a reaction helps understanding the nature of secondary processes and hence the mechanism of chemical reactions. If the absorption of radiation lies in the banded region, the electron is excited to the upper level without causing decomposition of the molecule. The excited molecule may deactivate itself by any one of the following steps.

- The excited molecule may simply emit the radiation of the frequency which it absorbed. The emitted radiation is called *resonance radiation*.
- The absorbed energy may be re-emitted as fluorescence or phosphorescence. The intensity of fluorescence depends on the concentration or pressure of the system. The frequency of fluorescent light is different from that of the absorbed light.
- The molecule may collide with other molecules and pass on them some or all of its excitation energy. This energy either can cause a reaction in the other molecule or can gradually be degraded into heat.
- The excited molecule may react with other molecules.
- The excited molecule may decompose through predissociation.

On the other side, if the absorption lies in the continuous region, the molecule dissociates to produce active species which react with the reactant molecules or other molecules in the secondary processes.

With the above facts, it is easy to understand the reasons for obtaining the low and high quantum efficiency. Some of the reasons are as follows.

Low Quantum Yield

A few reasons are:

1. The excited molecule is deactivated through fluorescence or phosphorescence.
2. The excited molecule is deactivated by converting its energy into the kinetic energy of other molecules (heating effects are produced).
3. The secondary process may involve a step which produces the reactant molecule as one of the products.
4. The energy absorbed might not be sufficient to cause any fruitful excitation of the molecule.

High Quantum Yield

The high quantum yield is attributed to the chain reactions caused by the generation of atoms or free radicals in the primary process. The quantum yield depends on the length of the chain propagating steps.

Example 3.5.1 In the photochemical decomposition of ethylene iodide

$$C_2H_4I_2 + h\nu \longrightarrow C_2H_4 + I_2$$

with radiation of 424 nm, the iodine formed after 20 minutes required 41.14 cm^3 of 0.002 5 mol dm^{-3} solution of $Na_2S_2O_3$. The intensity of the light source was 9.15×10^{-4} J s^{-1}. Calculate the quantum yield assuming absorption of the energy was complete.

Solution The quantity of energy consumed in 20 minutes

$$= (9.15 \times 10^{-4}\ \text{J s}^{-1})\ (20 \times 60\ \text{s}) = 1.098\ \text{J}$$

Energy associated with 1 mol of photons of wavelength 424 nm

$$= \frac{N_A hc}{\lambda} = \frac{(6.023 \times 10^{23}\ \text{mol}^{-1})(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(424 \times 10^{-9}\ \text{m})}$$

$$= 2.823 \times 10^{5}\ \text{J mol}^{-1}$$

Amount of radiation consumed

$$= \frac{1.098\ \text{J}}{(2.823 \times 10^{5}\ \text{J mol}^{-1})} = 3.890 \times 10^{-6}\ \text{mol}$$

Amount of $S_2O_3^{2-}$ consumed

$$= (0.002\,5\ \text{mol dm}^{-3})\ (0.041\,14\ \text{dm}^3) = 1.028 \times 10^{-4}\ \text{mol}$$

From the reaction $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$, we get

Amount of ethylene iodide reacted = amount of iodine formed

$$= \frac{1.028 \times 10^{-4}\ \text{mol}}{2} = 0.514 \times 10^{-4}\ \text{mol}$$

Hence, Quantum yield $= \dfrac{\text{Amount of ethylene iodide reacted}}{\text{Amount of radiation absorbed}}$

$$= \frac{(0.514\,5 \times 10^{-4}\ \text{mol})}{(3.890 \times 10^{-6}\ \text{mol})} = 13.225$$

Example 3.5.2 The photochemical dissociation of gaseous HI to form hydrogen and iodine atoms requires radiation of 404 nm or less. (a) Determine the molar energy of dissociation of HI. (b) If radiation of 253.7 nm is used, how much energy will appear as kinetic energy of atoms?

Solution **(a)** On absorbing one photon of wavelength 404 nm, one molecule of HI is dissociated. For the decomposition of one mole of HI, we will require N_A photons. Hence, energy carried by these photons is

$$E = \frac{N_A hc}{\lambda} = \frac{(6.023 \times 10^{23}\ \text{mol}^{-1})(6.626 \times 10^{-34}\ \text{J s})\ (3 \times 10^{8}\ \text{m s}^{-1})}{(404 \times 10^{-9}\ \text{m})}$$

$$= 2.963 \times 10^{5}\ \text{J mol}^{-1}$$

which is molar energy of dissociation of HI.

(b) If the wavelength of the incident light is less than 404 nm, the atoms after dissociating will fly apart with the total kinetic energy equivalent to the excessive energy. One mole of radiation of wavelength 253.7 nm will carry an energy

$$\frac{N_A hc}{\lambda} = \frac{(6.023 \times 10^{23}\ \text{mol}^{-1})(6.626 \times 10^{-34}\ \text{J s})\ (3 \times 10^{8}\ \text{m s}^{-1})}{(253.7 \times 10^{-9}\ \text{m})}$$

$$= 4.719 \times 10^{5}\ \text{J mol}^{-1}$$

Hence, extra energy which appear as kinetic energy

$$= (4.719 \times 10^{5} - 2.963 \times 10^{5})\ \text{J mol}^{-1} = 1.756 \times 10^{5}\ \text{J mol}^{-1}$$

Example 3.5.3 When acetone vapour is irradiated with light of wavelength 313 nm it decomposes to form ethane and carbon monoxide.

$$(CH_3)_2CO + h\nu \longrightarrow C_2H_6 + CO$$

Using a reaction cell of 60.3 cm^3 capacity and a temperature of 329 K irradiation for 23 000 s at the rate of 8.52×10^{-3} J s^{-1} produced a change in pressure from 760.0 to 790.4 mmHg. Calculate (a) the number of molecules of acetone decomposed, and (b) the quantum yield.

Solution **(a)** Change in pressure = 790.4 mmHg – 760.0 mmHg = 30.4 mmHg. This increase in pressure is due to the increase in the number of gaseous molecules. There is an increase of one molecule per molecule of acetone dissociated. Hence, number of molecules of acetone dissociated as given by ideal gas law is

$$\frac{(\Delta p)V}{RT}N_A = \frac{\left(\dfrac{1.013\times10^5}{760}\times 30.4\ \mathrm{N\ m^{-2}}\right)\left(\dfrac{60.3}{10^6}\ \mathrm{m^3}\right)}{(8.314\ \mathrm{N\ m\ K^{-1}\ mol^{-1}})(329\ \mathrm{K})}\times(6.023\times10^{23}\ \mathrm{mol^{-1}})$$

$$= 5.38\times10^{19}$$

(b) Quantity of energy absorbed

$$= (8.52\times10^{-3}\ \mathrm{J\ s^{-1}})\ (23\ 000\ \mathrm{s}) = 195.96\ \mathrm{J}$$

Number of photons absorbed

$$= \frac{(195.96\ \mathrm{J})}{hc/\lambda} = \frac{(195.96\ \mathrm{J})(313\times10^{-9}\mathrm{m})}{(6.626\times10^{-34}\ \mathrm{J\ s})(3\times10^8\ \mathrm{m\ s^{-1}})}$$

$$= 3.086\times10^{20}$$

Hence, $\Phi = \dfrac{5.38\times10^{19}}{3.086\times10^{20}} = 0.174$

Example 3.5.4 In the photochemical combination of $H_2(g)$, and $Cl_2(g)$, a quantum efficiency of about 1×10^6 is obtained with a wavelength of 480 nm. What amount of HCl(g) would be produced under these conditions per calories of radiant energy absorbed?

Solution Energy associated with 1 mol of photons of wavelength 480 nm

$$= \frac{N_A hc}{\lambda} = \frac{(6.023\times10^{23}\ \mathrm{mol^{-1}})(6.626\times10^{-34}\ \mathrm{J\ s})\ (3\times10^8\ \mathrm{m\ s^{-1}})}{(480\times10^{-9}\ \mathrm{m})}$$

$$= 2.494\times10^5\ \mathrm{J\ mol^{-1}}$$

Amount of photons in 1 cal (i.e. 4.184 J)

$$= \frac{(4.184\ \mathrm{J})}{2.494\times10^5\ \mathrm{J\ mol^{-1}}} = 1.677\times10^{-5}\ \mathrm{mol}$$

Since $\Phi = \dfrac{\text{Amount of substance reacted}}{\text{Amount of photons absorbed}}$, we have

$$1\times10^6 = \frac{\text{Amount of } Cl_2 \text{ reacted}}{1.677\times10^{-5}\ \mathrm{mol}}$$

Hence,

Amount of Cl_2 reacted = $(1\times10^6)(1.677\times10^{-5}\ \mathrm{mol})$ = 16.77 mol

1 mol of Cl_2 on reacting produces 2 mol of HCl. Hence, amount of HCl produced is 33.54 mol.