Properties of light

3- Dispersion

Define light scattering (dispersion)

It is the separation of light into its colors of different values, as each color is uniquely characterized **by a degree of refraction** that differs from the other color, and when the white color is dispersed, it is divided into the colors of the visible spectrum, through **a glass prism**, in addition to diffraction and scattering caused by the scattering of light.

To understand the effects that dispersion can have on light, consider what happens when light strikes a prism, as shown in Figure 7.

A ray of single-wavelength light incident on the prism from the left emerges refracted from its original direction of travel by an angle **δ**, called the **angle of deviation**.

Now suppose that a beam of ***white light*** (a combination of all visible wavelengths) is incident on a prism, as illustrated in Figure 7.

The rays that emerge spread out in a series of colors known as **the visible spectrum**.

These colors, in order of decreasing wavelength, are red, orange, yellow, green, blue, and violet. Clearly,

The angle of deviation **δ** depends on (wavelength) , Violet light deviates the most, red the least, and the remaining colors in the visible spectrum fall between these extremes.

Newton showed that each color has a particular angle of deviation and that the colors can be recombined to form the original white light.

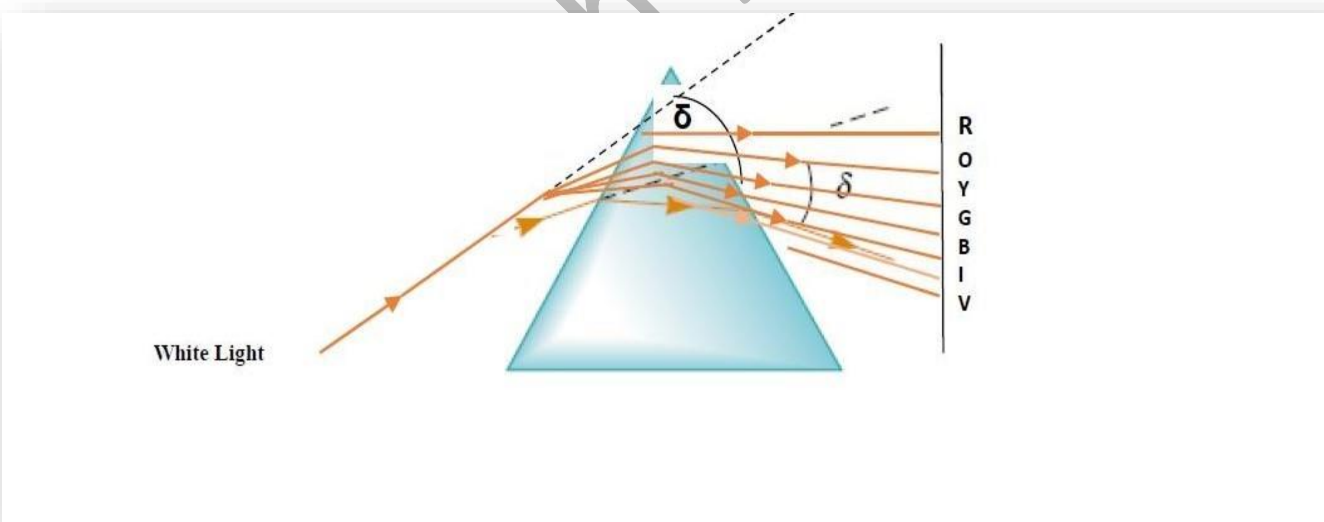

Fig (7) A prism refracts a single-wavelength light ray through an angle δ.

4- Velocity of light

Galileo made the first effort to measure the velocity of light in 1667. Two observers stood on the crests of two hills about 1.5 kilometers apart. Each observer was given one lamp, and the experiment was conducted at night. One witness, say A, uncovered his lamp, sending a brief flash of light to the other observer, say B, and recorded the moment he did so. As soon as he noticed the flare from B's bulb, the second observer B uncovered his lamp. The time spent for light to cover the distance AB twice is plainly equal to the gap between these two instants of time denoted by A.

Galileo deduced from this that the velocity of light, if finite, was extraordinarily fast.

C=2.3×10^{8}m/sec

H. L. Fizeau, a French scientist, performed the first experimental measurement of the speed of light in 1849. Later, several experimenters using various approaches measured C.

C=2.997924×10^{8}m/sec ≈ 3×10^{8}m/sec

Laws of of Photochemistry:

There are two basic laws governing photochemical reactions :

(a) The Grothus-Draper law

(b) The Stark-Einstein law of Photochemical Equivalence

(a) 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.

(b) The 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.

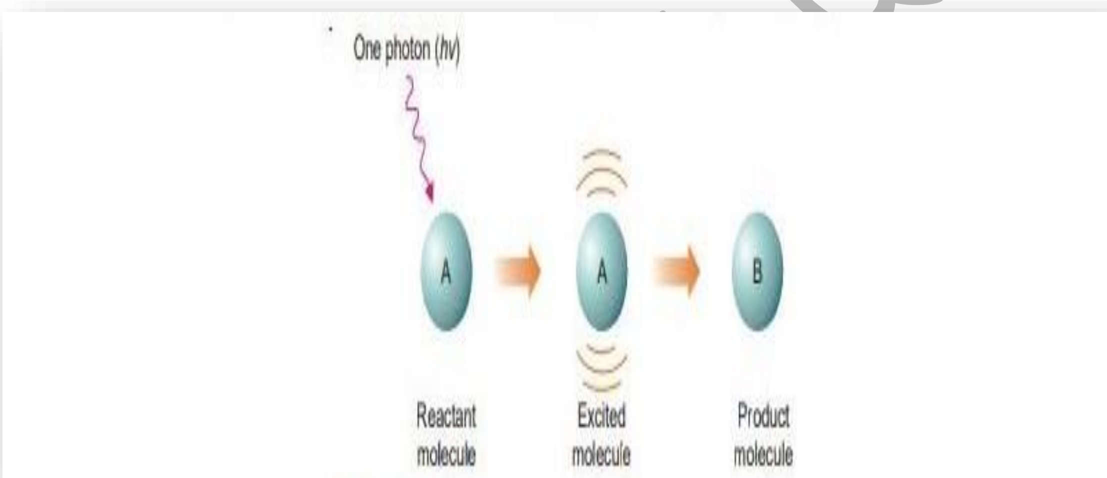

Fig. (8) Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule

The Stark-Einstein law of photochemical equivalence may be stated as :

(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. (8)

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:

$A + h\nu \rightarrow A^*$

$A^* \rightarrow B$

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overall $A + h\nu \rightarrow B$

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:

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

M. Bodenstein proposed that photochemical processes involve two distinct processes.

(a) a primary reaction (b) secondary reaction.

1. Primary Process: -

Primary processes are those processes in which quantum of energy (hv) is absorbed by a molecule, resulting in the excitation of the molecule.

Thus A + hv—→ A*

The molecule which absorbs light may get dissociated yielding.

excited state atoms or free radicals.

(The primary process may also involve loss of vibrational energy of excited molecules by collision with other molecules as well as by fluorescence and phosphorescence.

Thus A + hv —→A*

2. Secondary Process: -

Those processes which involve the excited atoms, or free radicals produced in the primary steps or primary process.

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:

$HBr + h\nu \longrightarrow H + Br$ Primary reaction

$HBr + H \longrightarrow H_2 + Br$ Secondary reaction

$Br + Br \longrightarrow Br_2$ Secondary reaction

$2HBr + h\nu \longrightarrow H_2 + Br_2$ Overall reaction

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)

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

φ =No. of molecules reacted or formed / No. of photons absorbed

It has been shown that not always a photochemical reaction obeys the Einstein law.

High and low Quantum yield (ф):

A- The various photochemical reactions can be divided into three categories:

The quantum yield is a small integer such as 1, 2, 3. Examples are:

1- Combination between SO_2 and Cl_2 to give SO_2Cl_2 (ф = 1),

2- Dissociation of HI and HBr (ф = 2),

3- Ozonation of O_2 (ф = 3).

Ozonation

(is the process of introducing ozone gas (O_3) into a substance, typically water, to purify and disinfect it).

Ozone is an unstable form of oxygen (O_2) that has a powerful oxidizing effect, which makes it effective at destroying a wide range of pollutants and harmful microorganisms such as bacteria, viruses, and algae.

Ozonation replaces chlorine and other chemical disinfectants in water treatment, as ozone treatment is an environmentally friendly and efficient alternative.

B- The quantum yield is less than 1, examples are:

1- dissociation of NH_3 (ф = 0.25)

2- combination between H_2 & Br_2 (ф = 0.01)

C- The quantum yield is very high, as for example:

1- combination of hydrogen and chlorine (ф =106)

2- combination between CO and Cl2 (ф =103).

<u>Reasons for high quantum yield:</u>

1. The excited atoms or free radicals produced in the primary process initiate a series of chain reactions, as for example, in combination of H2 and Cl2 to give HCl, when the resulting quantum yields are of the order of 106 or more.

2. If the secondary reaction is exothermic, the heat of the reaction may activate molecules thereby causing them to react and thus result in a high quantum yield.

Reason for low quantum yield:

1. Excited molecules may get deactivated before they form products.

2. Collisions of excited molecules with non-excited molecules may cause the former to lose energy.

3. The primary photochemical process may get reversed.

4. The dissociated fragments may recombine to form the original molecule.