

❖ Photochemical Reactions (Hydrogen-Bromine & Hydrogen-Chlorine Reactions)

There are many chemical reactions which occur also when the reactants are exposed to light. These reactions are called as photochemical reactions. Now before we discuss the nature and types of photochemical reactions, we need to discuss two laws first; the first is Grotthuss-Draper law while the second one is Stark-Einstein law.

The first law of photochemistry was given by Theodor Grotthuss and John W. Draper, and therefore, got its unique name.

The first law of photochemistry states that when the light is allowed to strike the reactions mixture, it can be partially transmitted, reflected and absorbed; and it is the absorbed portion of the incident light which is responsible to carry out any chemical change.

The second law of photochemistry was given by Johannes Stark and Albert Einstein, and therefore, is popularly known as Stark-Einstein law.

The second law of photochemistry states that one photon of light must be absorbed for one molecule to get activated in a photochemical reaction by a chemical system.

The quantum yield of a reaction is simply the ratio of number of molecules reacting in a given time to the number of photons absorbed in the same time i.e.

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$$\text{Quantum yield}(\phi) = \frac{\text{Number of moles of reactant reacting per second}}{\text{Number of einsteins absorbed per second}} \quad (79)$$

Where one einstein represents one mole of photons (6.022×10^{23}). The quantum yield is of two types in photochemical reactions; one for the primary process and the second one for the secondary process. During the course of the primary process, light is absorbed by the reactant and the quantum yield of this part is always unity. Therefore, we can say that the number of radiation-absorbing molecules consumed per unit time in the primary process is equal to intensity of absorbed radiation i.e. I_{ab} (number of photons striking the sample per unit time). For instance, consider the photo-decomposition



Then, the quantum yield will be

$$\phi = \frac{\text{Number of moles of Br}_2 \text{ decomposed per unit time}}{\text{Number of einsteins absorbed per unit time}} \quad (81)$$

or

$$\phi = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (82)$$

Since $\phi = 1$ for primary process, we have

$$1 = \frac{-d[\text{Br}_2]/dt}{I_{ab}} \quad (83)$$

or

$$-\frac{d[\text{Br}_2]}{dt} = I_{ab} \quad (84)$$

$$-\frac{d[\text{Br}_2]}{dt} = k[\text{Br}_2] = I_{ab} \quad (85)$$

If rate of formation of Br is asked, then

$$-\frac{d[\text{Br}_2]}{dt} = +\frac{1}{2} \frac{d[\text{Br}]}{dt} = k[\text{Br}_2] = I_{ab} \quad (86)$$

$$\frac{d[\text{Br}]}{dt} = 2k[\text{Br}_2] = 2I_{ab} \quad (87)$$

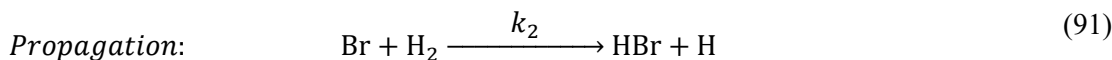
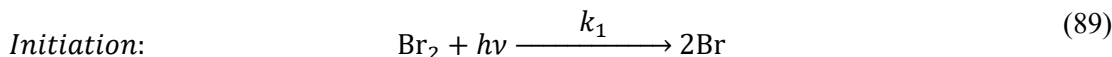
Two of the most common examples of photochemical reactions are hydrogen-bromine and hydrogen-chlorine reactions whose kinetics and nature will be discussed in this section.

➤ **Kinetics of Photochemical Reaction Between Hydrogen and Bromine**

The hydrogen-bromine or the $\text{H}_2\text{-Br}_2$ reaction is a typical case of photochemical reactions for which the overall reaction can be written as given below.



Since it is a chain reaction, the elementary steps for the same can be proposed as



The net rate of formation of HBr must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (95)$$

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the H and Br first i.e.

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad (96)$$

Similarly,

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0 \quad (97)$$

Taking negative both side of equation (96), we have

$$-k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] = 0 \quad (98)$$

Using the above result in equation (97), we get

$$2k_1[\text{Br}_2] + 0 - 2k_5[\text{Br}]^2 = 0 \quad (99)$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2] \quad (100)$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2} \quad (101)$$

Similarly, rearranging equation (96) again

$$k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] \quad (102)$$

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \quad (103)$$

Now using the value of $[Br]$ from equation (101), the above equation takes the form

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (104)$$

Now rearranging equation (96) again in different mode i.e.

$$k_2[Br][H_2] - k_4[H][HBr] = k_3[H][Br_2] \quad (105)$$

Using the above result in equation (95), we have

$$\frac{d[HBr]}{dt} = k_3[H][Br_2] + k_3[H][Br_2] \quad (106)$$

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2] \quad (107)$$

After putting the value of $[H]$ from equation (104), the equation (107) takes the form

$$\frac{d[HBr]}{dt} = \frac{2k_3k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad (108)$$

Taking $k_3[Br_2]$ as common in the denominator and then canceling out the same form numerator, we get

$$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \quad (109)$$

Now since $2k_1[Br_2] = 2I_{ab}$, then

$$k_1^{1/2}[Br_2]^{1/2} = (I_{ab})^{1/2} \quad (110)$$

Using the above result in equation (109), we get

$$\frac{d[HBr]}{dt} = \frac{2k_2(I_{ab}/k_5)^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]} \quad (111)$$

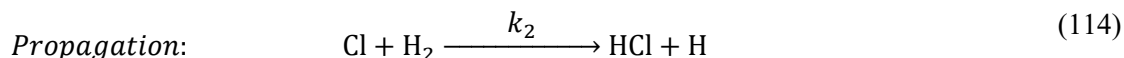
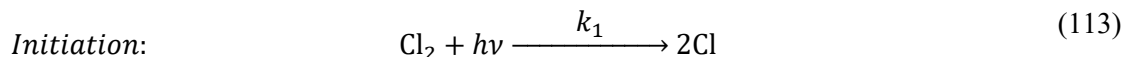
Hence, the rate of hydrogen-bromine reaction is directly proportional to the square root of the intensity of absorbed radiation.

➤ **Kinetics of Photochemical Reaction Between Hydrogen and Chlorine**

The hydrogen-bromine or the H_2-Cl_2 reaction is a typical case of photochemical reactions for which the overall reaction can be written as given below.



Since it is a chain reaction, the elementary steps for the same can be proposed as



The net rate of formation of HCl must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2] \quad (117)$$

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the H and Cl first i.e.

$$\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] = 0 \quad (118)$$

Similarly,

$$\frac{d[Cl]}{dt} = 2k_1[Cl_2] - k_2[Cl][H_2] + k_3[H][Cl_2] - 2k_4[Cl] = 0 \quad (119)$$

Taking negative both side of equation (118), we have

$$-k_2[Cl][H_2] + k_3[H][Cl_2] = 0 \quad (120)$$

Using the above result in equation (119), we get

$$2k_1[Cl_2] + 0 - 2k_4[Cl] = 0 \quad (121)$$

or

$$2k_1[Cl_2] = 2k_4[Cl] \quad (122)$$

or

$$[Cl] = \frac{k_1}{k_4} [Cl_2] \quad (123)$$

Similarly, rearranging equation (118) again

$$k_2 [Cl][H_2] - k_3 [H][Cl_2] = 0 \quad (124)$$

or

$$[H] = \frac{k_2 [Cl][H_2]}{k_3 [Cl_2]} \quad (125)$$

Now using the value of $[Cl]$ from equation (123), the above equation takes the form

$$[H] = \frac{k_2 [H_2] k_1}{k_3 [Cl_2] k_4} [Cl_2] = \frac{k_1 k_2 [H_2]}{k_3 k_4} \quad (126)$$

Using values of $[Cl]$ and $[H]$ from equation (123, 126) in equation (117), we have

$$\frac{d[HCl]}{dt} = k_2 \frac{k_1}{k_4} [Cl_2][H_2] + k_3 \frac{k_1 k_2 [H_2]}{k_3 k_4} [Cl_2] \quad (127)$$

or

$$\frac{d[HCl]}{dt} = \frac{k_1 k_2 [Cl_2][H_2]}{k_4} + \frac{k_1 k_2 [H_2][Cl_2]}{k_4} \quad (128)$$

Now since $2k_1 [Cl_2] = 2I_{ab}$, then

$$k_1 [Cl_2] = I_{ab} \quad (129)$$

Using the above result in equation (129), we get

$$\frac{d[HCl]}{dt} = \frac{k_2 I_{ab} [H_2]}{k_4} + \frac{k_2 I_{ab} [H_2]}{k_4} \quad (130)$$

or

$$\frac{d[HCl]}{dt} = \frac{2k_2 I_{ab} [H_2]}{k_4} \quad (131)$$

Hence, we can conclude that the rate of hydrogen-bromine reaction is directly proportional to the intensity of absorbed radiation. It is also worthy to note that the quantum yield of the hydrogen-chlorine reaction is much higher than that of hydrogen-bromine reaction which may simply be attributed to the exothermic nature of the second step in H_2-Cl_2 reaction which makes it spontaneous in nature.

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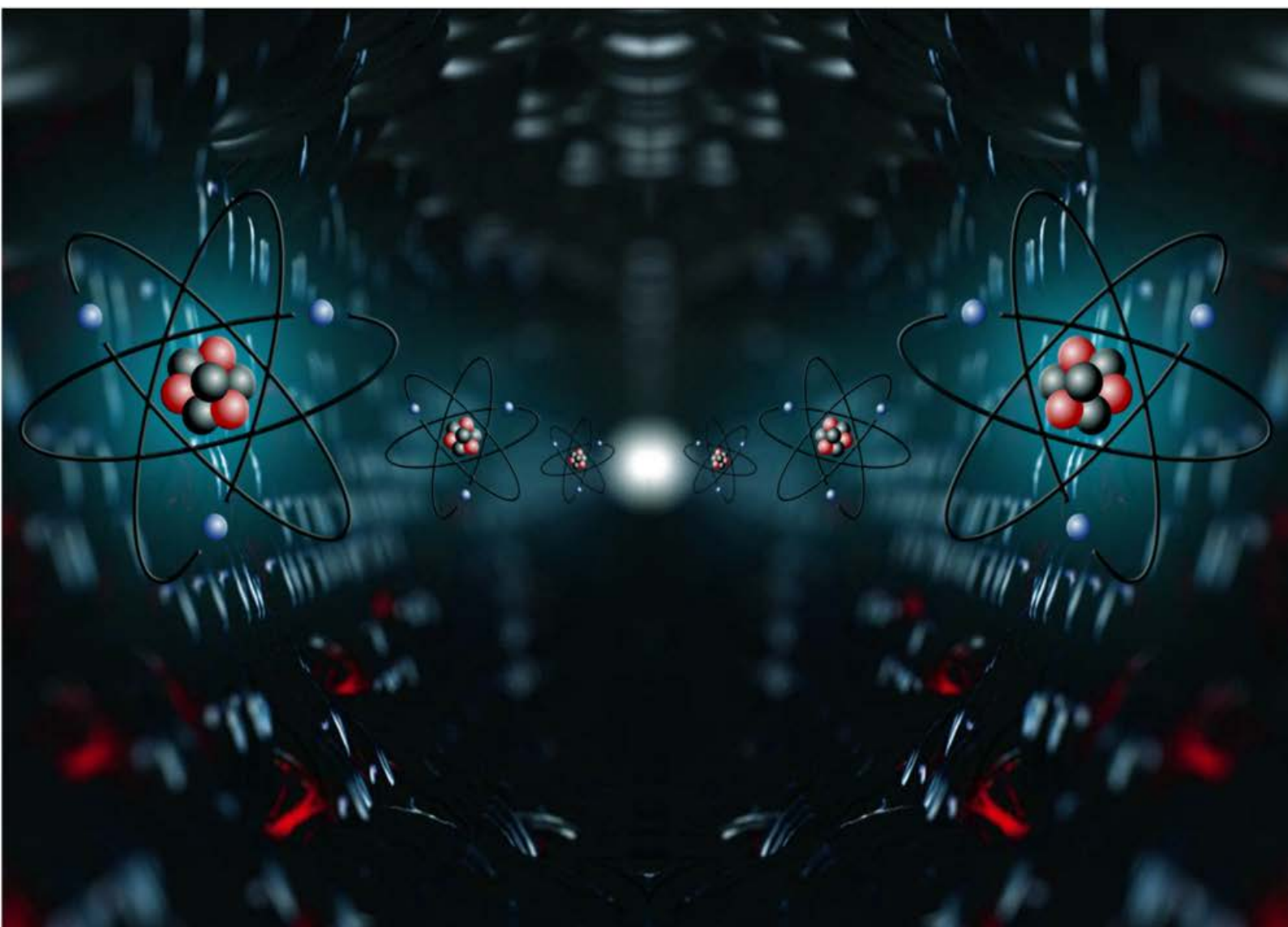
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A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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