No.

1 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction. (10 Marks)

Don't write anything in this margin

Don't write anything in this margin

$\longrightarrow$

The relation between half life and rate constant for First order reaction is given by,

$$t_{1/2} = \frac{0.693}{K}$$

$$23 = \frac{0.693}{K}$$

$$K = \frac{0.693}{23}$$

$$\underline{K = 0.0301 \, min^{-1}}$$

The Integrated rate law for First order reaction,

$$Kt = 2.303 \log \frac{[A_0]}{[A]} \quad \text{——} ①$$

Here,
[A₀] is the initial concentration &
[A] is the concentration at time t.

when 90% of the reaction is complete 10% of the reactants remains.

$\therefore$ rearranging the equation ①

$$t = \frac{2.303}{k} \cdot \log\left[\frac{[A_0]}{[A]}\right]$$

$$\therefore t = \frac{2.303}{0.0301} \log[10] \text{ --- } \left[\frac{[A]}{[A_0]} = 0.1\right]$$

$$\underline{t = 76.51 \text{ min.}}$$

$\therefore$ 76.51 minutes will be required for 90% complition of the reaction.

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2 The rate constant of a reaction is 5.70×10^{-5} dm^3 mol^{-1} s^{-1} at 25°C and 1.64×10^{-4} dm^3 mol^{-1} s^{-1} at 40°C. Calculate the activation energy and the Arrhenius pre-exponential factor.

(15 Marks)

$\longrightarrow$

Given Data:-

Rate constants:-

$K_1 = 5.70 \times 10^{-5} dm^3 mol^{-1} s^{-1}$

at 25°c i.e 298K

$K_2 = 1.64 \times 10^{-4} dm^3 mol^{-1} s^{-1}$

at 40°c i.e 313K.

∴ By using Arrhenius equation at two different temperature we can calculate Ea

$$\log \frac{K_2}{K_1} = \frac{Ea}{2.303 R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{(1.64 \times 10^{-4})}{(5.70 \times 10^{-5})} = \frac{Ea}{2.303 R}\left[\frac{313 - 298}{298 \times 313}\right]$$

$$\log(1.64 \times 10^{-4}) - \log(5.70 \times 10^{-5}) = \frac{Ea}{2.303 \times 8.314}[0.00016]$$

$$-3.7851 - (-4.2441) = \frac{Ea}{2.303 \times 8.314}[0.00016]$$

$$0.459 = \frac{Ea}{2.303 \times 8.314}[0.00016]$$

$$0.459 = \frac{Ea}{2.303 \times 8.314}[0.00016]$$

$$0.459 = \frac{Ea}{19.14}[0.00016]$$

$$\frac{0.459 \times 19.14}{0.00016} = Ea$$

$$\therefore \boxed{Ea = 54{,}907.875 \text{ J mol}^{-1}}$$

∴ The Activation energy of the ~~ra~~ reaction i.e Ea is 54,907.875 J mol^{-1}

or

$$\boxed{Ea = 54.90 \text{ kJ mol}^{-1}}$$

calculation of Arrhenius pre-exponential Factor using Arrhenius equation

$$\log k = \log A - \frac{Ea}{2.303RT}$$

Here
A = Arrhenius pre-exponential Factor.

using the value of k_1 & Ea we will calculate A.

$$\log(5.7 \times 10^{-5}) = \log A - \frac{Ea}{2.303\,RT}$$

$$-4.2441 = \log A - \frac{54907.87}{2.303 \times 8.314 \times 298}$$

$$= \log A - \frac{54907.87}{5705.84}$$

$$-4.2441 = \log A - 9.62$$

$$-4.2441 + 9.62 = \log A$$

$$5.3790 = \log A$$

$$\therefore A = \text{Antilog}(5.3790)$$

$$A = 239331.57$$

$$\therefore \boxed{A = 2.39 \times 10^{5}\ dm^3\,mol^{-1}\,s^{-1}}$$

∴ The Activation energy = 54907.87 $J\,mol^{-1}$

∴ Arrhenius pre-exponential factor = $2.39 \times 10^{5}\ dm^3\,mol^{-1}\,s^{-1}$

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Q. No.

3

Explain the transition-state theory for reaction rates. How this theory is considered superior to collision theory in providing a much more complete interpretation of the pre-exponential factor A in the Arrhenius equation?

(20 Marks)

→ Transition - state theory provides a description of how chemical reactions occure at moleculer level.

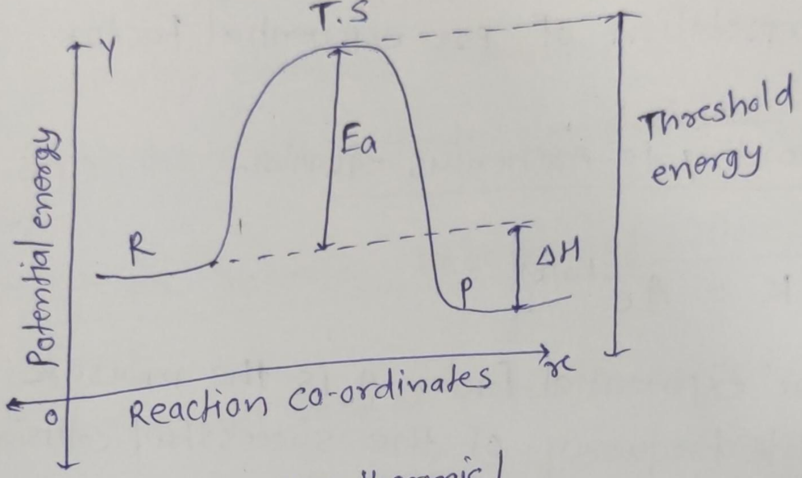
- It explains the reaction rate in terms of the Formation of an activated complex.

$$\underbrace{A-B+C}_{\text{Reactants}} \longrightarrow \underset{\text{transition state}}{ABC^{\#\ddagger}} \longrightarrow \underbrace{A+B-C}_{\text{product.}}$$

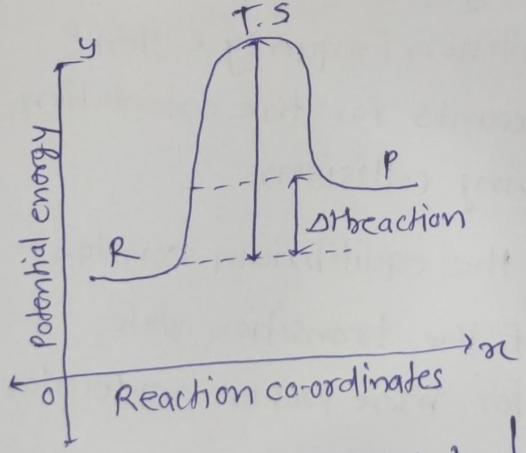
- This theory tells that when the molecules gradually comes near to each other they start to repel before the collision.
- In this process kinetic energy is converted into potential energy.
- A partial bond is formed between b&C atoms with corresponding weakning of A-b bond.

$$A-B+C \longrightarrow A \underset{\substack{\downarrow \\ \text{weakend} \\ \text{bond}}}{\text{-----}} B \underset{\substack{\downarrow \\ \text{Partial} \\ \text{bond.}}}{\text{-----}} C \longrightarrow A+B-C$$

Formation of transition state



(Exothermic)



(Endothermic)

T.S = Transition state

Ea = Activation energy

ΔH = Enthalpy

2) supuriority of transition state theory over collision theory in terms of interpretation of pre-exponential Factor A.

* According to Arrhenius equation:-

$$K = Ae^{-Ea/RT}$$

.The pre-exponential Factor A is the measure of the frequency of the successful collisions leading reaction.

- In collision theory A is described as the product of collision frequency & steric factor, which accounts for the orientation of molecules during collisions.
- But, in TST, the equilibrium constant for formation of the transition state, which accounts for more proper molecular orientation.
- This interpretation is superior because it accounts for thermodynamic properties.

- This interpretation is more accurate because of inclusion of entropy and enthalpy changes associated with the formation of activated complexes.

- It is superior beacause of following points.

a) The full rage of molecular interactions
b) The formation of activated complex.
c) The influence of thermodynamic quantities like enthalpy.

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4

The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of the reaction?

(10 Marks)

$\longrightarrow$

The relation between half life period and initial concentration can be determined From ~~In~~ Half life Formula's.

1) For zero order reaction;

$$t_{1/2} = \frac{[A_0]}{2K}$$

$\therefore t_{1/2} \propto [A_0]$ — ①

Here, $t_{1/2}$ is directly proportional to initial concentration it means half life time will increase w.r.t increase in concentration.

2) For First order reaction.

$$t_{1/2} = \frac{0.693}{K}$$

$\therefore t_{1/2}$ = constant. — ②.

$\therefore$ Here, half life time is independent of the initial concentration.

3) For second order reaction;

$$t_{1/2} = \frac{1}{K[A_0]}$$

$$\boxed{\therefore t_{1/2} \propto = \frac{1}{[A_0]}} \longleftarrow ③$$

Here, $t_{1/2}$ is inversly proportional to the initial concentration it means half life time will decrease w.r.t increase in intial concentration.

so,
case ③ i.e of second order reaction resembles with the condition given in the question.

$\therefore$ For, the second order reaction $t_{1/2}$ is halved as the initial concentration of reaction is double.
According to the statement given in the question the order of rection is $\boxed{\text{second-order reaction}}$

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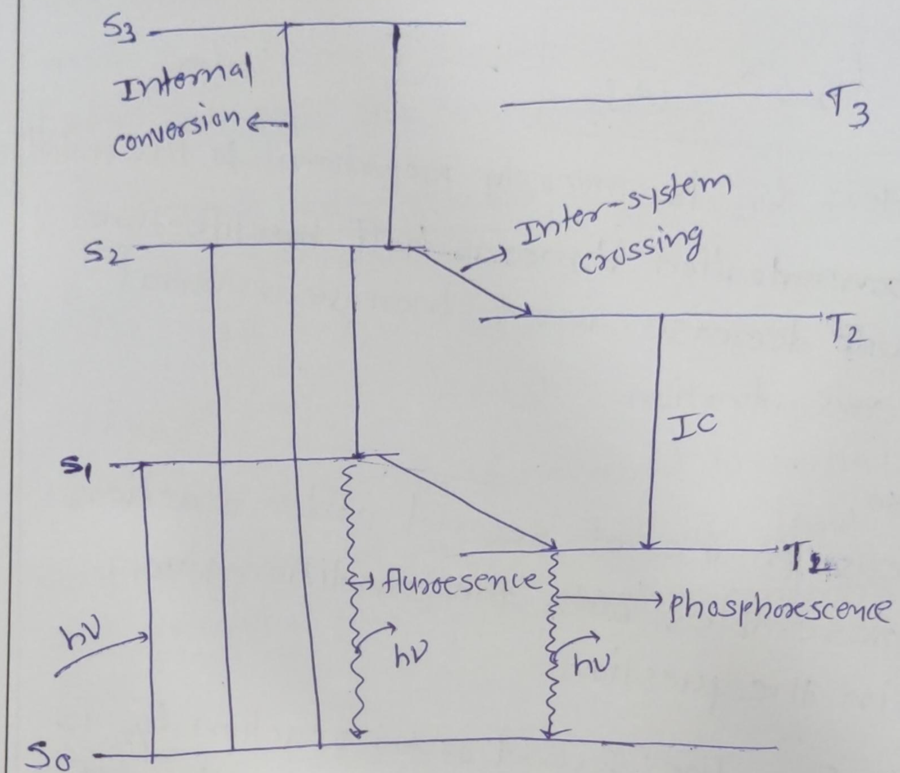
Q. No.

5 Discuss all the possible decay routes of an electronically excited molecule with the help of a neat Jablonski diagram.

(10 Marks)

- on absorption of light photon (hν)



Jablonski Diagram

- Non-radiative transitions! -

- These transitions involve the return of activated molecule from higher excited states two first excited state.

e.g. from $S_3 \rightarrow S_2 \rightarrow S_1$

a) Internal conversions (IC):-

- The energy of the activated molecule is dessipited in the form. of heat due to molecular collisions, this process is known as Internal conversions (IC)

b) Inter-system crossing:-

- The loss of energy can also occure through a process called Inter-system crossing, in this process the transition between different multiplicity states takes place.

- Radiative transitions:-

1) Phosphorescence:- The transition from the triplet excited state T_1 to the ground state S_0.

2) Flurorescence:-

- These transition involve the return of activated molecule from the excited (S or T) state to the ground state S_0 through emission of radiations.

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6

The relaxation time for the fast reaction is 10 μs (i.e., microseconds) and the equilibrium constant is 1.0×10^{-3}. Calculate the rate constants for the forward and the reverse reactions.

⟶

(10 Marks)

The relaxation time = $10 \mu s = 10 \times 10^{-6}$ cm

$K_{eq} = 1.0 \times 10^{-3}$

let,

k_1 be the rate of Forward reaction.

k_{-1} be the rate of backward reaction.

& τ be the relaxation time

→ The relation between relaxation time and Rate constants:

$$\tau = \frac{1}{k_1 + k_{-1}} \quad — ①$$

→ Equilibirium constants in terms of rate constant

$$K_{eq} = \frac{k_1}{k_{-1}} \quad — ②$$

using equations ① & ②.

$$K_{eq} \times k_{-1} = k_1$$

$$1.0 \times 10^{-3} \times k_{-1} = k_1 \quad — ③$$

Plug this value in eqⁿ ①.

$$\tau = \frac{1}{k_1 + k_{-1}}$$

~~$10\times10^{-6} = \frac{1}{k_1 \times 10\times10^{-3} + k_{-1}}$~~

$$k_1 + k_{-1} = \frac{1}{\tau}$$

$$\therefore k_1 + k_{-1} = \frac{1}{10\times10^{-6}} \quad \text{— ④}$$

$$\boxed{k_1 + k_{-1} = 10^5\, s^{-1}}$$

$1\times10^{-3} \times k_{-1} + k_{-1} = 10^5$ — from eq^n ①

$$\therefore \boxed{k_{-1} = 9.99\times10^{4}\, s^{-1}} \quad \text{— ⑤}$$

Now, plug this value in eq^n -①.

$$1\times10^{-3} \times k_{-1} = k_1$$

$$\therefore k_1 = 1.0\times10^{-3} \times 9.99\times10^{-4}$$

$$\boxed{k_1 = 99.9\, s^{-1}}$$

∴ The ~~the~~ rate of Forward reaction

$$\boxed{k_1 = 99.9\, s^{-1}}$$

The rate of backward reaction

$$\boxed{k_{-1} = 9.99\times10^{4}\, s^{-1}}$$

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7 A substance when dissolved in water at 10^{-3} M concentration absorbs 10% of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90% of the same radiation?

$\longrightarrow$

(10 Marks)

case-I :.

Here, absorbed light is given in the For of Percentage light absorbed.

$\therefore$ 10% light absorbed means light transmitted is 90%

$\therefore$ Transmittane(T) = $1 - \frac{10}{100}$

$\therefore \boxed{T = 0.9}$ — ①

To find absorbane in relation to transmittance we have,

$A_1 = -\log(T)$

$\therefore A_1 = -\log(0.9)$ - - - From ①

$\boxed{A_1 = 0.0457}$ — ②

case-II

Here,

90% light is absorbed means light transmitted is 10%.

$\therefore$ Transmittance (T) = $1 - \frac{90}{100}$

$\boxed{T = 0.1}$

$$A_2 = -\log(T)$$

$$A_2 = -\log(0.1)$$

$$\boxed{A_2 = 1} \quad - ③.$$

From lambert-Beer's law,

$$A = \varepsilon . C . l$$

where,
A = Absorbane
c = concentration
l = path length
ε = molar absorptivity constant

we can say that,
Absorbance is directly proportional to concentration.

$$\therefore \frac{A_2}{A_1} = \frac{C_2}{C_1} \quad / \quad \frac{A_1}{A_2} = \frac{C_1}{C_2}$$

$$\frac{1}{0.04} = \frac{C_2}{10^{-3}}$$

$$C_2 = \frac{1}{0.04} \times 10^{-3}$$

$$\therefore \boxed{C_2 = 0.025M}$$ → This much concentration will be required for 90% absorption

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8 For the photochemical formation of ethylene from di-n-propylketone using a radiation of wave length 313 nm, the quantum yield is 0.21. Calculate the number of moles of ethylene formed when the sample is irradiated with 50 watt (Js^{-1}) of this radiation assuming that all the radiation is absorbed by the sample.

(10 Marks)

$\longrightarrow$

Given data:-

wavelength $(\lambda) = 313\ nm = 313 \times 10^{-9}\ m$

Quantum yield $(\phi) = 0.21$

Total Energy $= 50\ JS^{-1}$

① To calculate energy of 1 photon

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{313 \times 10^{-9}\ m}$$

Here
h = plank's constant
c = speed of light
E = Energy
λ = wavelength

$\boxed{E = 6.35 \times 10^{-19}\ J}$ — Energy of 1 photon

② To calculate Number of photons absorbed per second:-

$$\therefore \text{No. of photons} = \frac{\text{Total energy}}{\text{Energy of 1 photon}}$$

$$= \frac{50\ Js^{-1}}{6.35 \times 10^{-19} J}$$

$\boxed{N_{photons} = 7.87 \times 10^{19}\ \text{photons/sec}}$

7.87×10^{19} photons absorbed per second.

3) To Calculate Number of moles of ethylene Formed

$$\phi_{ethylene} = \frac{\text{No. of molecules of ethylene Formed}}{\text{No. of Photons absorbed per second.}}$$

(Nphotons)

$\phi \times N_{photons}$ = No. of molecules formed.

$$0.27 \times 7.87 \times 10^{19} = 2.12 \times 10^{19}$$

∴ No. of molecules of ethylene Formed are $\boxed{2.12 \times 10^{19}}$

To convert these molecule to moles we need to divide by Avagadro's Number.

$$\therefore \frac{2.12 \times 10^{19}}{6.022 \times 10^{23}} = \text{moles of ethylene}$$

$$\boxed{= 2.75 \times 10^{-5}}$$

∴ The number of moles of ethylene Formed when the sample is irradiated with $50 Js^{-1}$ of energy per second are $\boxed{2.75 \times 10^{-5}}$

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9 Show that a surface catalysed decomposition reaction follows zero order kinetics with respect to reactant when its pressure is high enough.

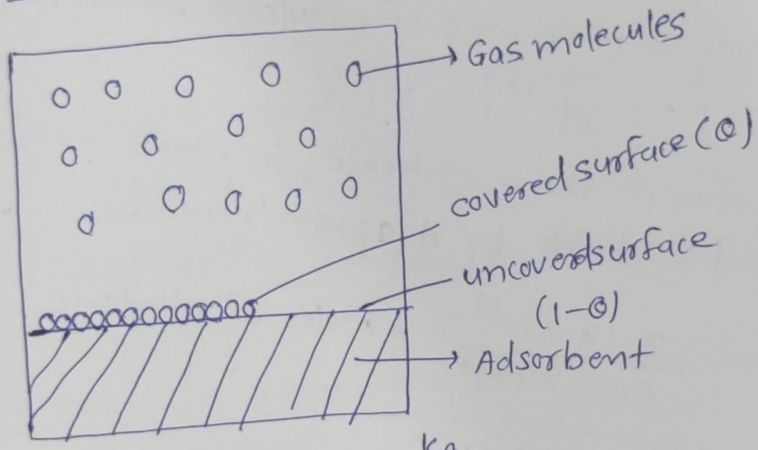
(10 Marks)

⟶

In surface-catalysed reactions the rate of reaction is influenced by the adsorption of reactants on the surface of the catalysts.

- The rate of adsorption depends upon the pressure.

- By referring to langmuir adsorption isotherm



$$A_{(g)} + M\text{-surface} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} Am$$

Thus,

$$\theta = \frac{K_{eq}.\ P}{1 + K_p}$$

where,

K_{eq} = Equilibrium constant

θ = covered surface

p = pressure of gas.

Now,

At high pressure,

$$Kp >>> 1$$

$$\therefore Kp + 1 = Kp$$

$$\boxed{\theta = 1}$$

∴ At high pressure, langmuir adsorption isotherm ~~re~~ simplifies to $\theta = 1$

- This means that at high pressure, nearly all the active sites on the catalytic surface are occupied. & will become independent of pressure.

$\therefore \underline{r = K}$ -- as reaction becomes independent of reactant pressure.

$$\boxed{\therefore \frac{d[R]}{dt} = -K}$$

Thus, the rate of reaction becomes independent of the reactant concentration, which corresponds to zero order kinetics

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11 Explain the dependence of rate of photochemical formation of HBr on intensity of absorbed light.

(10 Marks)

⟶

The rate of photochemical formation of HBr depends upon the intensity of absorbed light due to nature of photochemical reactions.

- photochemical reactions are ~~absorbed~~ initiated by absorbed light which provides them energy to break bonds.

* General photochemical reaction for formation of HBr:-

1. Initiation step:-

1. In this step the absorption of light takes place ~~which~~ By (Br_2) molecule which leads to formation of $2Br^{\cdot}$ radicals

$$Br_2 + h\nu \longrightarrow 2Br^{\circ}$$

-This step is very crucial as it leads to formation of HBr.

2. Propogation step:-

- The bromine radicals react with hydrogen molecule to form HBr.

$$Br^{\cdot} + H_2 \longrightarrow HBr + H^{\cdot}$$

$$H^{\circ} + Br_2 \longrightarrow HBr + Br^{\cdot}$$

-This a chain reactions where Hydrogen & Bromine radicals reacts to Form HBr.

3. Termination Step:

$Br^{\cdot} + Br^{\cdot} \longrightarrow Br_2$

- In this case not all bromine molecules contribute to Formation HBr but some of them Forms Br_2.

• conclusion:-

Rate of Formation of HBr $\propto$ Intensity of absorbed light.

~~ab~~

- At low light intensities, the rate of photochemical Formation of HBr. increases linearly with ~~increase~~ the intensity of absorbed light, as the reaction is limited with to generate bromine radicals
- At higher intensities, the rate becomes ~~stagnet~~ stagnent due to radical recombination.

Hence, the rate of photochemical Formation of HBr, depends on the intensity of absorbed light which is required to initiate the reaction.

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