Kinetics

⑥ a)

③ i) Rate law of $A \longrightarrow product$

can be, $Rate = k[A]^m$

ii)

$A \longrightarrow product$

Initial concentration: $a \qquad 0$

Final concentration: $(a-x) \qquad x$

By integration,

$Kt = \ln \dfrac{[A]_0}{[A]} \qquad\longrightarrow\qquad Kt = \ln \dfrac{a}{a-x}$

$\Rightarrow Kt = 2.303 \dfrac{1}{t} \log \dfrac{[A]_0}{[A]} \qquad\longrightarrow\qquad Kt = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)}$

iii) we know,

$$Kt = \dfrac{2.303}{} \log \dfrac{[A]_0}{[A]} \quad \text{in first order.}$$

or, $t = \dfrac{2.303}{K} \log \dfrac{[A]_0}{[A]}$

when, $t = t_{1/2}, [A] = [A_0]/2$

or, $x = \dfrac{a}{2}$
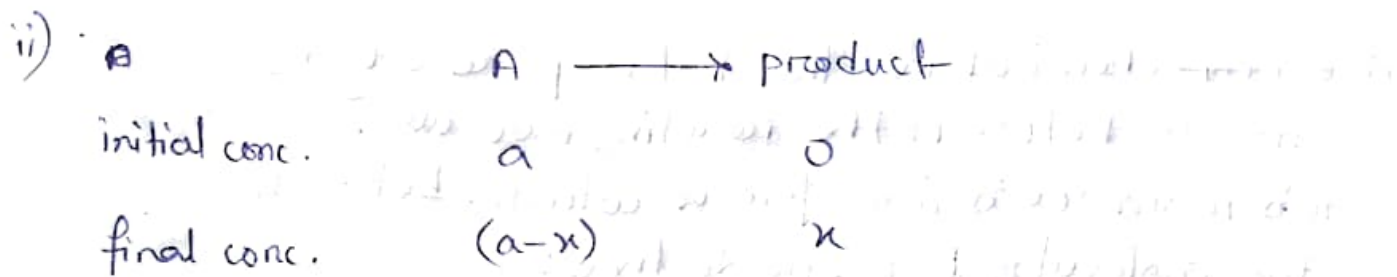
So, we can write,

$$t_{1/2} = \dfrac{2.303}{K} \log \dfrac{[A]_0}{[A]_0/2}$$

$$\Rightarrow t_{1/2} = \dfrac{2.303}{K} \log \dfrac{a}{a - a/2}$$

$\Rightarrow t_{1/2} = \dfrac{2.303}{k} \log 2$.

$\Rightarrow t_{1/2} = \dfrac{2.303}{k}$.

$\therefore$ Half life of a first order is concentration independent.

ii)

$$A \longrightarrow product$$

initial conc. a 0

final conc. $(a-x)$ x

Rate of reaction $= -\dfrac{d[A]}{dt} = k_0$

We know, $\dfrac{dx}{dt}$ is directly proportional to the concentration of the reactant. So,

$$\dfrac{dk}{dt} = k(a-x)$$

$$\Rightarrow \dfrac{du}{a-x} = kdt.$$

$$\Rightarrow \int \dfrac{du}{a-x} = \int kdt \cdot \left[\text{By integration}\right]$$

$$\Rightarrow -\ln(a-x) = kt + I \quad\text{————(11)}$$

I is integration constant. Putting $t=0$ and $x=0$, we get,

$$I = -\ln a.$$

Putting value of I in ⑪,

$$-\ln(a-x) = kt - \ln a.$$

$$\Rightarrow \ln a - \ln(a-x) = kt$$

$$\Rightarrow kt = \ln\dfrac{a}{(a-x)}$$

$$\Rightarrow k = \frac{1}{t} \ln \frac{a}{(a-x)}$$

$$\Rightarrow k = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad \text{(Derived)}.$$

|3/b| Collision Theory of Reaction Rates :

A ~~collisi~~ chemical reaction takes place only by collisions between the reacting molecules,

The two main conditions for a collision between the reacting molecules to be productive :

① The colliding molecules must-posses sufficient kinetic energy to cause a reaction.

② The reacting molecules must collide with proper orientation.

|3/d| Activation Energy Calculation :

From Arrhenius Equation, we get,

$K = A e^{-Ea/RT}$ where, A is experimetally determined quantity
E_a is activation energy
R is gas constant
T is Temperature.
K is rate constant.

So, $\ln K = -\frac{E_a}{RT} + \ln A$

$\Rightarrow \log k = -\frac{E_a}{2.303 RT} + \log A$

If there were two temp, then,

$$\log k = \frac{-E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Definition: E_a is defined as the minimum amount of energy required by a reacting molecule to get converted into product.

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3/b $\text{Rate} = k \left[Br_2 \right]^m \left[H COOH \right]^n$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k \left[Br_2 \right]_2^m \left[HCOOH \right]^n}{k \left[Br_2 \right]^m \left[1 + COOH \right]^n} \quad \left[\because HCOOH = \text{constant} \right]$$

$\Rightarrow \dfrac{3.52}{4.2} = \dfrac{(0.0101)^m}{\cancel{120}(0.0120)^m}$

$\Rightarrow \ln \dfrac{3.52}{4.2} = m \ln \left(\dfrac{0.0101}{0.0120} \right)$

$\Rightarrow m = 1.02 \cdot \approx 1$

3/d $\ln \dfrac{k_1}{k_2} = \dfrac{-E_A}{R} \left(\dfrac{1}{T_1} - \dfrac{1}{T_2} \right)$

$\Rightarrow \ln \dfrac{2.46 \times 10^{-5}}{1.65 \times 10^{-3}} = \dfrac{-E_A}{8.314} \times \dfrac{303 - 273}{303 \times 273}$

$\Rightarrow -4.205 = -E_A \times$

$\Rightarrow E_A = 96.396 \times 10^3 \text{ J mol}^{-1}$

3a(iv)

$$T_{1/2} = 18.5 \text{ min}$$

$$= (18.5 \times 60) = 1110 \text{ sec}.$$

$$T_{1/2} = \frac{0.693}{k}$$

$$\Rightarrow 1110 = \frac{0.693}{k}$$

$$\Rightarrow k = 6.243 \times 10^{-4}$$

Here, $A = \frac{80}{100} A_0$.

So, we know,

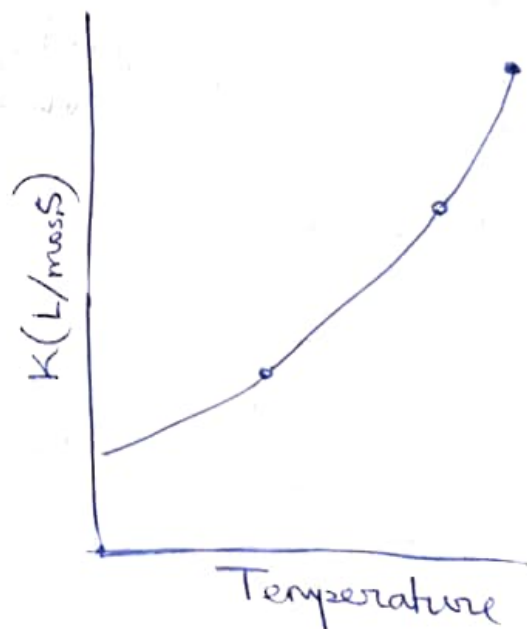$$k = \frac{1}{t} \ln \frac{A_0 \times 100}{A_0 \cdot 80}$$

$$t = 357.43 \text{ sec}.$$

3.c Graphical illustration of effect of temperature on rate constant:
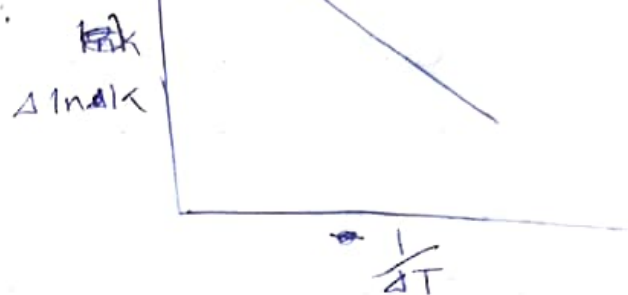
From Arrhenius equation
$K = Ae^{-E_a/RT}$ we get to
know K increases.
exponentially as T increases.

we can calculate E_a from the graph too. If we draw a graph of $\frac{\Delta \ln K}{}$ and inverse ΔT, we get a downward slope.

So, the slope will be $\frac{\Delta \ln K}{\Delta T}$.

And from the equation,

$$\Delta \ln K = -\frac{E_a}{R}\left(\frac{1}{\Delta T}\right) + \ln A.$$

we can assume $\Delta \ln K$ as y and $-\frac{E_a}{R}$ as m and $\frac{1}{\Delta T}$ as x and rest as intercept of equation of straight line $y = mx + c$.

The slope is $\frac{y}{x} = \frac{\Delta \ln K}{1/\Delta T}$.

and so the slope is $-\frac{E_a}{R}$.

So, we can calculate E_a.