

Chemical Kinetics

~~Ther~~, for the reacⁿ.



Ratio of disappearance of A = $-\frac{d[A]}{dt}$

Ratio of appearance of B = $\frac{d[B]}{dt}$.

$$-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$$

Let, when time $t=0$, $[A] = a$ & $[B] = 0$.

At time t , let the extent of reaction $= x$. (unit: mol/lit)

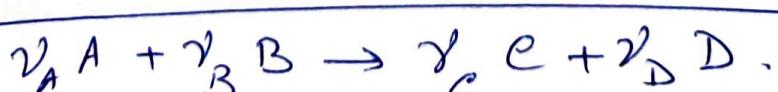
Hence, At time t , $[A]_t = (a-x)$

$$[B]_t = 2x.$$

$$\therefore -\frac{d[A]}{dt} = -\frac{d(a-x)}{dt} = \frac{dx}{dt}.$$

$$2 \quad \frac{1}{2} \frac{d[B]_t}{dt} = \frac{1}{2} \frac{d(2x)}{dt} = \frac{dx}{dt}.$$

$$\therefore \gamma = \frac{dx}{dt} = -\frac{d[A]_t}{dt} = \frac{1}{2} \frac{d[B]_t}{dt}$$



$$\frac{dx}{dt} = -\frac{1}{\gamma_A} \frac{d[A]}{dt} = -\frac{1}{\gamma_B} \frac{d[B]}{dt} = \frac{1}{\gamma_C} \frac{d[C]}{dt} = \frac{1}{\gamma_D} \frac{d[D]}{dt}.$$

Here,

Let at time $t=0$, $[A]_0 = a$; $[B]_0 = b$; $[C]_0 = 0$; $[D]_0 = 0$.

At at time t , $[A]_t = (a - \gamma_A x)$; $[B]_t = (b - \gamma_B x)$; $[C]_t = \gamma_C x$; $[D]_t = \gamma_D x$.

$$\therefore -\frac{d[A]_t}{dt} = -\frac{d(a - \gamma_A x)}{dt} = \gamma_A \frac{dx}{dt}$$

$$-\frac{d[B]_t}{dt} = \gamma_B \frac{dx}{dt}$$

$$\frac{d[C]_t}{dt} = \gamma_C \frac{dx}{dt}$$

$$\frac{d[D]_t}{dt} = \gamma_D \frac{dx}{dt}$$

\therefore Overall rate of the reaction \Rightarrow
Rate of change in the extent of reaction.

$$\gamma = \frac{dx}{dt} = -\frac{1}{\gamma_A} \frac{d[A]_t}{dt} = -\frac{1}{\gamma_B} \frac{d[B]_t}{dt} = \frac{1}{\gamma_C} \frac{d[C]_t}{dt} = \frac{1}{\gamma_D} \frac{d[D]_t}{dt}.$$

(2)

that Thermodynamics depend is based on macroscopic properties of system \Rightarrow like energy, T , P , V , heat capacity and others.

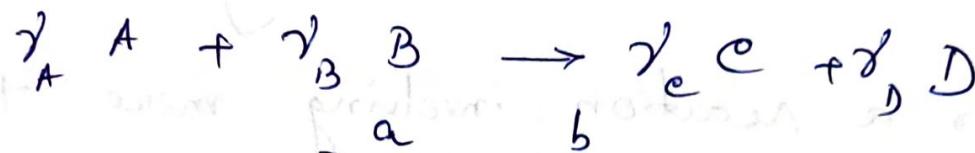
It deals with equilibrium state of a system, i.e. in terms of a chemical red^{2} , it can tell you what is the equilibrium const of the reactants and how it is changed with T , P and other variables. From this, we can calculate the amount of product and amount of unreacted reactant at eq^m at a given set of experimental variables.

But classical thermodynamics is silent on the time required for any chemical red^{2} to establish the equilibrium \Rightarrow This is the domain of chemical kinetics.

From the study of chemical kinetics, we can determine the rate of the red^{2} , we can predict on the mechanism of the reactants and also we can know how the rate of a red^{2} depends on various experimental parameters, like temp, pressure, dielectric const. of the medium, ionic strength of the medium, etc.

How does the rate depend on reactant concentrations?

The rate of a reaction is proportional to the product of effective concentrations of the reacting species, each raised to a power like \Rightarrow



$$\text{Rate} = \propto [A]^a [B]^b \dots$$

$a, b \Rightarrow$ experimentally obtained number values, $a, b \Rightarrow$ can be (+), (-) ^{integer}, fractional no. or even zero.

Total order of the reacⁿ $\Rightarrow (a+b+\dots)$

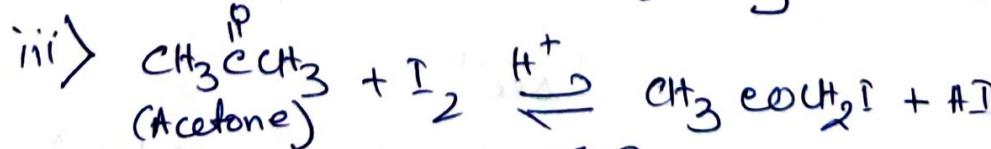
Ex: i) Reacⁿ betw. H_2 & Br_2 ; $H_2 + Br_2 \rightarrow 2HBr$

$$\frac{1}{2} \frac{d[HBr]}{dt} = \frac{k [H_2] [Br_2]^{1/2}}{1 + k' \frac{[HBr]}{[Br_2]}}$$

ii) Reacⁿ betw. Hypochloride and iodide:

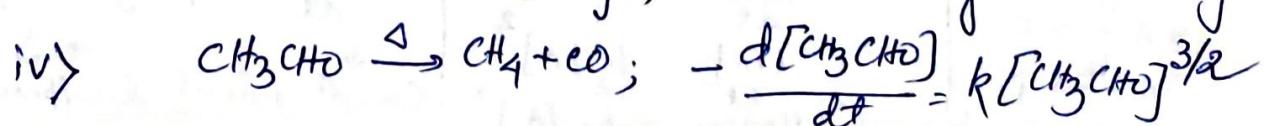


$$\frac{d[Cl^-]}{dt} = \frac{k [OCl^-] [I^-]}{[OH^-]} ; OH^- \text{ acting as an inhibitor.}$$



$$-\frac{d[I_2]}{dt} = k [CH_3COCH_3] [H^+]$$

Reacⁿ is '0' order w.r.t $[I_2]$; H^+ acting as catalyst.



For elementary reacⁿ (single step reaction) \rightarrow
 order = stoichiometric number of molecules
 involved in the reaction.

Order \Rightarrow Molecularity

For a reaction involving more than one step, overall reaction is obtained by adding these elementary reactions (steps).

In these cases, order may not be equal to the molecularity.

Rate Constant or Specific-reaction
 rate constant:

$$r \propto [A]^a [B]^b \dots$$

$$r = k [A]^a [B]^b \dots; k \Rightarrow \text{proportionality}$$

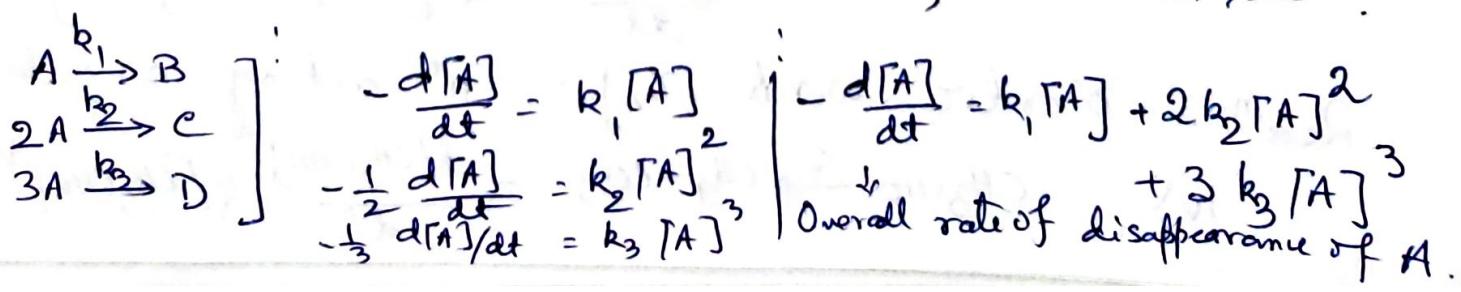
const. \Rightarrow Rate constant.

order unit of k

0 $\text{con}^n \cdot \text{time}^{-1}; \text{mole dm}^{-3} \text{sec}^{-1}$

1 sec^{-1}

2 $\text{con}^{-1} \cdot \text{time}^{-1}; \text{mole}^{-1} \text{dm}^3 \text{sec}^{-1}$



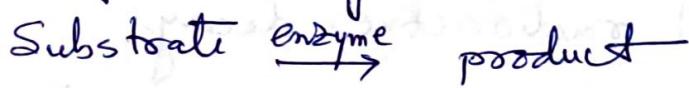
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Differential And Integrated Rate expressions:

i)

Zero order Reacⁿ:

A) Enzyme catalysed reacⁿ:



$$\text{Rate} = k [\text{enzyme}]^1 [\text{substrate}]^0 = k [\text{enzyme}]$$

B) Decomposition of HI on Gold surface

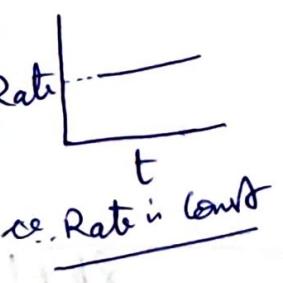
Here, rate does not depend on pressure of HI; it depends on the number of active sites (adsorption sites) present on Gold surface. As this number is fixed, rate is independent on gas pressure.



$$-\frac{1}{\gamma} \frac{d[\gamma A]}{dt} = k \quad ; \quad d[\gamma A] = -\gamma k dt$$

Integrating: $\int_{[\gamma A]_0}^{[\gamma A]_t} d[\gamma A] = -\gamma k \int_0^t dt$

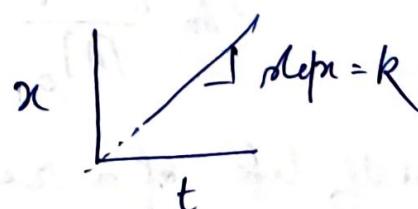
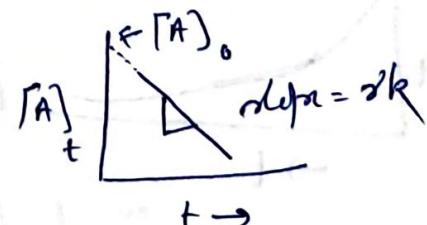
$$[\gamma A]_t - [\gamma A]_0 = -\gamma k t ; \boxed{[\gamma A]_t = [\gamma A]_0 - \gamma k t}$$



$$, \quad [\gamma A]_0 - [\gamma A]_t = \gamma k t$$

$$, \quad [\gamma A]_0 - \{ [\gamma A]_0 - \gamma k t \} = \gamma k t$$

$$\boxed{x = kt}$$

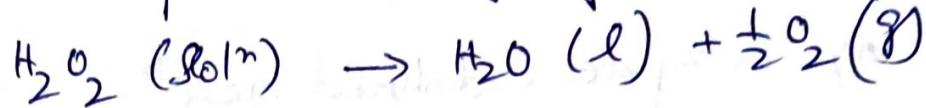


$$\boxed{t_{\text{completion}} = \frac{[\gamma A]_0}{\gamma k}} \Rightarrow \text{time at which } [\gamma A]_t = 0.$$

1st Order Reacⁿ

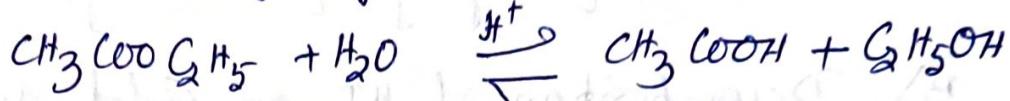
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Example: i) Decomposition of Hydrogen-peroxide.

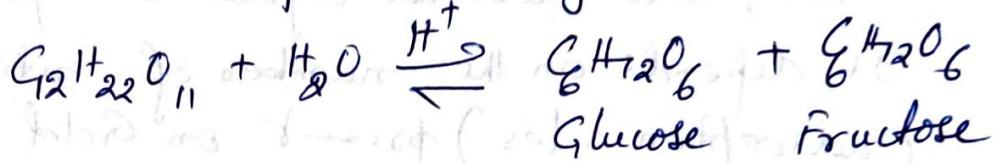


ii) All radioactive decay

iii) Acid hydrolysis of an ester



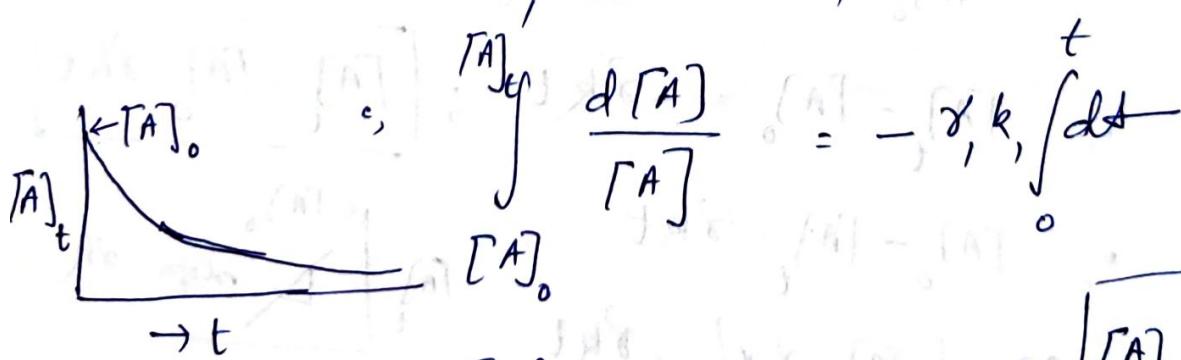
iv) Inversion of cane-sugar



Reacⁿs (iii) & (iv) \Rightarrow Example of pseudo-unimolecular reactions, where concn. of water is much higher than thi. Other reacting species present.



$$\text{Rate} ; -\frac{1}{\gamma_1} \frac{d[A]}{dt} = k_1 [A] \quad \left[\begin{array}{l} \text{0 concn} \\ \text{w.r.t. B} \end{array} \right]$$



$$[A]_t = [A]_0 e^{-\gamma_1 k_1 t}$$

$$\ln \frac{[A]_t}{[A]_0} = -\gamma_1 k_1 t \Rightarrow \frac{[A]_t}{[A]_0} = e^{-\gamma_1 k_1 t}$$

Wilhelmy's eqⁿ.

At, Half-life of a reaction ($t_{1/2}$) ; $[A]_t = [A]_0/2$

$$\Rightarrow t_{1/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k}$$

How does concn. of product increase with time? ⑥

$$[A]_t = [A]_0 \cdot e^{-kt}$$

Rate of increase in concn. of product, P:

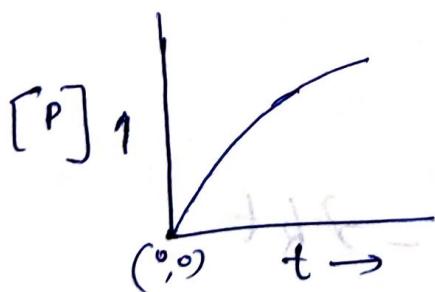
$$\frac{d[P]}{dt} = k[A] = k[A]_0 \cdot e^{-kt}$$

Integrating: $[P] = \frac{k[A]_0 e^{-kt}}{(-k)} + I.C.$

when time $t=0$; $[P]=0$.

$$\therefore I.C. = [A]_0$$

$$\therefore [P] = [A]_0 \left\{ 1 - e^{-kt} \right\}$$



2nd order Reacⁿ

Example: i) Thermal dissociation of acetaldehyde



ii) Saponification of an ester



Concⁿ

$\rightarrow A \rightarrow \text{product}$

$$-\frac{1}{2} \frac{d[A]}{dt} = k[A]^2$$

$$\int \frac{d[A]}{[A]^2} = -2k \int dt$$

$$-\left[\frac{1}{[A]} \right]_t - \left[\frac{1}{[A]} \right]_0 = -2kt$$

$$\frac{1}{[A]}_t - \frac{1}{[A]}_0 = kt \quad (\gamma=1)$$

$$\therefore \frac{1}{(a-x)} - \frac{1}{a} = kt$$

$$a = [A]_0$$

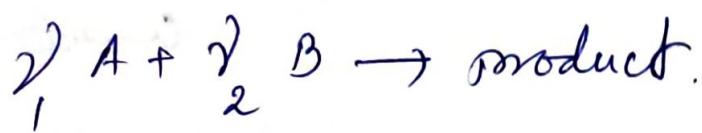
$x = \text{extent of redn}$
at time t .

$$\therefore \boxed{\frac{x}{a(a-x)} = kt}$$

$$\text{when } t = t_{1/2}, x = \frac{a}{2};$$

$$t_{1/2} = \frac{1}{ka}$$

(7)



Let initial concn. of A & B are different; $a \& b$ respectively.

$$\therefore \frac{dx}{dt} = k (a - \gamma_1 x) (b - \gamma_2 x)$$

$$\text{or, } \frac{dx}{(a - \gamma_1 x)(b - \gamma_2 x)} = k dt$$

$$\text{or, } \frac{1}{(\gamma_1 b - \gamma_2 a)} \left[\int \frac{\gamma_1}{(a - \gamma_1 x)} dx - \int \frac{\gamma_2}{(b - \gamma_2 x)} dx \right] dt = k dt$$

$$\text{or, } \frac{1}{(\gamma_1 b - \gamma_2 a)} \left[\ln \frac{(b - \gamma_2 x)}{(a - \gamma_1 x)} \right] = kt + I.C.$$

when $t = 0$; $x = 0$

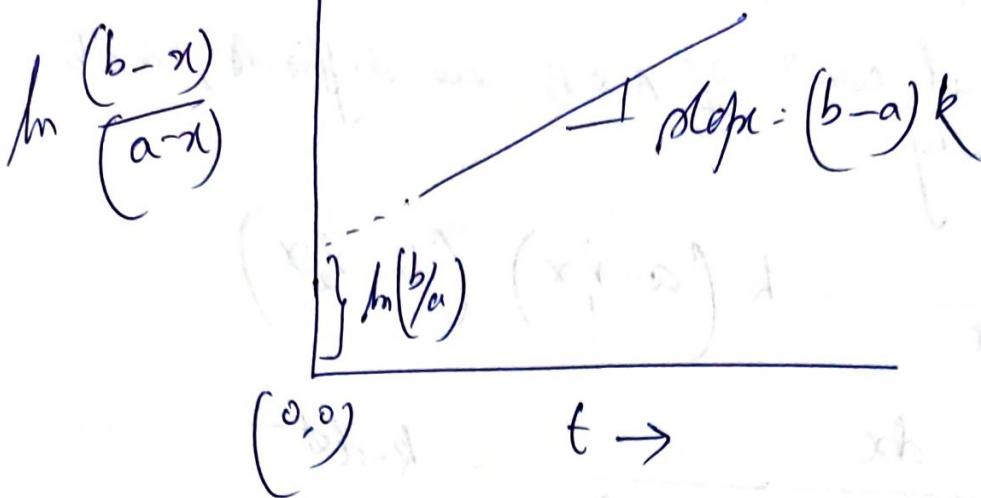
$$\therefore I.C. = \frac{1}{(\gamma_1 b - \gamma_2 a)} \ln \left(\frac{b}{a} \right)$$

$$\text{or, } \frac{1}{(\gamma_1 b - \gamma_2 a)} \left[\ln \frac{(b - \gamma_2 x)}{(a - \gamma_1 x)} + \ln \left(\frac{a}{b} \right) \right] = kt$$

$$\gamma_1 = \gamma_2 = L$$

$$\frac{1}{(b-a)} \ln \left[\frac{a(b-x)}{b(a-x)} \right] = kt$$

$$\Rightarrow \ln \frac{(b-x)}{(a-x)} = \ln \left(\frac{b}{a} \right) + k(b-a)t$$



Again; $\frac{1}{(b-a)} \ln \frac{a(b-x)}{b(a-x)} = kt$

Under the condition of $b \gg a$

we will get: $\ln \left(\frac{a}{a-x} \right) = k't \Rightarrow$

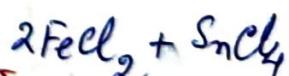
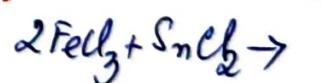
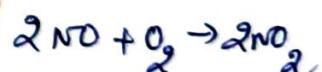
pseudo-first order kinetics.



Show that $\left(\frac{1}{a-x} \right)^2 = \frac{1}{a^2} + 2kt$

$$\therefore t_{1/2} = \frac{3}{2ka^2}$$

e.g.



Rate exp: $\frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] = kt$

Also show:

$$\frac{t_{3/2}}{t_{1/2}} = 2^{\frac{n-1}{2}} + 1 \quad \& \quad t_{1/2} \propto \frac{1}{a^{n-1}} \quad \begin{array}{l} [\text{Not applicable}] \\ \text{for } n=1 \end{array}$$

③ For a 1st order reaction at the start, $x = akt$.

Hint: $(a-x) = a e^{-kt} \approx a(1-kt)$; $\therefore x = akt$

Some numerical problems:

(8)

D) Determine the rate law for the reaction $A + B \rightarrow \text{prod}$, from the fact that when the initial concn. of A is doubled, the initial rate of the reactⁿ doubles; but doubling the initial concn. of B cuts off the reaction rate by half.

Ans: $r = k [A]^n [B]^m$ - ①

Case I: $2r = k\{2[A]\}^n [B]^m$ - ②

Dividing ② with ①

$2 = 2^n \Rightarrow n = 1$.

Case II: $\frac{1}{2}r = k [A]^n \{2[B]\}^m$ - ③

Comparing ① & ③

$\frac{1}{2} = 2^m ; m = -1$.

∴ Rate expression: $r = k [A] [B]^{-1}$

(2)

② A drug is known to be ineffective when it has decomposed 30%. The original concn. of the sample is 500 units/mL. When it is analysed 20 months later, the concn. has been found to be 420 units/mL. Assuming that the decomposition is 1st order, what will be expiration time of the sample? What is the half life of this drug?

Solⁿ:

$$k = \frac{1}{20} \ln \frac{500}{420}; k = 8.717 \times 10^{-6} \text{ month}^{-1}$$

The expiration time t is (when $x = 0.3a$)

$$t_{\text{exp.}} = \frac{1}{k} \ln \left(\frac{a}{a-0.3a} \right) \approx 41 \text{ months.}$$

Half life of the drug \Rightarrow when it decomposes to the extent of 15%.

$$t_{1/2} = \frac{1}{8.717 \times 10^{-6}} \ln \left(\frac{a}{0.85a} \right) \approx 19 \text{ months.}$$

③ A piece of wood buried by a glacier had 25.6% as much C¹⁴ as a recently grown piece of wood. If the amount of C¹⁴ in the atmosphere was the same when the old wood died as it is now, when was the wood buried? [Given $t_{1/2}$ for C¹⁴ = 5600 yrs]

Solⁿ: Assume decay of C¹⁴ starts when the wood was buried
Radioactive decay is 1st order.

$$t = \frac{1}{k} \ln \left(\frac{N_0}{N} \right); k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5600} \text{ yrs}^{-1}$$

$$\therefore t = \frac{5600}{0.693} \ln \left(\frac{1}{0.256} \right) = 11011 \text{ yrs.}$$

⑤ At 25°C , the specific rate constant for the hydrolysis of ethyl acetate by NaOH is $6.36 \text{ lit mol}^{-1} \text{ min}^{-1}$ (1st and order reaction). Starting with 10 ml of base and ester of 0.02 moles/lit , what proportion of ester will be hydrolysed in 10 mins ? [Ans: 55%]

⑥

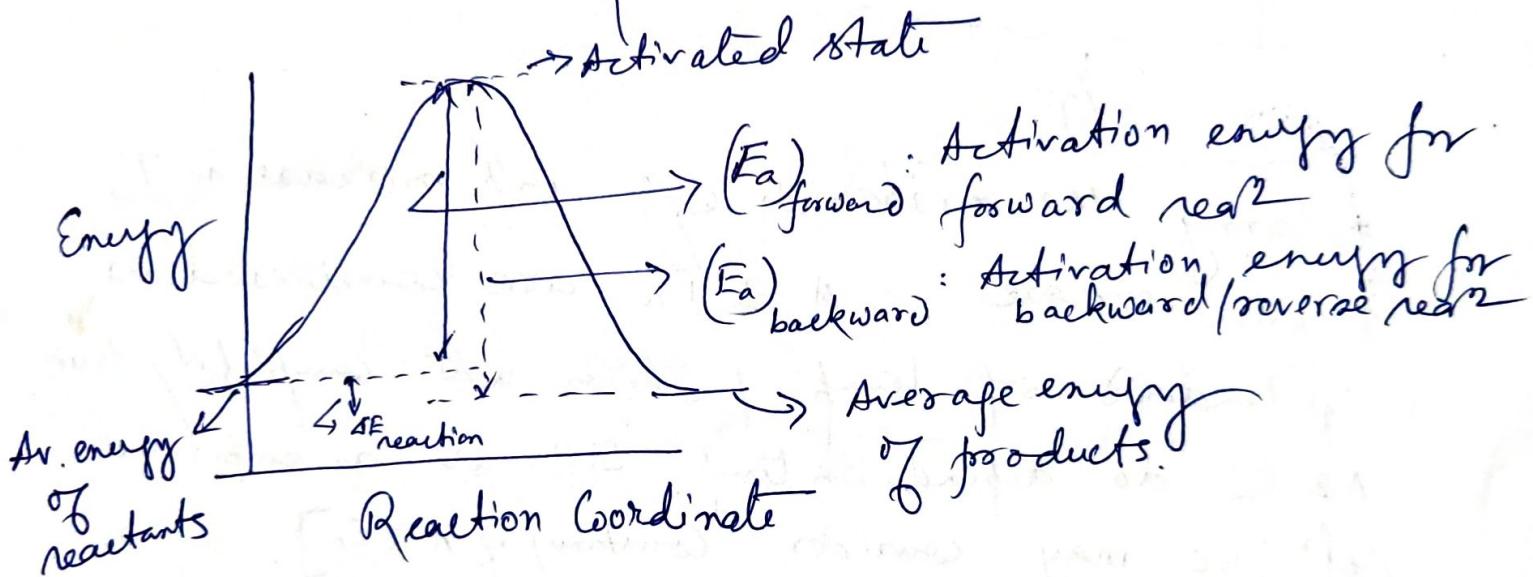
Effect of temperature on the rate of a reaction:

For all simple elementary reactions, rate of the reaction increases with temperature.

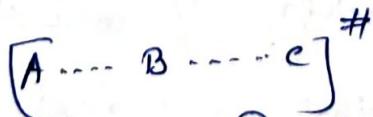
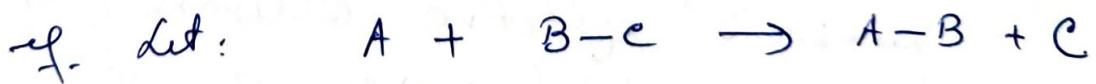
Arrhenius eqⁿ:

$$\text{Rate const}, k = A \cdot e^{-E_a/RT}$$

A: Pre-exponential factor, sometimes called as frequency factor.



Reaction coordinate: closeness of approach of reactants and products,



Activated state/transition state

Distance b/w A & BC and then A-B & C may be considered as reaction coordinate.

OR

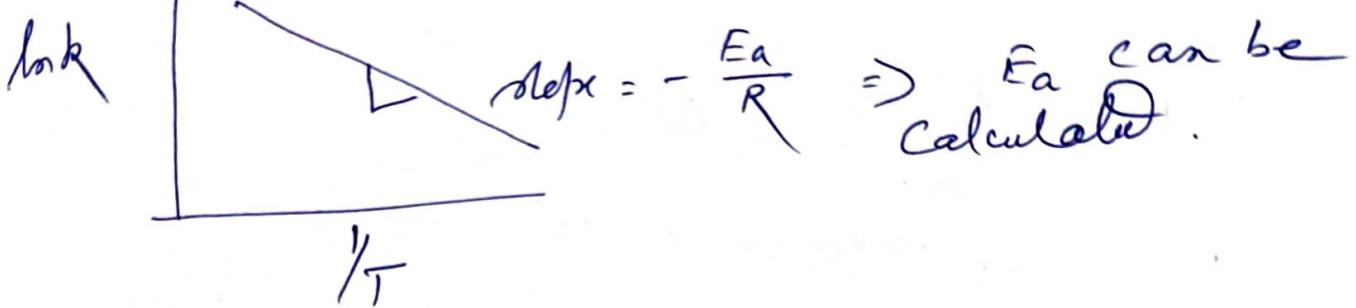


Here angle of rotation along c=c bond may be considered as the reaction coordinate.

$$\text{or, } \ln k = \ln A - \frac{E_a}{RT}$$

$$\therefore \left[\frac{\partial \ln k}{\partial T} \right]_P = - \frac{E_a}{RT^2}; \quad ; \quad \begin{aligned} E_a &= RT^2 \left(\frac{d \ln k}{dT} \right) \\ &= -R \cancel{\left(\frac{d \ln k}{d(T)} \right)} \end{aligned}$$

$\leftarrow \ln(A) \rightarrow$ From this intercept, A can be calculated



Following the Arrhenius eqn, with increase in T, k will increase. A & E_a are considered as independent of temp. [This is not completely true, A & E_a do depend on temp. Still, as an empirical ref], we may consider [constancy of A & E_a].

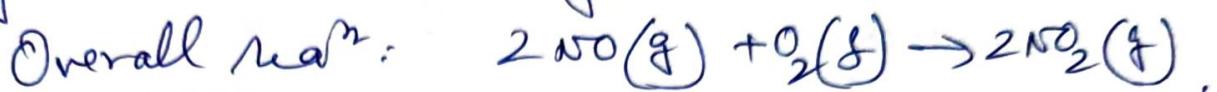
With increase in temp, average energy of colliding reactant molecules increases. Hence, number of effective collisions (those collisions for which total energy of colliding reactant molecules exceed the required activation energy) increases. As a result, rate of the reaction increases.

You should keep in mind that this explanation is over-simplified. Because, not only the number of effective collisions but also the specific orientation of colliding molecules is an important factor for reaction to proceed.

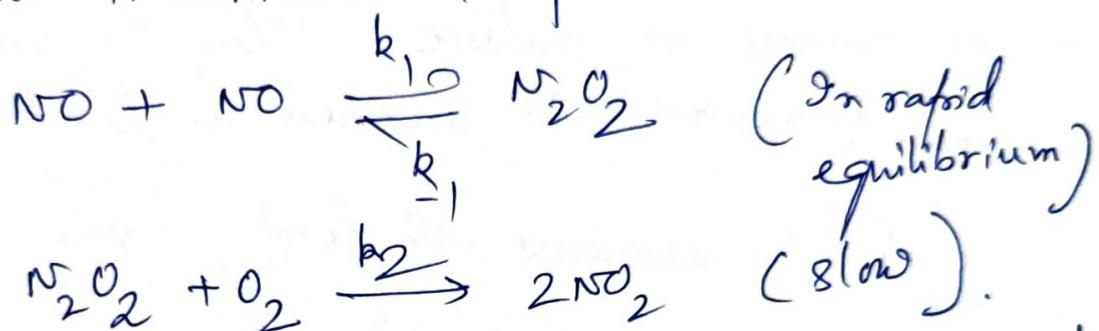
Though for the elementary reactions, rate increases w/ temp, this simple correlation may not be valid for multi-step complex reaction.

e.g., consider the reaction betw.

nitric oxide (NO) and oxygen (O_2) to produce nitrogen-di-oxide (NO_2) gas.



Here, the intermediate steps are:



As, in the second step the product is formed, we can write:

Rate of formation of the product:

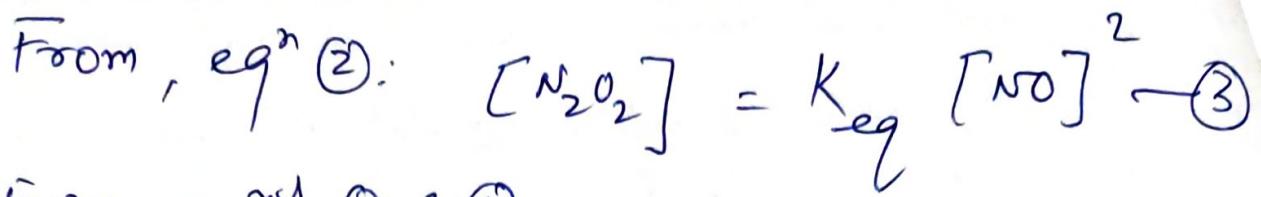
$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2 [\text{N}_2\text{O}_2] [\text{O}_2] \quad \text{--- (1)}$$

Now, N_2O_2 is an reactive intermediate. This term should be replaced either by reactant or product molecule concn.

For the first dimerisation eq^m rxn^r:

$$\text{Eq}^m \text{ const} \Rightarrow K_{\text{eq}} = \frac{k_1}{k_{-1}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad \text{--- (2)}$$

[Eq^m const is the ratio of forward and backward rate constant \Rightarrow we will prove it later]



From eq^{ns} ① & ③:

$$-\frac{1}{2} \frac{d[NO_2]}{dt} = k_2 K_{eq} [NO]^2 [O_2]$$

Thus, Overall reactⁿ is obeys the third order kinetics.

Now, the dimerisation reactⁿ (step 1) is exothermic in nature. Thus, the value of K_{eq} decreases with increase in temp.

Though k_2 increases with temp., the decrease in K_{eq} is sufficiently large to make the term ($k_2 K_{eq}$) to decrease with increase in temperature.

The temperature Coefficient of a reaction: It is defined as the ratio of the rate constants at two temperatures differing by $10^\circ C$. The two temperatures chosen usually are $25^\circ C$ & $35^\circ C$.

$$\frac{k}{T} = A \cdot e^{-E_a/RT}$$

$$\frac{k}{T+10} = A \cdot e^{-E_a/R(T+10)}$$

$$\frac{k}{T+10} = A \cdot e^{-E_a/RT+10}$$

$$\therefore \frac{\frac{k}{T+10}}{k_T} = e^{\frac{-10E_a}{RT(T+10)}}$$

If E_a is taken as 80 kJ mol^{-1} and $T = 298 \text{ K}$,

$$(T+10) = 308 \text{ K}, \text{ then:}$$

$$\frac{\frac{k}{T+10}}{k_T} = 2.85$$

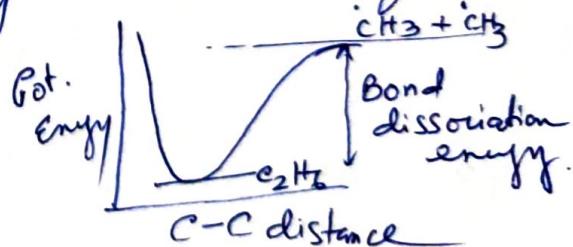
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

For most reactions, the temp coeff. lies betw. 2 and 3. i.e. rate of a redⁿ (elementary redⁿ) increases by a factor betw. 2 and 3 for $\times 10^\circ$ rise in temp at around 298 K.

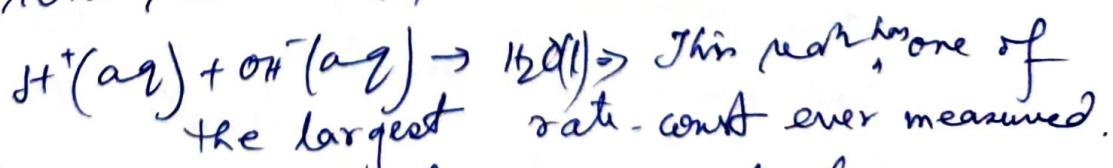
[Ans.]

There are certain special types of redⁿs which do occur with zero activation energy.

e.g. i) Combination of methyl radicals to form ethane. Here, no bond dissociation is involved.



ii) Some ionized redⁿ in so/n.



iii) Attachment of electrons to molecules (e^- transfer redⁿ)

iv) Some excited state redⁿs are also barrierless.

Problems

① Consider two reactions I & II. Frequency factor (A) of I is 100 times that of II. The activation energy of I is 4600 cal. higher than that of II. Show that at 227°C , the rate constants have very nearly the same value.

Sol/m:

$$\frac{k_I}{k_{II}} = \frac{A_I e^{-E_I/RT}}{A_{II} e^{-E_{II}/RT}}$$

$$; A_I = 100 A_{II} \\ E_I = E_{II} + 4600 \quad] \text{in cal.}$$

$$\therefore \frac{k_I}{k_{II}} = 100 \cdot e^{-\frac{4600}{R \times 500}}$$

$$[227^{\circ}\text{C} = 500\text{K}]$$

$$\ln \frac{k_I}{k_{II}} = \ln 100 - \frac{4600}{R \times 500} \\ \approx 0$$

$$\therefore k_I \approx k_{II}$$

② At 378.5°C , the $t_{1/2}$ for a 1st order thermal decomposition of ethylene oxide is 363 min and energy of activation is 52000 cal/mole. From these data, estimate the time required for ethylene oxide to be 75% decomposed at 450°C .

Sol/m: If k' is the rate const at 378.5°C , then as the reactn is 1st order, we know.

$$k = \frac{0.693}{t_{1/2}} ; k' = \frac{0.693}{363} \text{ min}^{-1} \\ = 1.91 \times 10^{-3} \text{ min}^{-1} \quad \text{at } 378.5^{\circ}\text{C}$$

Set k_2 is the rate const at 450°C . (7)

$$\left. \begin{array}{l} k_1 = A e^{-E_a/RT_1} \\ k_2 = A e^{-E_a/RT_2} \end{array} \right\} \begin{array}{l} k_1 \text{ is the rate const at } T_1 \\ k_2 \text{ - - - at } T_2 \\ \text{Assuming } A \text{ & } E_a \text{ are} \\ \text{independents of temp.} \end{array}$$

$$\ln k_1 = \ln A + \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\therefore \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\therefore \ln \left(\frac{k_2}{(1.91 \times 10^3)} \right) = \frac{52000}{1.987} \times \frac{71.5}{651.5 \times 723}$$

$$\therefore \frac{k_2}{k_1} = 0.101 \text{ min}^{-1}, \text{ i.e. rate const at } 450^\circ\text{C.}$$

$$R = \frac{1}{t} \ln \left(\frac{a}{a-x} \right) \leftarrow \text{1st order rate expression.}$$

$$(a-x) \Rightarrow \text{Amount of unreacted reactant} = \frac{1}{4}a$$

(as $\frac{3}{4}$ has reacted)

$$\therefore 0.101 = \frac{1}{t} \ln \frac{a}{(\frac{1}{4}a)}$$

$$\therefore t = 13.7 \text{ min.}$$

\therefore 13.7 mins will be required for 75% decomposition of ethylene oxide at 450°C .

③ A mechanism involving three elementary steps for a certain complex reaction, the respective rate constants being k_1 , k_2 & k_3 and the corresponding activation energies being E_1 , E_2 and E_3 . According to the mechanism, rate const for the overall reactⁿ (k) is $k = \frac{k_1 k_3}{k_2}$. Show that the activation energy (E) for the overall reactⁿ, $E = E_1 - E_2 + E_3$.

Solⁿ Given, $k = \frac{k_1 k_3}{k_2}$; $\ln k = \ln k_1 - \ln k_2 + \ln k_3$

Following Arrhenius eqn; $\ln k = \ln A - \frac{E}{RT}$

$$\therefore \ln A - \frac{E}{RT} = \ln \frac{A_1 A_3}{A_2} - \frac{1}{RT} (E_1 - E_2 + E_3)$$

Equating energy terms on both sides

$$E = (E_1 - E_2 + E_3)$$

T.H.W. Overall rate const for a complex reactⁿ is given by
 ④ $k = k_2 \left(\frac{k_1}{2k_3} \right)^{1/2}$ k_1, k_2 & $k_3 \Rightarrow$ rate constant of intermediate steps.

$$\text{Show that, overall activation energy } E = E_2 + \frac{1}{2} (E_1 - E_3)$$

⑤ A first order reactⁿ is 25% complete in 30 mins at 227°C and in 10 mins at 237°C . Find the energy of activation and the frequency (Pre-exponential) factor.

⑥