

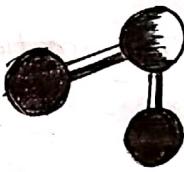
#2

Chemical Kinetics

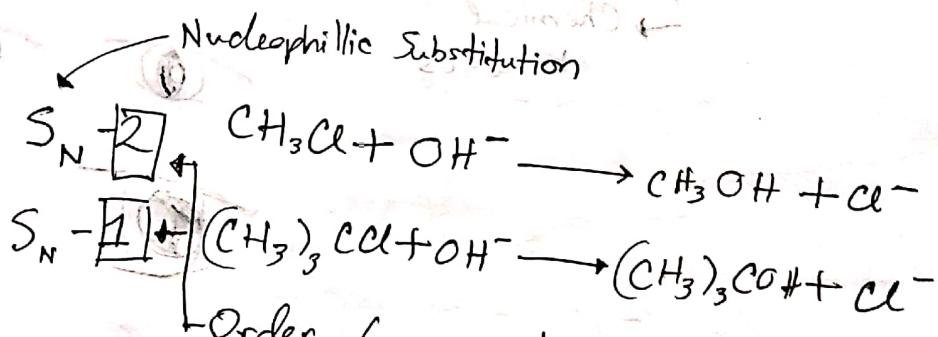
06-09-19
Friday

Chemical Kinetics: Factors influencing value.

- (i) Temperature
- (ii) P/V
- (iii) Catalyst
- (iv) Sound
- (v) $\text{h}\nu$
- (vi) Surface Area



Final objective of kinetics is to use the factors to find out the chemical mechanism.



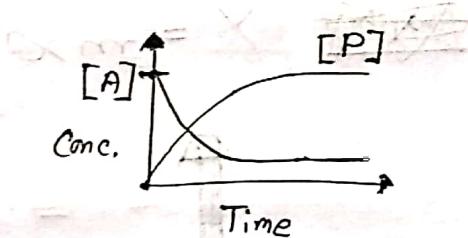
Order of a reaction shows the number of components which actively take part in a reaction.

Order: 0, 1, 2, 3, 4 (rarely).

Order 0: photosynthesis, catalytic reactions.

Terms

- i) Rate
- ii) Rate constant
- iii) Order
- iv) Molecularity



$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[P]}{dt}$$

→ Remember that order is an experimental paramental parameter but molecularity is a theoretical one. You can't derive the order from the reaction.



$$\text{Rate} = -\frac{1}{x} \cdot \frac{d[A]}{dt} = \frac{1}{y} \cdot \frac{d[P]}{dt}$$

Law of mass action:

$$\text{rate} \propto a_A^x \cdot a_B^y$$



$$\Rightarrow \text{rate} = k a_A^x \cdot a_B^y$$

(a means active mass)

$$\text{rate} = -\frac{1}{x} \frac{d[A]}{dt} = -\frac{1}{y} \frac{d[B]}{dt} = \frac{1}{m} \frac{d[C]}{dt} = \frac{1}{n} \frac{d[D]}{dt}$$

$$\text{Now, rate} = k [A]^x [B]^y = k [A]^x [B]^y$$

$$\Rightarrow \text{Let, } [A] = [B]$$

$$\therefore \text{rate} = k [A]^{x+y} = k [A]^n$$

↑ Rate constant

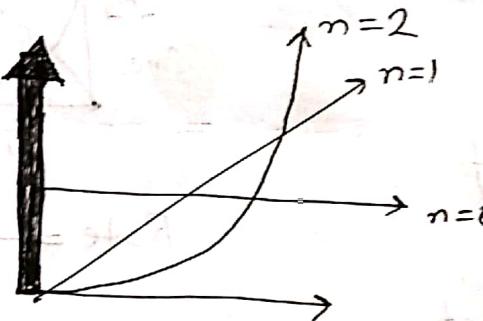
$$\text{rate} = k \cdot C^n$$

Assuming,

n represents the
order of the reaction.

Graph: ~~of time~~

$$Y = m x^n$$



Unit of k ?

$$\text{rate} = k C^n$$

$$\Rightarrow \frac{\text{Conc}}{\text{time}} = k \cdot \text{conc}^n$$

$$\Rightarrow k = \text{conc}^{1-n} / \text{time}$$

For $n = 0$, $k = \text{Ms}^{-1}$ (M means mol/dm³)

$$n = 1, k = \text{s}^{-1}$$

$$n = 2, k = \text{M}^{-1}\text{s}^{-1}$$

$$n = 3, k = \text{M}^{-2}\text{s}^{-1}$$

$$[E] = [E_0] + \nu t$$



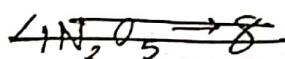
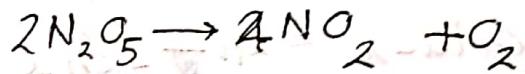
$$\text{rate} = k[A]^x[B]^y$$

$$= k[A]^{x+y}$$

~~Rate~~ = $k \cdot C^n$ → Molar conc.

Quiz-3

20-07-19 (Next Friday)
chemical bond + Molecular Orbital theory
and Applications



First Order Reaction

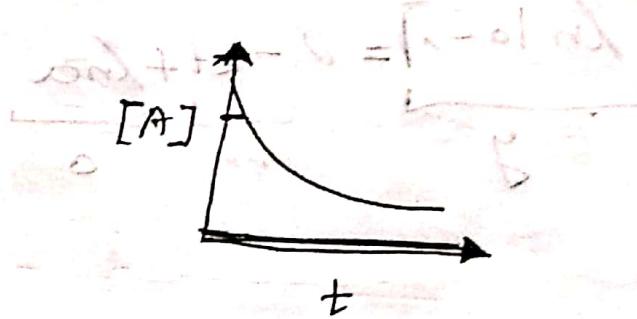


Let, at $t = 0$, 'a' moles

$t = t$, $(a-x)$ moles

0 moles

~~x~~ moles



Applying Law of Mass action:

$$\text{rate} = -\frac{d(a-x)}{dt} = k_1(a-x)$$

$$\Rightarrow \frac{dx}{dt} = k_1(a-x) \Rightarrow -\frac{dx}{a-x} = k_1 dt$$



Integrating, we get,

$$\int \frac{dx}{a-x} = \int k_1 dt$$

$$\Rightarrow -\ln|a-x| = kt + c$$

When, $t=0, x=0$

$$\Rightarrow -\ln|a| = c$$

So, $-\ln|a-x| = kt - \ln a$

$$\Rightarrow \ln \frac{a-x}{a} = -kt$$

$$\Rightarrow \frac{a-x}{a} = e^{-kt}$$

$$\Rightarrow a-x = a \cdot e^{-kt}$$

Kinetic equation for
First order reaction

$$\ln|a-x| = \theta - kt + \ln a$$

y

mx

c

Kinetic equation for First Order
Reaction in the form of
integral factors

Re-arranging,

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x} \quad [k_1 = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}]$$

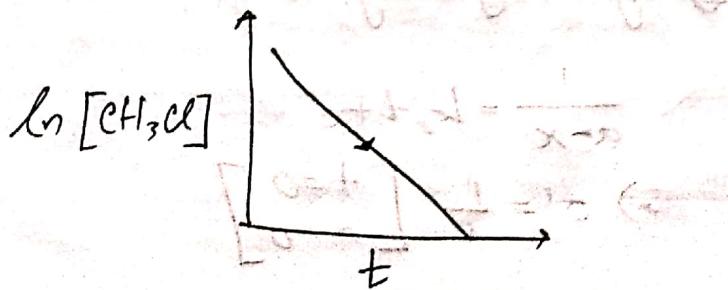
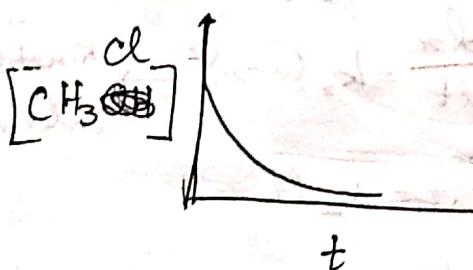
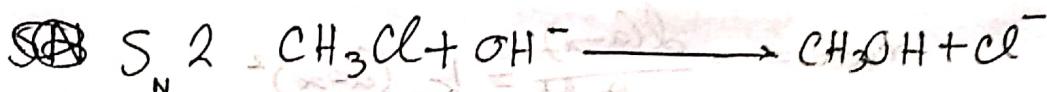
Test for first order reaction,

- i) Integral method
- ii) Graphical method
- iii) Half-life method

$$\textcircled{1} \quad t = \frac{1}{k_1} \ln \frac{a}{a-x}$$

$$t_{1/2} = \frac{1}{k_1} \ln \frac{a}{a-a/2} = \frac{\ln 2}{k_1} = \text{const.}$$

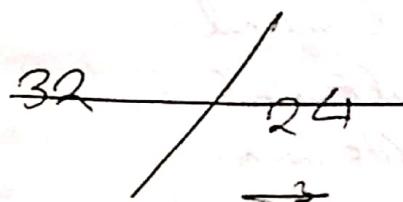
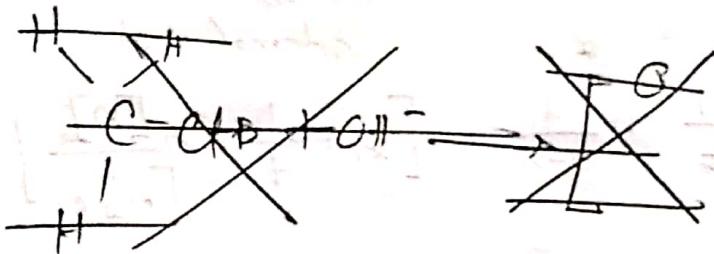
A first order ~~reac~~ reaction is never complete.



#4

Second Order Reaction

13-09-19
Friday



Second order reaction:



Let, at $t=0$, "a" moles | 0' moles

at ~~at~~ $t=t$, $a-x$ moles | x moles

Applying law of mass action,

$$\text{rate} = -\frac{d(a-x)}{dt} = k_2 (a-x)^2$$

$$\Rightarrow \frac{dx}{dt} = k_2 (a-x)^2 \rightarrow \text{Kinetic eqn. for 2nd order reaction in diff form.}$$

$$\Rightarrow \frac{dx}{(a-x)^2} = k_2 dt$$

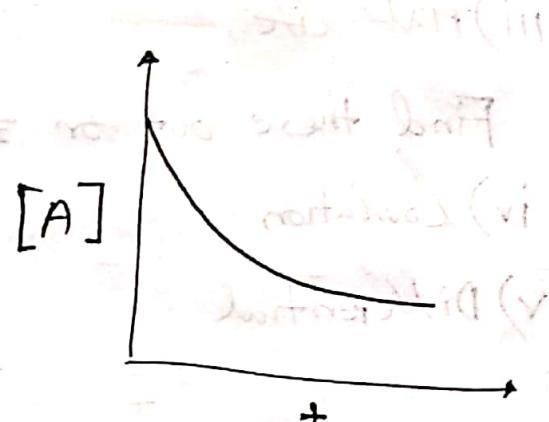
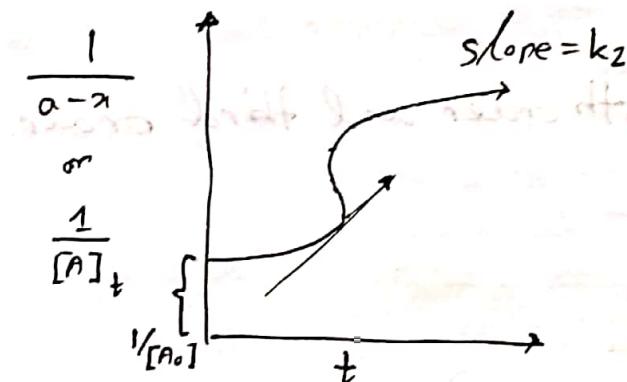
⇒ By integrating, we get,

$$\frac{1}{a-x} = k_2 t + c'$$

$$\Rightarrow c' = \frac{1}{a} \left[\begin{matrix} t=0 \\ a=0 \end{matrix} \right]$$

$$\Rightarrow \frac{1}{a-x} = k_2 t + \frac{1}{a}$$

$$\Rightarrow \frac{1}{[A]_t} = k_2 t + \frac{1}{[A]_0} \rightarrow \text{Kinetic equation for a second order reaction in linear form}$$



Applied examples:

$$\text{Intercept} = 5 \times 10^3 \text{ (say)}$$

Caution: $\frac{1}{[A]_0}$ is the intercept, not $[A]_0$

(I'm not sure about it, check back's examples)

Rearranging, we get,

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} \rightarrow \text{In intercept form}$$

Tests for Second Order

i) Integral method $k_c = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

ii) Graphically

$$\boxed{iii) \text{ Half-life} \quad t_{1/2} = \frac{1}{k_2} \cdot \frac{a/2}{a(a-x_2)} = \frac{1}{k_2} \cdot \frac{1}{a} = \frac{1}{k_2 [A]_0}}$$

$$\Rightarrow t_{1/2} \propto \frac{1}{[A]_0}$$

Methods to determine order

i) Integral

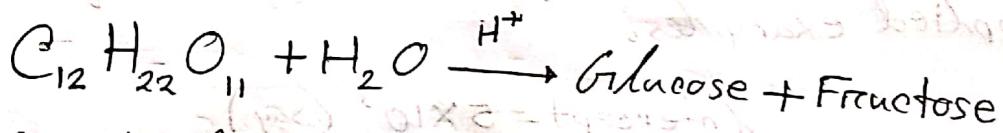
ii) Graphical

iii) Half-life

Find these out for zeroth order and third order

iv) Isolation

v) Differential

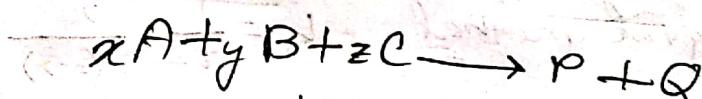


→ The rate doesn't depend on the concentration of catalyst, $[H^+]$.

rate $\propto [C_{12}H_{22}O_{11}]$

Through method of isolation (calculating rate for a single reagent) we find out that rate is only proportional to the concentration of sugar.

For example

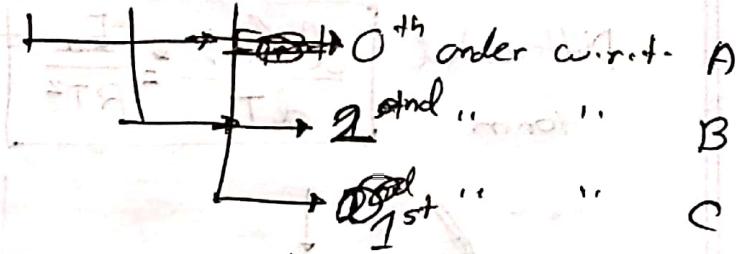


Hypothetically, rate $\propto [A]^x [B]^y [C]^z$

In order to isolate, we take excess of each reagent.

After isolation, for instance, we get,

$$\text{rate} = [A]^0 [B]^2 [C]^1 \quad n=0+2+1$$

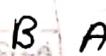


$$n = 0 + 2 + 1 = 3$$

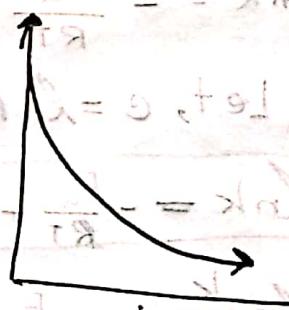
Hence, third order reaction

Differential

$$\text{rate} = k \cdot C^n$$



$$\ln r = \ln k + n \ln C$$



$$\text{conc. } A = 9 + 9t$$

$$\Delta E - \Delta E = \Delta \Delta E$$

$$\Delta E < \Delta E$$

$$(E_1 - E_2) = \Delta \Delta E$$

ln r

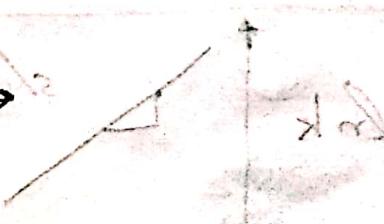
ln k

slope = n = order

$$\frac{\ln r}{t} = \frac{1}{k} + \frac{n}{k} \cdot \frac{\ln C}{t}$$

ln C

We find order through slope.



#5

Relationship between temperature and rate constant

19-09-19

Thursday

The dependency is exponential.

Arrhenius Equation:

Differential form

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Defⁿ of activation energy

[The minimum energy required for any reaction to take place.]



Derived from
thermodynamics

$$\Rightarrow d \ln k = \frac{E_a}{RT^2} dT$$

$$\Rightarrow \ln k = \frac{E_a}{R} \left(-\frac{1}{T} \right) + C \quad [\text{Integrating}]$$

$$\Rightarrow \ln k = -\frac{E_a}{RT} + C$$

Let, $C = \ln A \rightarrow$ [Arrhenius Parameter or Frequency Number]

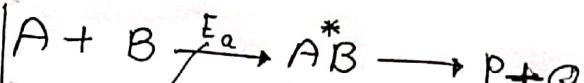
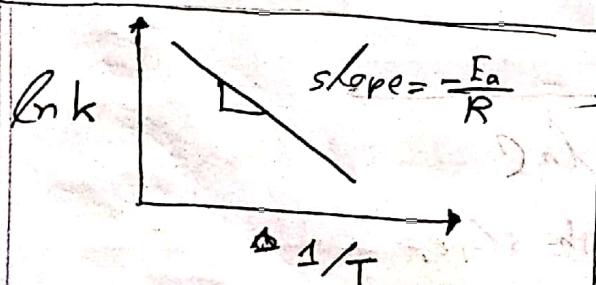
$$\Rightarrow \ln k = -\frac{E_a}{RT} + \ln A$$

$$\Rightarrow \ln \frac{k}{A} = -\frac{E_a}{RT}$$

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

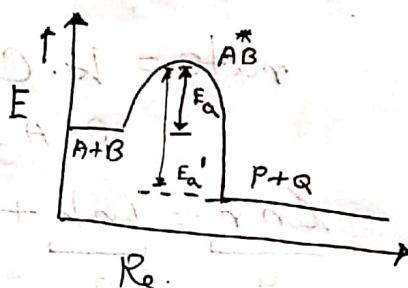
$$\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

$$y = m \cdot x + c$$



Deactivated
Complex

E_a is required to reach
deactivated complex

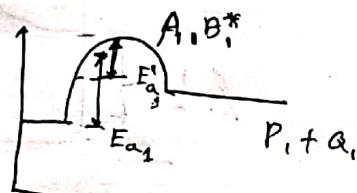


$$\Delta E = E_a - E_a'$$

But, $E_a > E_a'$

$$\therefore \Delta E = (-ve)$$

Hence, exothermic.

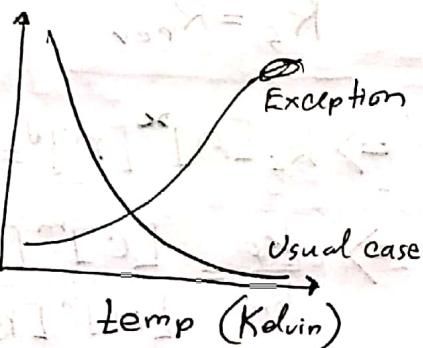


$$\Delta E_1 = E_{a_1} - E_{a_1'}$$

But, $E_{a_1} > E_{a_1'}$

$$\therefore \Delta E = (+ve), \text{ endothermic}$$

→ Catalyst doesn't increase the kinetic energy of a reaction.
It only changes the activation energy making the reaction faster or slower.



Case-I $E_a - k$ [E_a constant]

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

$$\Rightarrow k = \frac{A}{e^{\frac{E_a}{RT}}}$$

$$k \propto \frac{1}{e^{\frac{E_a}{RT}}}$$

E_a large then $e^{\frac{E_a}{RT}}$ large.
then Reaction ~~is~~ slower.

$\uparrow E_a \rightarrow \uparrow e^{\frac{E_a}{RT}} \rightarrow \downarrow k$ (slower)
and vice-versa

$\downarrow E_a \rightarrow \downarrow e^{\frac{E_a}{RT}} \rightarrow \uparrow k$ (faster)

Case-II $T - k$ [$E_a = \text{constant}$]

$$k = \frac{A}{e^{\frac{E_a}{RT}}}$$

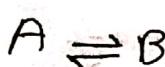
$$k \propto \frac{1}{e^{\frac{E_a}{RT}}}$$

$T \downarrow, e^{\frac{E_a}{RT}} \uparrow, k \downarrow$ (slower)

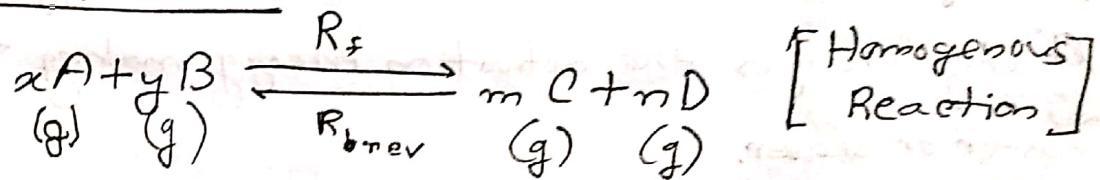
$T \uparrow, e^{\frac{E_a}{RT}} \downarrow, k \uparrow$ (faster)

Kinetics of : (i) Reversible Reaction / Reaction at Equilibrium

(ii) Consecutive Reaction



Chemical Equilibrium



$$R_f = R_{\text{rev}}$$

$$\Rightarrow k_f [A]^x [B]^y = k_m [C]^m [D]^n$$

$$\Rightarrow \frac{k_f}{k_m} = \frac{[C]^m [D]^n}{[A]^x [B]^y} = k_{\text{eq}}$$

$$\text{with } k_{\text{eq}} \rightarrow [P_i, t_i, \text{cat}]$$

$$k_c = \frac{C_c^m C_d^n}{C_a^x C_b^y}$$

$$k_p = \frac{P_c^m P_d^n}{P_a^x P_b^y}$$

$$PV = nRT$$

$$\Rightarrow P = \frac{n}{V} RT = CRT$$

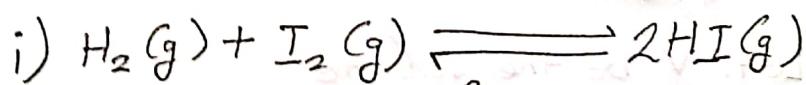
$$k_p = \frac{P_c^m P_d^n}{P_a^x P_b^y}$$

$$= \frac{(CRT)^m (CRT)^n}{(CRT)^x (CRT)^y}$$

$$= \frac{C_c^m C_d^n}{C_a^x C_b^y} \times (RT)^{m+n-x-y}$$

$$\therefore k_p = k_c \cdot (RT)^{\Delta n}$$

Computation of 'K'



$$\Delta n = 0, K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Let, at $t=0$, we have (initially)

$$H_2 = a \text{ moles}$$

$$I_2 = b \text{ moles}$$

$$HI = 0 \text{ moles}$$

And, at equilibrium, let ' x ' moles are produced in the reaction.
We have,

$$H_2 = (a-x) \text{ moles}$$

$$I_2 = (b-x) \text{ moles}$$

$$HI = 2x \text{ moles}$$

Let, total pressure be P .

$$i) P_{H_2} = X_{H_2} \cdot P = \frac{n_{H_2}}{n_{\text{Total}}} \times P$$

$$= \frac{a-x}{a-x+b-x+2x} \times P$$

$$= \frac{a-x}{a+b} \times P \text{ moles}$$

$$\text{ii) } P_{I_2} = \frac{b-x}{a+b} \times p$$

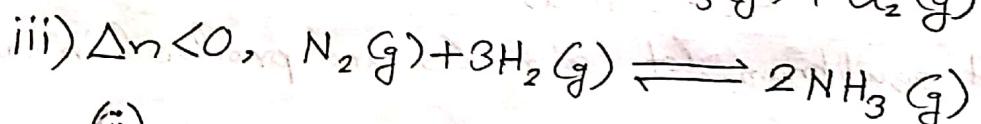
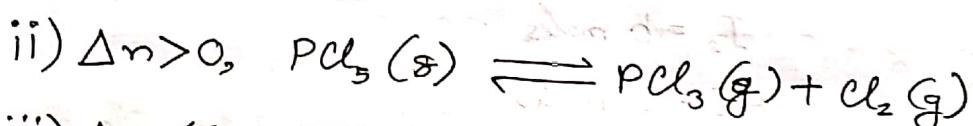
$$\text{iii) } P_{HI} = \frac{2x}{a+b} \times p$$

Let, V be the volume.

$$[HI] = \frac{2x}{V}; [I_2] = \frac{b-x}{V}; [H_2] = \frac{a-x}{V}$$

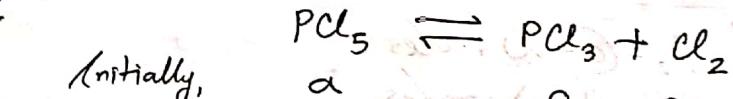
$$\Rightarrow K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{4x^2/V}{(a-x)(b-x)/V^2} = \frac{4x^2}{(a-x)(b-x)}$$

For $\Delta n = 0$, the effect of pressure and temperature is irrelevant.



(ii)

Initially,



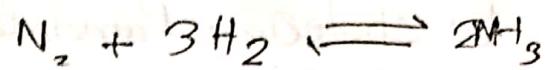
At equilibrium, $a-x$

$$K_p = \frac{\left(\frac{x}{a-x} \times p\right) \times \left(\frac{x}{a-x} \times p\right)}{\frac{a-x}{a+x} \times p}$$

$$= \frac{x^2}{a^2 - x^2} \times p$$

For $\Delta n > 0$, the pressure applied is directly proportional to ~~pressure applied~~.

(iii)



a	3a	0	Total = $3a - 3x + 2x$
$a-x$	$3a-3x$	$2x$	$= 3a-x$

$$K_p = \frac{\frac{2x}{3a-x} \times P}{\frac{3(a-x)}{3a-x} \times \frac{2x}{3a-x} \times P^2}$$

$$= \frac{3a-x}{3a-3x} \times \frac{1}{P}$$

For, $\Delta n < 0$, K_p is inversely proportional to applied pressure.

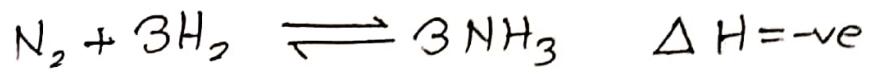
Le Chatelier Principle

→ Check the Principle from the book. (Defn.)

- ⇒ i) Change of P/V
- ii) Change of conc.
- iii) Catalyst (No effect)
- iv) Temperature Exothermic $T \uparrow \quad \downarrow R$
 $T \downarrow \quad \uparrow R$

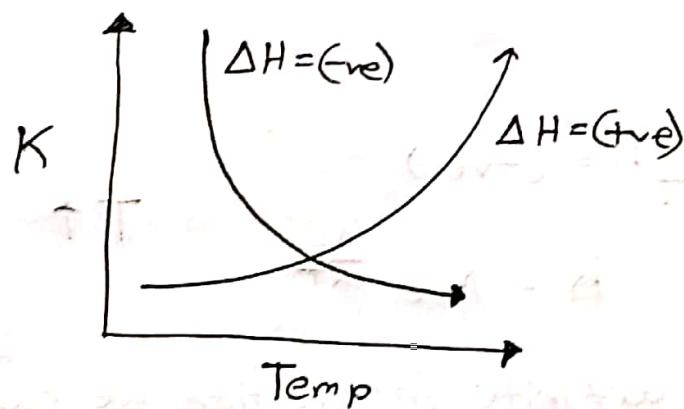
Catalyst doesn't increase kinetic energy, temperature only affects the kinetic energy of molecules.

For $n > 0$, i.e. the number of mole of products are greater than that of reactants. Since the volume of a gas is directly proportional to its mole number, the volume of products is greater than that of reactants. So, for $n > 0$, forward reaction increases volume. Pressure tries to decrease volume.



Since, it is exothermic, the reaction should be carried out at a lower temperature. Hence, it is carried out at 450°C.

450°C might seem too high to us but this figure is relative. For this reaction, 450°C is optimum as it provides the necessary kinetic energy for the reaction to take place and also maximize output through Le Chatelier's Principle.



Relationship between 'K' and 'Temp'

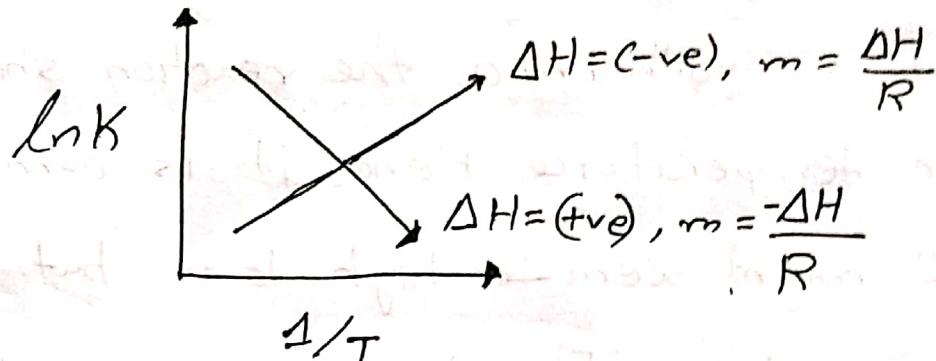
$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$

$$\Rightarrow d\ln K = \frac{\Delta H}{RT^2} dT \Rightarrow \int d\ln K = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\Rightarrow \ln K = -\frac{\Delta H}{RT} + \ln A$$

ΔH isn't independent to temperature. But as we have taken a small interval of time, dT ; ΔH can be considered constant.

$$\Rightarrow K = A e^{-\frac{\Delta H}{RT}}$$



i) If, $\Delta H = (+ve)$

$$K = \frac{N}{e^{\Delta H/RT}} \quad T \uparrow e^{\Delta H/RT} \downarrow K \uparrow$$

and vice-versa

and,

(ii) If, $\Delta H = (-ve)$

$$K = N e^{\frac{\Delta H}{RT}} \quad T \uparrow e^{\Delta H/RT} \downarrow K \downarrow$$

Through definite integration, we can derive,

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Class Test

Syllabus