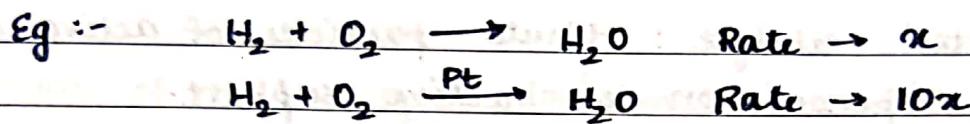


Catalysis and Catalytic Reactors

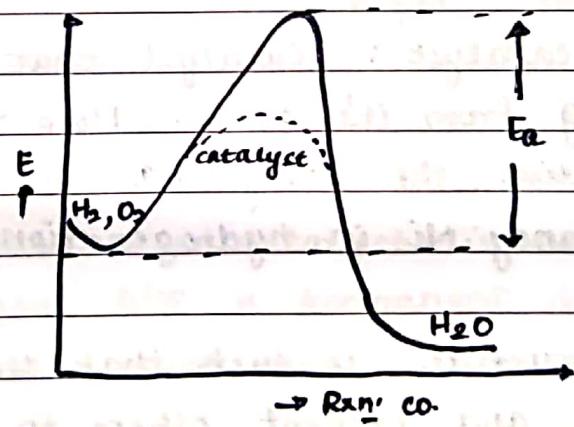
Catalyst is a reagent which either accelerates or retards a chemical reaction without being consumed or converted.

A catalyst usually changes a rxn. rate by promoting a different molecular path for the rxn.



A catalyst changes only the rate of rxn. of, it doesn't affect equilibrium. It lowers the activation energy of a rxn.

Catalysis is the occurrence, study and use of catalysts and catalytic processes.



Heterogeneous catalytic processes involve more than one phase; usually the catalyst is a solid and the reactants and products are in liquid or gaseous form.

Advantages of Heterogeneous catalysts :

- Simple and complete sep. of solid catalysts from rxn: medium
- Separation of catalysts makes the process economic as no wastage of valuable catalysts
- Separation makes the reuse of catalysts possible.

Supported catalyst : Minute particles of active catalyst are dispersed on less active support.

Eg :- Pt on alumina ($\text{Pt}/\text{Al}_2\text{O}_3$) , V_2O_5 on silica

Unsupported catalyst : No support is required, the material is as a whole a catalyst with similar activity throughout its area.

Eg :- Silica-Alumina in dehydrogenation rxn for butadiene prep.

Porous catalyst : Catalyst that has a large area resulting from its pores. More the surface area, more active, the catalyst (as rxn occurs on the surface)

Eg :- Raney Ni in hydrogenation of fats.

Pore structure is such that they allow some molecules and prevent others to enter into pores of catalyst, this way they act as sieves.

Note:-

- Heterogeneous catalytic rxn occurs at fluid solid interface. A porous catalyst has larger surface area resulting from its non-porous catalyst. Note all catalysts need the extended surface provided by a porous structure, some are suff. active.
- Most of the catalysts don't maintain their activity at same level for indefinite period of time, they get deactivated either slowly or rapidly. Deactivation may be caused by ageing phenomenon.

Gas Phase Solid Catalytic Rxn:

Gas phase solid catalytic rxn needs the reactants to attach to the surface of catalyst, this attachment is called adsorption.

Physical adsorption : Force of attraction between the gas molecules and solid catalyst is weak, either van der waal type, b/w a permanent dipole and an induced dipole or neutral atom or molecule. $\Delta H = -1 - 15 \text{ kcal/gmol}$

Chemical adsorption : Force of attraction is strong, (valence bond type force). Electronic structure of reactant molecules are distributed significantly, making them extremely active i.e $\Delta H = 10 - 100 \text{ kcal/gmol}$

The rxn isn't catalyzed by the entire solid surface. Adsorption of reactant molecules occurs on specific active centers or sites on the catalyst surface. The active surfaces originate from surface irreg, dislocations, edges, cracks. So active centers on the catalyst surface are able to make strong bonds.

Turnover frequency : It is the parameter to quantit catalyst activity. It is the no. of molecules reacting per active sites per second at the experimental cond.

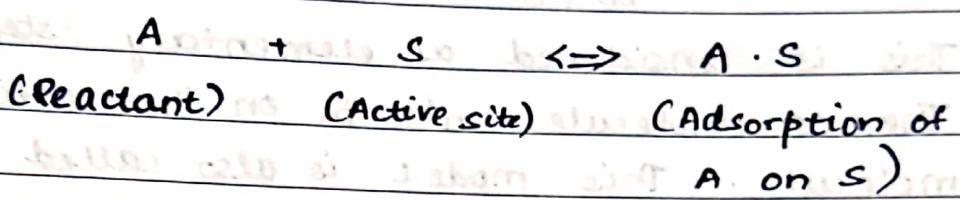
Dispersion of Catalyst : Fraction of metal ions present on the surface of catalyst.

Steps in a solid catalytic gas phase rxn:
(Porous)

Diffusion of react. from bulk to external surface of catalyst pellet. Diffusion of reactant from ext. surface to internal pore surface through the catalyst pore. Adsorption of reactant on the internal surface. Rxn. on surface to form pdt. Desorption of the pdt. from the surface. Diffusion of pdt. from internal surface of pore to external surface of catalyst. Mass transfer of pdt from catalyst external surface to bulk.

- The overall rate of the r_n' is equal to the rate of slowest step of r_n .
- Mass transfer/diffusion don't affect r_n' rate. Chemical r_n' step will be the rate limiting step. When rate of chemical r_n' is $>$ adsorption step, then rate limiting step may be the slowest step among them.

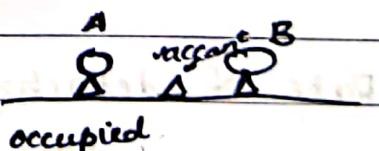
Absorption on active sites:



$C_t \rightarrow$ Total number of active site/unit mass of catalyst / Avg. no. = Total molar conc. of active sites (mol/g of catalyst)

$C_v \rightarrow$ Total no. of vacant sites/ unit mass of catalyst / Avg. no. = Total molar conc. of vacant sites (mol/g)

Similarly, total molar conc. of occupied sites can be expressed. In the absence of catalyst deactivation, total molar conc. of active sites is assumed to remain const.

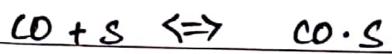


$$C_t = C_v + C_A \cdot S + C_B \cdot S$$

P_i - Partial pressure in gas phase

Consider adsorption of a non-reacting gas on surface of catalyst, it is reported in the form of adsorption isotherm (Adsorption curve formed by data of amt. of gas adsorbed on a solid surface at diff. pressures but at single temp.)

Molecular adsorption



This is considered as elementary step.

The CO molecule adsorbs on the active site as a molecule. This model is also called non-dissociative adsorption.

Rate of attachment is prop. to,

- ① No. of collisions of molecules making per sec
[No. of collisions/sec \propto P_{CO}]
- ② Conc. of vacant sites of catalysts (C_v)

$$\text{Rate of attachment} \propto C_v P_{CO}$$

$$\therefore \text{Rate of attachment} = k_A C_v P_{CO}$$

\hookrightarrow Adsorption rate const.

Rate of detachment \propto Conc. of occupied sites ($C_{CO \cdot S}$)

$$\therefore \text{Rate of detachment} = k_A C_{CO \cdot S}$$

∴ Overall, rate of adsorption

$$r_{AD} = k_A P_{CO} C_v - k_{-A} C_{CO \cdot s}$$

Let $K_A = \frac{k_A}{k_{-A}}$, adsorption eq. const.

$$r_{AD} = k_A \left(P_{CO} C_v - \frac{C_{CO \cdot s}}{K_A} \right)$$

At eq., rate of attachment = rate of detachment

$$P_{CO} C_v = \frac{C_{CO \cdot s}}{K_A}, C_{CO \cdot s} = K_A P_{CO} C_v$$

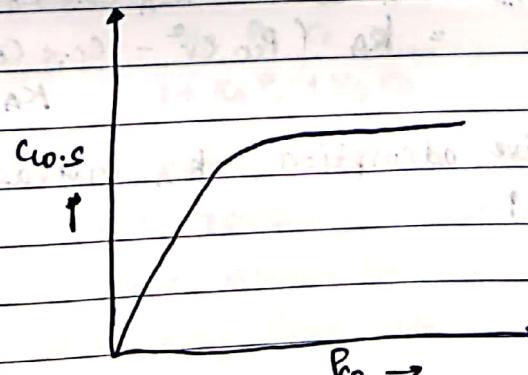
$$C_v = \frac{C_{CO \cdot s}}{K_A P_{CO}}$$

Consider site balance, $C_t = C_v + C_{CO \cdot s}$

$$C_{CO \cdot s} = K_A P_{CO} (C_t - C_{CO \cdot s})$$

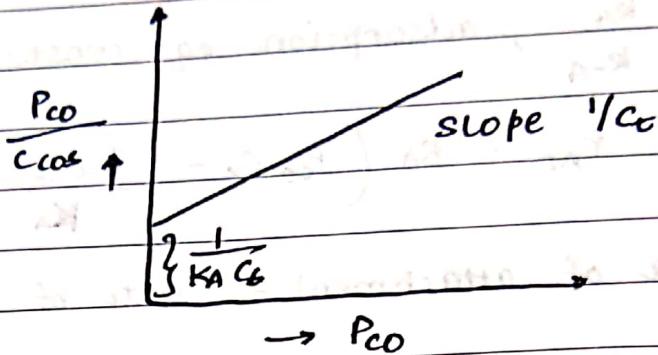
$$C_{CO \cdot s} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}} \quad \text{①}$$

This relation b/w conc. of occupied sites with partial pressure of gas is called Langmuir Adsorption Isotherm.



From ①,

$$\frac{P_{CO}}{C_{CO \cdot S}} = \frac{1}{K_A \cdot C_s} + \frac{P_{CO}}{C_s}$$



Dissociative Adsorption



Rate of attachment $\propto P_i$ of gass and square of vacant sites adjacent to each other

$$\text{Rate of attachment} = k_A P_{CO} C_v^2$$

Rate of detachment of two adjacent occupied sites

$$\text{Rate of detachment} = k_A C_{CS} C_{OS}$$

Total rate of adsorption,

$$\begin{aligned} r_{AD} &= k_A P_{CO} C_v^2 - k_A C_{CS} C_{OS} \\ &= k_A \left(P_{CO} C_v^2 - \frac{C_{CS} C_{OS}}{k_A} \right) \end{aligned}$$

For dissociative adsorption, k_A increases with $T \uparrow$ so $K_A \downarrow$ with $T \uparrow$

At eq., $P_{CO} C_r^2 = \frac{C_{O.S} C_{O.S}}{K_A}$

If $C_{O.S} = C_{O.R}$, $P_{CO} C_r^2 K_A = C_{O.R}^2$

$$\therefore C_{O.R} = (P_{CO} K_A)^{1/2} C_r$$

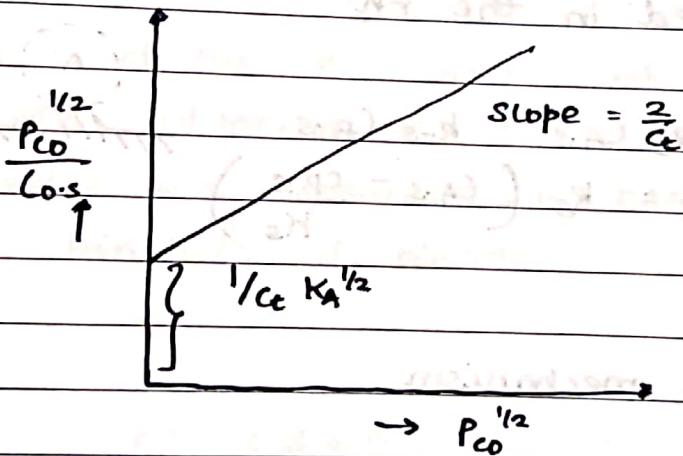
For site balance, $C_t = C_r + C_{O.S} + C_{O.R}$ or $C_t = C_t - 2 C_{O.S}$

$$C_{O.S} = (P_{CO} K_A)^{1/2} (C_t - 2 C_{O.S})$$

$$\therefore C_{O.S} = \frac{C_t (P_{CO} K_A)^{1/2}}{1 + 2 (P_{CO} K_A)^{1/2}}$$

Linearising,

$$\frac{1}{C_{O.S}} = \frac{1}{C_t (P_{CO} K_A)^{1/2}} + \frac{2}{C_t} \frac{1}{C_{O.S}}$$



When more than 1 molecule is present, say A, B,

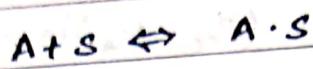
A (ad) B + (ad)

$$C_{O.S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B}$$

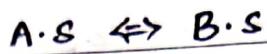
All the time, a uniform surface is assumed in deriving Langmuir Isotherm. This means any active site has the same attraction for an impinging molecule as does any other site.

Surface Reaction

Consider a chemical rxn: $A + B \rightarrow C + D$



Then m: step on solid catalyst surface,



If the m: is $A + B \rightleftharpoons C + D$,

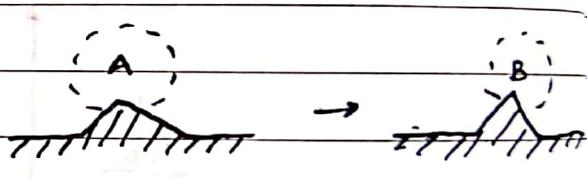


Single site mechanism

The surface m: may be a single site mech. where the single site on which the reactant is adsorbed is involved in the rxn:

$$r_s = k_s C_{A \cdot S} - k_{-s} C_{B \cdot S}$$

$$\therefore r_s = k_s \left(C_{A \cdot S} - \frac{C_{B \cdot S}}{k_s} \right)$$



Dual site mechanism

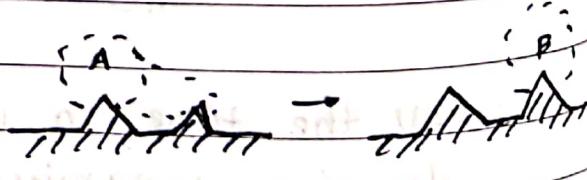
In this mechanism, the adsorbed molecule in one site may interact with an adjacent vacant or occupied site to form pdt.

Case 1:

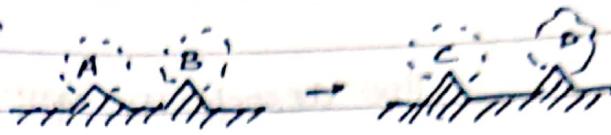
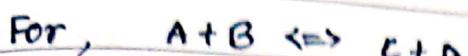


$$r_s = k_s C_{A \cdot S} C_V - k_{-s} C_{B \cdot S} C_V$$

$$= k_s \left(C_{A \cdot S} C_V - \frac{C_{B \cdot S} C_V}{k_s} \right)$$

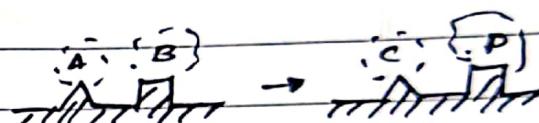
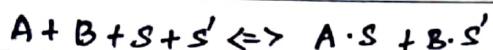


Case 2:



$$\begin{aligned} r_A &= k_s (c_{A \cdot S} c_{B \cdot S} - k_s c_{C \cdot S} c_{D \cdot S}) \\ &= k_s (c_{A \cdot S} c_{B \cdot S} - \frac{c_{C \cdot S} c_{D \cdot S}}{k_s}) \end{aligned}$$

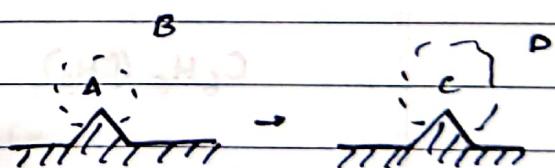
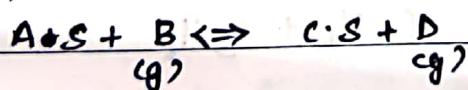
Case 3: Consider two reactants are adsorbed on two diff. types of active sites,



$$r_s = k_s (c_{A \cdot S} c_{B \cdot S'} - \frac{c_{C \cdot S} c_{D \cdot S'}}{k_s})$$

The kinetics of the rxn where all reactants and products are adsorbed on active sites either by single or dual site mechanism is named as Langmuir - Hinshelwood kinetics

Case 4: The rxn is



$$r_s = k_s (c_{A \cdot S} P_B - \frac{c_{C \cdot S} P_D}{k_s})$$

The rate kinetics is called Eley - Rideal kinetics

Desorption

The desorption eqn is,



Desorption rate eqn, $r_D = k_D \left(C_{c,s} - \frac{C_v P_c}{K_{Dc}} \right)$

K_{Dc} is desorption eq. const. of C

Rate of desorption = - Rate of adsorption

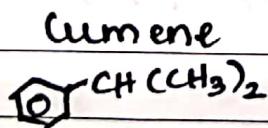
$$r_D = r_{AD}$$

$$K_{Dc} = \frac{1 + 21}{K_c}$$

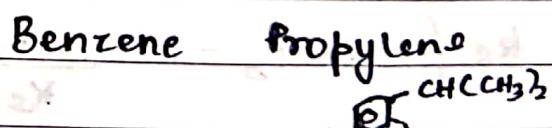
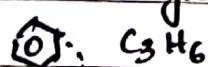
Synthesising a Rate law, Mechanism and Rate Limiting step.

We aren't considering any mass transfer step.

Only three steps, adsorption, surface m⁺ and desorption



Cumene in gas phase

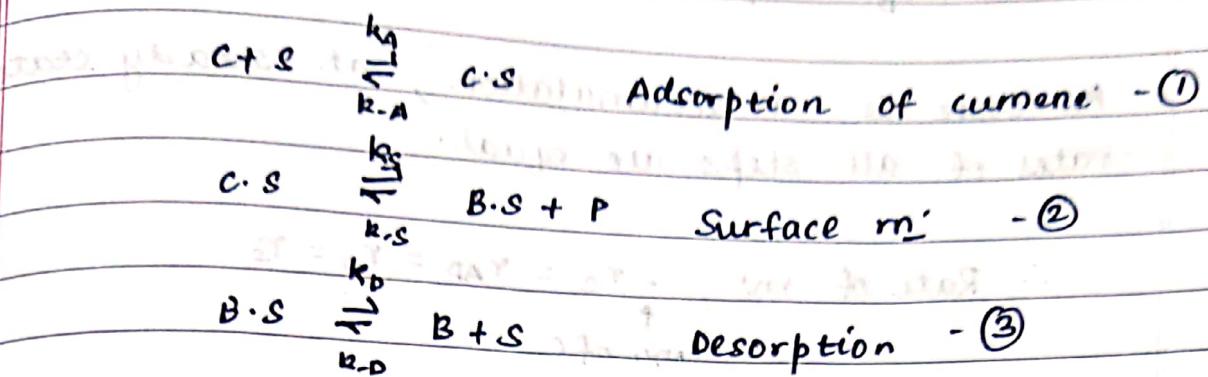


Absorption of cumene



Desorption

The rxn involved,



For (1),

$$\begin{aligned}
 r_{AD} &= k_A P_C C_V - k_A C_{C \cdot S} \\
 &= k_A \left(P_C C_V - \frac{C_{C \cdot S}}{K_{AD}} \right)
 \end{aligned}$$

$[r_{AD}] \rightarrow \text{mol/gs}$

$[C_{C \cdot S}] \rightarrow \text{mol of C/g}$

$[k_A] \rightarrow (\text{kPa} \cdot \text{s})^{-1}$

$[k_A] \rightarrow \text{s}^{-1}$

$[K_{AD}] = \text{atm}^{-1}$

For (2),

$$\begin{aligned}
 r_S &= k_S C_{A \cdot S} - k_S C_{B \cdot S} P_P \\
 &= k_S \left(C_{A \cdot S} - \frac{C_{B \cdot S} P_P}{K_S} \right)
 \end{aligned}$$

For (3),

$$\begin{aligned}
 r_D &= k_D C_{B \cdot S} - k_D P_B C_V \\
 &= k_D \left(C_{B \cdot S} - \frac{C_V P_B}{K_D} \right)
 \end{aligned}$$

As WKT,

$$K_B = \frac{1}{K_{DB}}$$

As desorption $B \cdot S \rightleftharpoons B + S$ is just the opp. of adsorption
eqn. of B

$$r_D = k_D (C_B \cdot s - k_B P_0 C_v)$$

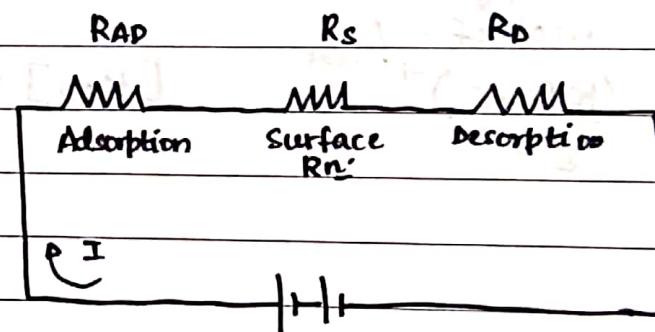
As there is no accumulation, at steady state, rates of all steps are equal.

\therefore Rate of r_m , $-r_c = r_{AD} = r_D = r_s$

\uparrow
conc. of C
is dec.

Rate limiting step.

We consider the heterogeneous process similar to electrical ckt.



$I \rightarrow$ rate of r_m ($-r_A$, mol/sq. of catalyst)

$$I = \frac{E}{Rt} = \frac{E}{R_{AD} + R_s + R_D}$$

More the resistance, lesser is current. Similarly, the step with largest resistance controls rate of the ran.

Hence, the step with largest resistance is rate limiting step.

To find out the R.L.C, each step can be assumed as R.L one by one and analysed then.

Conc. of gas phase is replaced by partial pressure.

① Rate law for adsorption limited rxn:

$$r_{AD} = k_A P_C C_V - k_{A^{-}} C_{C.S} = k_A \left(P_C C_V - \frac{C_{C.S}}{K_{AD}} \right)$$

(Adsorption)

$$r_S = k_S \left(C_{C.S} - \frac{C_{B.S} P_P}{k_S} \right)$$

↑
(Surface Rxn.)

$$r_D = k_D \left(C_{B.S} - \frac{P_B C_V}{k_{D.B}} \right)$$

(Desorption)

In adsorption limited rxn., $k_A \ll k_S, k_D$

$$\text{Thus, } \frac{r_{AD}}{k_A} \gg \frac{r_S}{k_S}, \frac{r_D}{k_D} \Rightarrow \frac{r_S}{k_S}, \frac{r_D}{k_D} \approx 0 \text{ comp. to } \frac{r_{AD}}{k_A}$$

$$\text{Surface rxn., } C_{C.S} = \frac{C_{B.S} P_P}{k_S} \quad \left(\frac{r_S}{k_S} = 0 \right)$$

$$\text{Desorption, } C_{B.S} = \frac{P_B C_V}{k_{D.B}} \quad \left(\frac{r_D}{k_D} \approx 0 \right)$$

$$C_{C.S} = \frac{C_{B.S} P_P}{k_S} = \frac{P_B C_V}{k_{D.B}} \frac{P_P}{k_S}$$

$$r_{AD} = k_A \left(P_C - \frac{P_B}{k_{D.B}} \frac{P_P}{k_A} \right) C_V$$

When there is no adsorption, $C \rightleftharpoons B + P$

k_1 — rate of fwd. m: $K_p \rightarrow$ eq. const.
 k_2 — rate of rev. rn:

$$r_{S1} = k_1 \left(P_C - \frac{P_B P_P}{K_p} \right)$$

Adsorption rate eqn:

$$r_{AD} = k_A \left(P_C - \frac{P_B}{K_{D_B}} \frac{P_P}{K_{AD} K_S} \right) C_V$$

$$\text{Let } K_p = \frac{K_{D_B} K_{AD} K_S}{B}$$

$$\therefore r_{AD} = k_A \left(P_C - \frac{P_B P_P}{K_p} \right) C_V$$

Now we have to eliminate C_V ,

$$\begin{aligned} C_t &= C_V + C_{BS} + C_{CS} \\ &= C_V \left(1 + K_B P_B + \frac{K_B P_P P_B}{K_S} \right) \end{aligned}$$

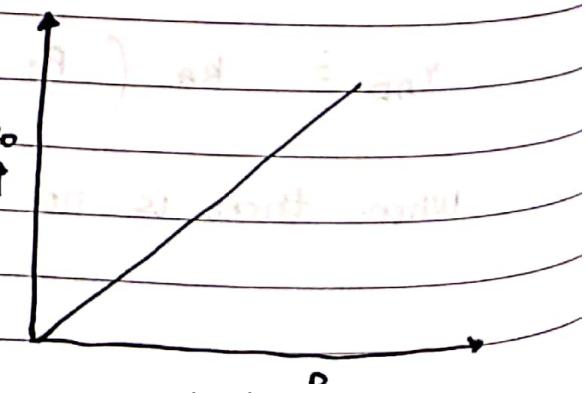
$$\therefore C_V = \frac{C_t}{\left(1 + K_B P_B + \frac{K_B P_P P_B}{K_S} \right)}$$

$$\therefore -r_C = r_{AD} = \frac{k_A C_t}{\left(1 + K_B P_B + \frac{K_B P_P P_B}{K_S} \right)} \left(P_C - \frac{P_B P_P}{K_p} \right)$$

Initial rate $(-r_{C0})$,

$$\begin{aligned} -r_{C0} &= (t k_A P_{C0} = k_p P_{C0}) \quad (1) \\ P_B, P_P &= 0 \text{ as initially there is no pdt.} \end{aligned}$$

If Cumene disprop. m:
is adsorption controlled,
then expt. data should
follow (1)



Surface Rn: Limited Rate law

$$-r_C = r_S = \frac{k_S C_t K_C}{1 + P_B K_B + K_P P_p} \left(P_C - \frac{P_p P_B}{K_p} \right)$$

Initially, $P_B = 0$, $P_p = 0$ and $k_S C_t K_C = K$

$$-r_{CO} = \frac{K P_{CO}}{1 + K_C P_{CO}}$$

At low P.P of cumene, $K_C P_{CO} \ll 1$

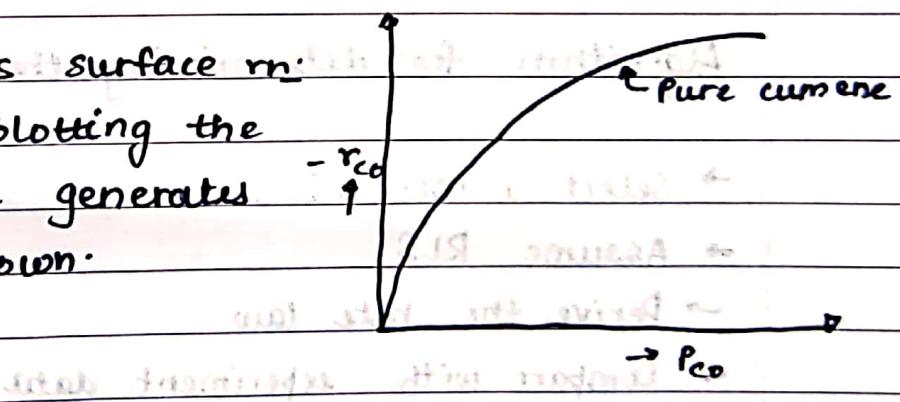
$\therefore -r_{CO} = K P_{CO}$, at this cond. rate linearly varies with P.P

At high partial pressure, $1 \ll K_C P_{CO}$

$$-r_C = \text{const.} = \frac{K}{K_C}$$

At this cond, rate is independent of partial pressure

If the process is surface rn. controlled, then plotting the experimental data generates the graph as shown.



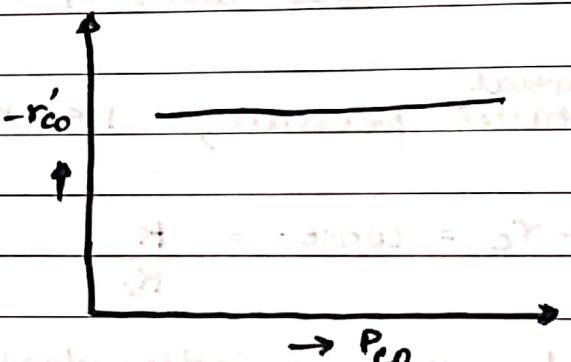
Desorption as RLS

$$-r_C = r_D = \frac{K_D C_t K_s K_C}{P_p + P_C K_e K_s + K_C P_p P_C} \left(P_C - \frac{P_p P_B}{K_p} \right)$$

Initially, $P_p = P_B = 0$

$$\therefore -r_{C_0} = K_D C_t = \text{const.}$$

When desorption is RLS, plotting experimental data will give a straight line parallel to x-axis



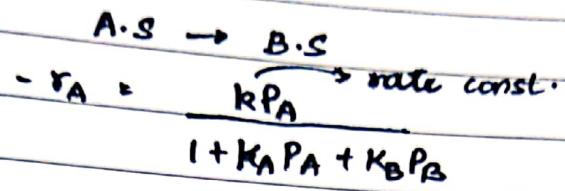
Algorithm for determining the mechanism and RLS

- Select a mechanism
- Assume RLS
- Derive the rate law
- Compare with experiment data

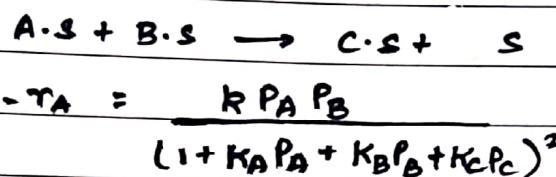
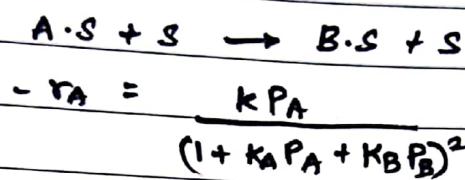
If the model and mechanism agree with the data, we can select the mechanism and rate model.

Irreversible surface m: limited rate law

single site



Dual site



Eley Rideal Kinetics

