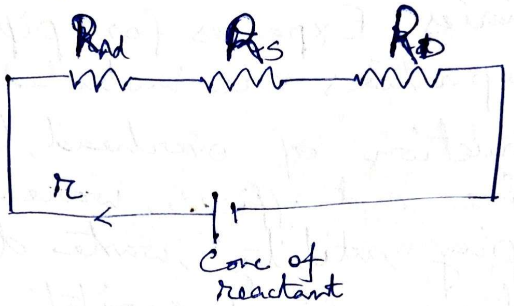
Chemical Reaction Engineering -II /Lecture -1

Rate Limiting Step - Explain steps in heterogeneous rxn.

Steps of heterogeneous rxn. - Adsorption, Surface rxn, desorpti



In steady state, these resistances are equal; in other terms, the rate of adsorption, surface rxn, desorption are equal.

$$\boxed{-r_A' = r_{Ad} = r_S = r_D}$$

Explain the analogy with a electrical ckt. and real life

~~Recap~~ Recap Langmuir-Hinshelwood kinetics.

↓

~~Ex~~ ~~Adsorption~~ Rate limiting step - Assumption - All sites are uniform.

Example

Adsorption Controlled rxn - NH_3 synthesis on iron catal

$$\text{Adsorption}\left|\begin{array}{l} H_2 + 2S \rightleftharpoons 2H.S \qquad \text{Rapid} \\ \left.\begin{array}{l} N_2 + S \rightleftharpoons N_2.S \\ N_2.S + S \rightleftharpoons 2N.S \end{array}\right\} \text{Rate-limiting} \end{array}\right.$$

$$\left.\begin{array}{l} \text{Surface rxn.}\left|\begin{array}{l} N.S + H.S \rightleftharpoons HN.S + S \\ NH.S + H.S \rightleftharpoons NH_2.S + S \\ NH_2.S + H.S \rightleftharpoons NH_3.S + S \end{array}\right. \\ \text{Desorption}\ |\ NH_3.S \rightleftharpoons NH_3 + S \end{array}\right\} \text{Rapid}$$

Surface-rxn. Rate limiting.

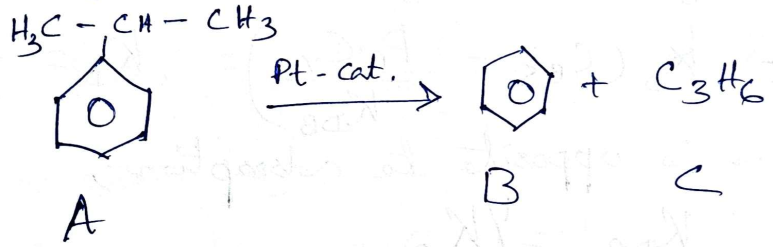
$CO + NO \rightarrow CO_2 + \frac{1}{2} N_2$ over Cu catalyst in automobile

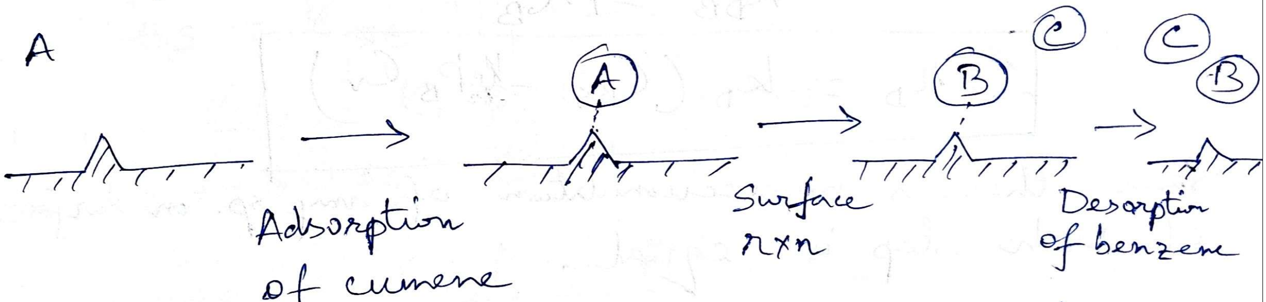
Adsorption | $CO + S \rightleftharpoons CO.S$
$NO + S \rightleftharpoons NO.S$ } Rapid

Surface rxn | $NO.S + CO.S \rightleftharpoons CO_2 + N.S + S$ | Rate limiting
$N.S + N.S \rightleftharpoons N_2.S$ }
desorption | $N_2.S \longrightarrow N_2 + S$ } Rapid

Synthesizing Rate-Law, Mechanism, Rate-limiting step.

Decomposition of cumene into benzene and propylene on Pt catalyst.





Adsorption on Pt cat. surface through π electrons of the benzene ring.

Langmuir-Hinshelwood kinetics

$$A + S \underset{k_{-Ad}}{\overset{k_{Ad}}{\rightleftharpoons}} A.S \quad \text{Adsorption}$$

$$A.S \underset{k_{-S}}{\overset{k_S}{\rightleftharpoons}} B.S + C \quad \text{Surface rxn}$$

$$B.S \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} B + S \quad \text{Desorption}$$

Assumption - 1. Each step is elementary rxn.
2. Species conc. in gas phase is replaced by partial pr. $C_A \rightarrow P_A$
$C_B \rightarrow P_B$
3. Ideal gas law: $P = CRT$

Adsorption of A

$$r_{AD} = k_{Ad} P_A C_v - k_{-Ad} C_{A.S}$$

$$\boxed{\therefore\ r_{Ad} = k_{Ad}\left(P_A C_v - \frac{C_{AS}}{K_{A}}\right)}$$

$$K_A = \frac{k_{Ad}}{k_{-Ad}}\Big|_{\text{For comp}}$$

Surface rxn.

$$r_S = k_S C_{AS} - k_{-S} C_{B.S} P_C$$

$$\boxed{r_S = k_S\left(C_{AS} - \frac{C_{BS} P_C}{K_S}\right)}$$

Desorption

$$r_D = k_D C_{B.S} - k_{-D} P_B C_v$$

$$r_D = k_D\left(C_{BS} - \frac{P_B C_v}{K_{DB}}\right) \qquad K_D = \frac{k_D}{k_{-D}}\Big|_{\text{For compl}}$$

Since, desorption is opposite to adsorption,

$$K_{DB} = 1/K_B$$

$$\boxed{\therefore\ r_D = k_D\left(C_{BS} - K_B P_B C_v\right)}$$

Since, there is no accumulation of any sp. on surface, rate of each step is equal.

$$-r_A = r_{Ad} = r_S = r_D$$

In next ~~step~~ stage, we will assume that one of the steps to be rate-limiting and formulate rate law in terms of partial pr. of species present. From the expressio how rxn rate varies with total pr will be postulated. If the ~~dat~~ prediction matches with experimental data the assumed mechanism and rate-limiting step are correct.

Adsorption is Rate-limiting

Let us assume adsorption step is rate limiting. In this case, k_{Ad} is small and k_S and k_D are large.

$$\therefore \frac{r_S}{k_S} \simeq 0 \quad , \quad \frac{r_D}{k_D} \simeq 0$$

Revisit adsorption eq^n —

$$r_{Ad} = k_{Ad}\left(P_A C_v - \frac{C_{AS}}{K_A}\right) \quad \text{———} \quad ①$$

C_{AS} and C_v are non-measurable entities and hence, should be replaced.

$$C_{AS} - \frac{C_{BS} P_C}{K_S} = 0$$

$$C_{AS} = \frac{C_{BS} P_C}{K_S} \quad \text{———} \quad ②$$

From desorption eq^n —

$$C_{BS} - K_B P_B C_v = 0$$

$$C_{BS} = K_B P_B C_v \quad \text{———} \quad ③$$

Replacing C_{BS} in eq^n ② —

$$C_{AS} = \frac{K_B P_B C_v P_C}{K_S} \quad \text{———} \quad ④$$

Replacing C_{AS} in eq^n ① —

$$r_{Ad} = k_{Ad}\left(P_A C_v - \frac{K_B P_B P_C C_v}{K_S K_A}\right)$$

$$r_{Ad} = k_{Ad}\left(P_A - \frac{P_B P_C K_B}{K_S K_A}\right) C_v \quad \text{———} \quad ⑤$$

Now, if $r_{Ad} = 0$, $\frac{P_A}{P_B P_C} = \frac{K_B}{K_S K_A} = K_P$ $\quad P_A - \frac{P_B P_C K_B}{K_S K_A} = 0$

K_P is ~~dependent~~ overall partial pr. equili. const. for the rxn.

$$A \rightleftharpoons B + C$$

$$K_p = \frac{K_S K_A}{K_B} = \frac{P_C P_B}{P_A}$$

Equili const. can be determined from thermodynamics -

$$\boxed{\ln K = -\frac{\Delta G^\circ}{RT}}$$

Site balance ~~gives~~ -

$$C_t = C_v + C_{AS} + C_{BS}$$

$$= C_v + \frac{K_B P_B P_C C_v}{K_S} + K_B C_v P_B$$

$$\therefore C_v = \frac{C_t}{1 + \frac{K_B P_B P_C}{K_S} + K_B P_B} \quad \text{—— ⑥}$$

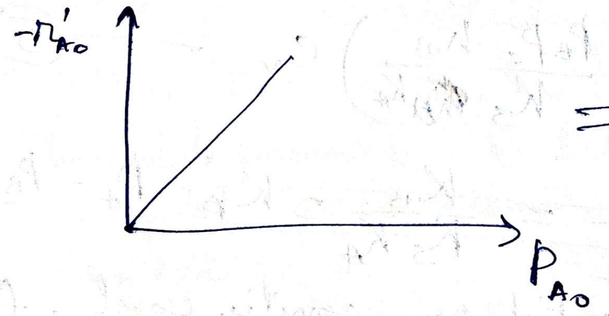
Combining eq^n ⑤ and ⑥ we get —

$$\boxed{-r'_A = r_{Ad} = \frac{C_t k_{Ad}\left(P_A - \frac{P_B P_C}{K_p}\right)}{1 + \frac{K_B P_B P_C}{K_S} + K_B P_B}}$$

Langmuir - Hinshelwood - Hougen - Watson kinetics

Initially, no B and C are produced, P_B, P_C are zero.

$$\therefore -r'_{A0} = C_t k_{Ad} P_{A0} = k P_{A0}$$



$\Rightarrow$ Check this plot ~~is~~ if adsorption is rate controlling.

Surface Rxn is Rate-limiting

$$r_S = k_S\left(C_{AS} - \frac{C_{BS}\,P_C}{K_S}\right) \quad \text{——} ①$$

C_{AS} and C_{BS} should be replaced since adsorbed comp conc. can't be measured.

If surface rxn is rate limiting, k_S is small and k_{Ad}, k_D are large.

$$\therefore \frac{r_{Ad}}{k_{Ad}} \simeq 0 \quad , \quad \frac{r_D}{k_D} \simeq 0$$

From adsorption eqn —

$$P_A C_v - \frac{C_{AS}}{K_A} = 0$$

$$C_{AS} = K_A P_A C_v \quad \text{——} ②$$

Similarly, from desorption eqn —

$$C_{BS} - K_B P_B C_v = 0$$

$$C_{BS} = K_B P_B C_v \quad \text{——} ③$$

Substituting C_{AS} and C_{BS} in eqn ① —

$$r_S = k_S\left(K_A P_A C_v - \frac{K_B P_B C_v P_C}{K_S}\right)$$

$$= k_S K_A\left(P_A - \frac{K_B}{K_S K_A} P_B P_C\right) C_v$$

$$r_S = k_S K_A\left(P_A - \frac{P_B P_C}{K_P}\right) C_v \qquad \left[K_P = \frac{K_S K_A}{K_B}\right]$$

—— ④

Site balance —

$$C_t = C_v + C_{AS} + C_{BS}$$

$$C_v = \frac{C_t}{1 + K_A P_A + K_B P_B} \quad \text{——} ⑤$$

Substituting C_v in eqn ④ —

$$\boxed{r_S = \frac{C_t\, k_S K_A}{k}\left(P_A - \frac{P_B P_C}{K_P}\right)\frac{\text{[illegible]}}{1 + K_A P_A + K_B P_B}}$$

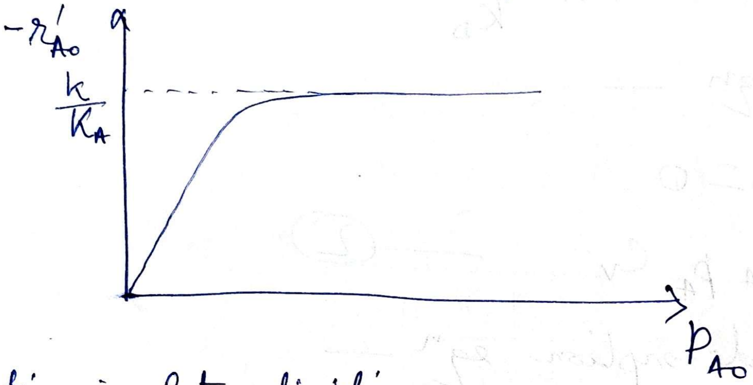
Initial stage, $P_B = 0$, $P_C = 0$, $P_A = P_{A0}$

$$-r'_{A0} = r_S = \frac{k P_{A0}}{1 + K_A P_{A0}}$$

At low partial pr. of A, $-r'_{A0} = r_S = k P_{A0}$ $[\because 1 >> K_A P_{A0}]$

At high partial pr. $K_A P_{A0} >> 1$

$$\therefore -r'_{A0} = \frac{k}{K_A}$$



Desorption is Rate-limiting

$$r_D = k_D(C_{BS} - K_B P_B C_v) \quad \text{--- (1)}$$

C_v, C_{BS} should be replaced.

k_S, k_{Ad} are large and k_D is small.

$$\frac{r_S}{k_S} \simeq 0, \quad \& \quad \frac{r_{Ad}}{k_{Ad}} \simeq 0$$

From Surface rxn eqn —

$$C_{AS} - \frac{C_{BS} P_C}{K_S} = 0$$

$$C_{BS} = \frac{K_S C_{AS}}{P_C} \quad \text{--- (2)}$$

From adsorption eqn —

$$P_A C_v - \frac{C_{AS}}{K_A} = 0$$

$$C_{AS} = K_A P_A C_v \quad \text{--- (3)}$$

Substituting C_{AS} into eqn ② we get —

$$C_{BS} = \frac{K_S K_A P_A C_v}{P_c} \qquad \text{——} \textcircled{4}$$

Substituting into eqn ① —

$$r_D = k_D\left(\frac{K_S K_A P_A C_v}{P_c} - K_B P_B C_v\right)$$

$$= k_D K_B\left(\frac{K_S K_A}{K_B}\frac{P_A}{P_c} - P_B\right) C_v$$

$$= k_D K_B C_v\left(K_P \frac{P_A}{P_c} - P_B\right)$$

$$= k_D K_A K_S\left(\frac{P_A}{P_c} - \frac{P_B}{K_P}\right) C_v \qquad \text{——} \textcircled{5}$$

Site balance —

$$C_t = C_v + C_{AS} + C_{BS}$$

$$= C_v + K_A P_A C_v + \frac{K_S K_A P_A C_v}{P_c}$$

$$C_v = \frac{C_t}{1 + K_A P_A + \frac{K_S K_A P_A}{P_c}} \qquad \text{——} \textcircled{6}$$

Replacing C_v in eqn ⑤ —

$$r_D = k_D K_A K_S\left(\frac{P_A}{P_c} - \frac{P_B}{K_P}\right)\frac{C_t}{\left(1 + K_A P_A + \frac{K_S K_A P_A}{P_c}\right)}$$

$$\boxed{r_D = \frac{\underset{k}{\underline{k_D K_A K_S C_t}}\left(P_A - \frac{P_B P_c}{K_P}\right)}{\left(P_c + K_A P_A P_c + K_S K_A P_A\right)}}$$

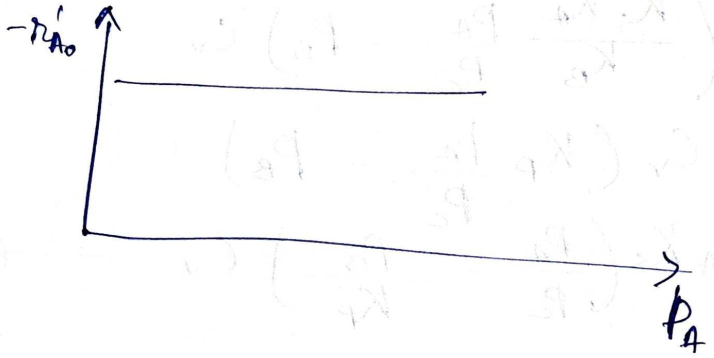
~~Initial Ra~~

Initial stage

$P_A = P_{A0}$, $P_B = 0$, $P_C = 0$

$$r_D = \frac{k_D K_S K_A C_t P_A}{K_S K_A P_A}$$

$$\therefore r_D = k_D C_t = -r'_{A0}$$



Summary of Cumene decomposition

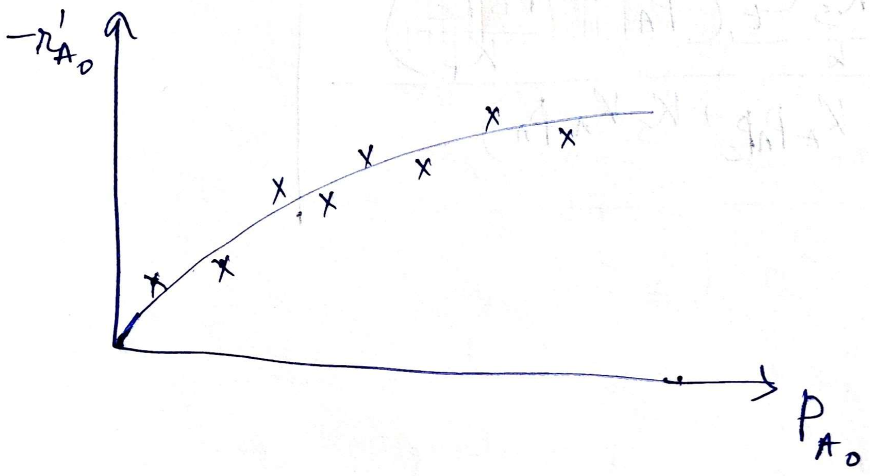
$$A + S \rightleftharpoons A.S$$

$$A.S \rightleftharpoons B.S + C$$

$$B.S \rightleftharpoons B + S$$

Assumption – 1. No inerts are adsorbed
2. Surface rxn rate limiting.
3. Single site

$$-r'_A = \frac{k\left(P_A - \dfrac{P_B P_C}{K_P}\right)}{1 + K_B P_B + K_A P_A}$$



Pseudo S.S. Hypothesis

Net rate of formation of reactive intermediates are zero.

Each sp. adsorbed on cat. surface is a reactive intermediate.

$$\frac{r_{AD}}{k_A} \simeq 0$$

Net rate of sp. i adsorbed on surface will be zero.

$$r^*_{i.S} = 0$$

This works well for both single rate limiting and where multiple steps are rate limiting (e.g. adsorption and surface rxn.)

$$N + S \underset{k_{-N}}{\overset{k_N}{\rightleftarrows}} N.S$$

$$N.S \xrightarrow{k_S} I.S$$ — irreversible as the conversion is fast.

$$I.S \underset{k_{-I}}{\overset{k_I}{\rightleftarrows}} I + S$$

$$-r'_N = r_S = k_S C_{N.S}$$

$$r^*_{NS} = k_N P_N C_v - k_{-N} C_{NS} - k_S C_{NS} = 0$$

$$r^*_{IS} = k_S C_{N.S} - k_I C_{I.S} - k_{-I} P_I C_v = 0$$

PSSH assumption —

$$r^*_{NS} = 0, \quad r^*_{IS} = 0$$

$$C_{N.S} = \frac{k_N P_N C_v}{k_{-N} + k_S}, \quad C_{I.S} = \frac{k_S C_{NS} + k_{-I} P_I C_v}{k_I}$$

$$\cancel{C_{I.S} = \frac{k_{-I} P_I C_v}{k_S + k_I}} \qquad = \left(\frac{k_S k_N P_N}{k_I (k_{-N} + k_S)} + \frac{k_{-I}}{k_I} P_I\right) C_v$$

Site balance —

$$C_t = C_v + C_{NS} + C_{I.S}$$

$$-r'_N = \frac{K_N k_S C_t}{\left(1 + \frac{k_S}{k_{-N}}\right)} \frac{P_N}{1 + \frac{1}{1 + \frac{k_S}{k_{-N}}} K_N P_N + K_I P_I}$$