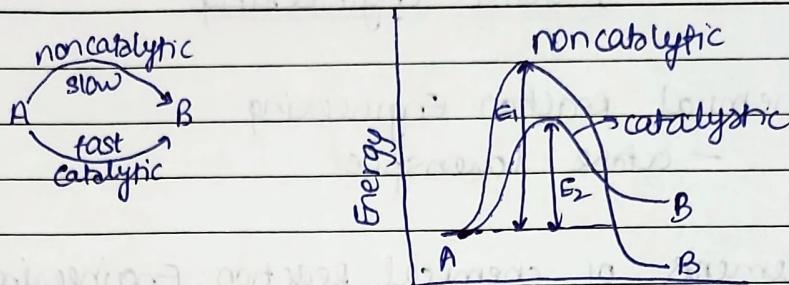


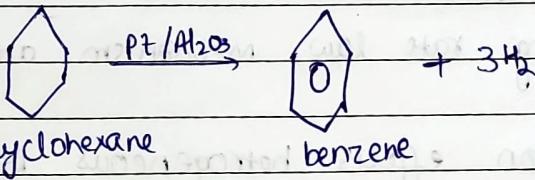
Reaction engineering

1. Chemical Reaction Engineering
 - Octave Levenspiel
2. Elements of chemical Reaction Engineering
 - H. Scott Fogler
3. Chemical Engineering kinetics - J.M Smith
4. Catalysis and catalytic Reactions
 - a) steps in reaction
 - b) Synthesising rate law, mechanism and rate limiting step
5. External diffusion effects heterogeneous Reactions
 - a) external resistance to mass transfer
6. Diffusion and Reactions in a catalyst pellet - internal diffusion to mass transfer on reaction.
7. Solid catalysts and their characterisation
 - a) surface area
 - b) pore volume, void fraction, solid density etc.
8. Fluid particle reactions (non catalytic)
 - a) progressive conversion model
 - b) shrinking core model
 - c) determination of rate controlling steps

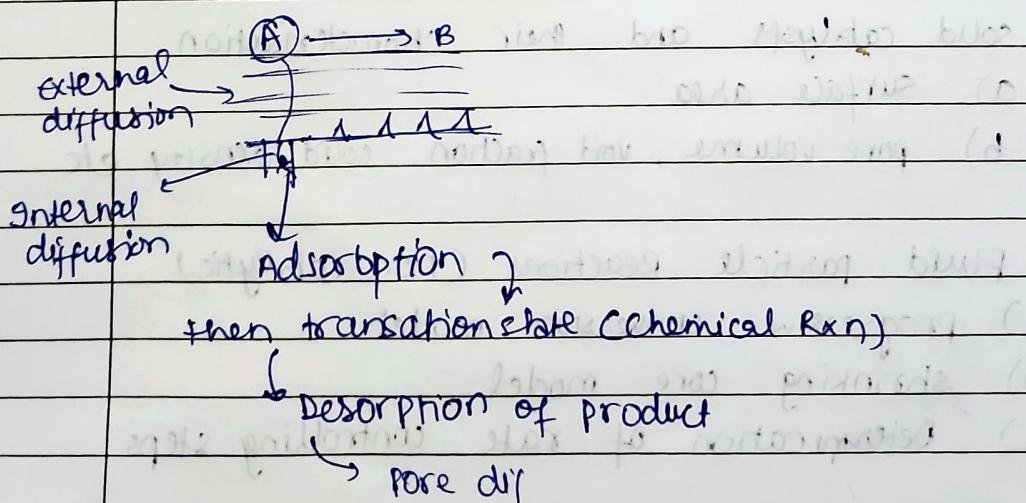


Reaction Pathway →

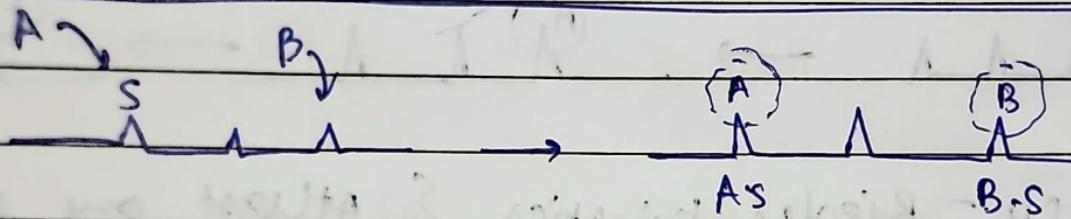
Activation Energy for non catalytic $\rightarrow E_1$
 " " " " catalytic $\rightarrow E_2$



→ porous catalysts are effective due to large surface area.



- 1) External diffusion of reactants from bulk to the external catalyst surface
- 2) Internal/pore diffusion of the reactants into the pores.
- 3) Chemical adsorption of the reactants on the active centres of the catalyst surface



c_t = Total concentration of active sites
 when there is no adsorption

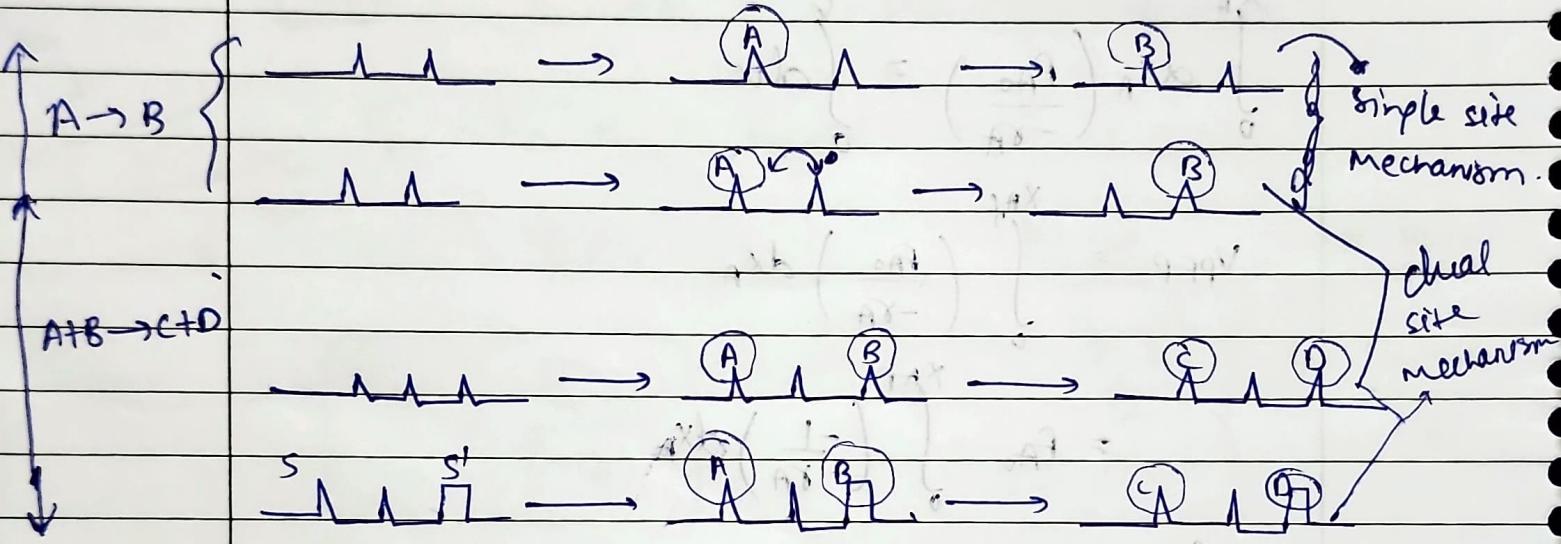
$$\left(\text{moles of active sites unit wt. of catalyst} \right) = \frac{\text{number of active sites}}{\text{Avogadro's number}} / \text{unit wt. of catalyst}$$

$$\text{Concentration of } c_v = \frac{\text{no. of vacant site}}{\text{Avogadro's no.}} / \frac{\text{unit mass of the catalyst}}{\text{unit mass of the catalyst}}$$

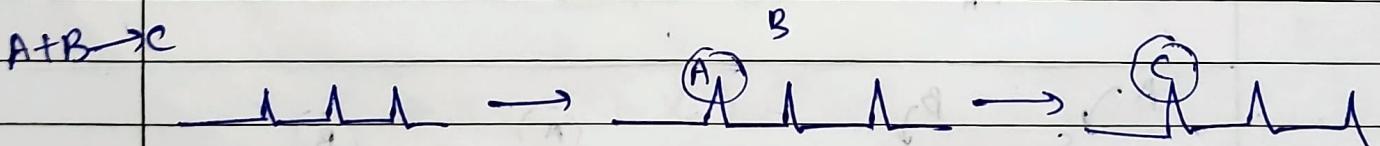
Concentration of occupied site ($c_{A,S}$)

Site balance

$$c_t = c_{A,S} + c_{B,S} + c_v$$

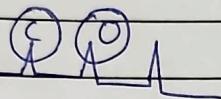
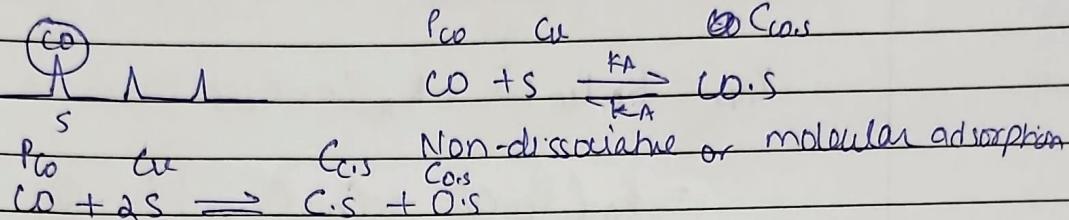


Langmuir-Hinshelwood kinetics = All the reactants should be absorbed on the active site for product formation.



Eley-Riedel kinetics { At least one of the reactants shouldn't be absorbed on the active site }

$$C = 0$$



Dissociative adsorption

rate of attachment $r' \propto P_{CO}$
 $\propto C_V$

$$r' = k_A P_{CO} C_V$$

rate of detachment $r'' \propto C_{CO\cdot S}$

$$r'' = K_A C_{CO\cdot S}$$

rate of Adsorption $r_{AD} = k_A P_{CO} C_V - k_A C_{CO\cdot S}$

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

where $k_A = \frac{k_A}{K_A}$

$$r_{AD} = k_A \left(P_{CO} C_V - \frac{C_{CO\cdot S}}{K_A} \right) \quad (1)$$

Adsorption equilibrium constant.

Dissociative adsorption

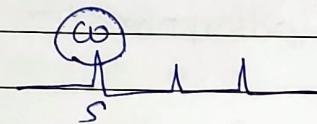
rate of attachment $r' \propto P_{CO}$
 $\propto C_V^2$ $r' = k_A P_{CO} C_V^2$

rate of detachment $\Rightarrow r'' \propto C_{CO\cdot S}$ $r'' = k_A C_{CO\cdot S} C_{CO\cdot S}$
 $\propto C_{CO\cdot S}$

rate of adsorption

$$r_{AD} = k_A P_{CO} C_U - k_A C_{CO.S} C_{CO.S}$$

$$= k_A \left(P_{CO} C_U^2 - \frac{C_{CO.S} C_{CO.S}}{K_A} \right) \quad \text{--- (2)}$$



$$C_U = C_{CO.S} + C_U$$

$$C_U = C_U - C_{CO.S}$$

~~partial pressure~~

At equilibrium rate of adsorption

$$r_{AD} \approx 0$$

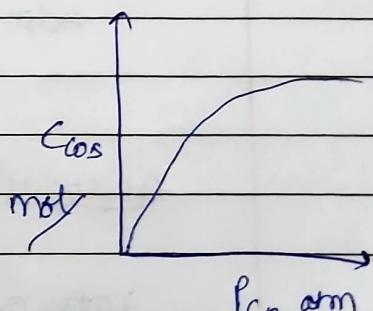
from eqn (1)

$$P_{CO} C_U = \frac{C_{CO.S}}{K_A}$$

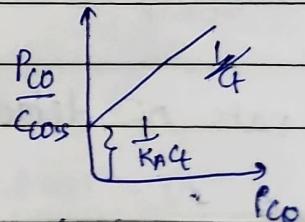
$$\text{Putting } C_U \text{ in } \rightarrow P_{CO} (C_U - C_{CO.S}) = \frac{C_{CO.S}}{K_A}$$

$$C_{CO.S} = \frac{k_A P_{CO} \cdot C_U}{1 + k_A P_{CO}}$$

Langmuir adsorption isotherm



$$\frac{P_{CO}}{C_{CO.S}} = \frac{1}{k_A C_U} + \frac{P_{CO}}{C_U}$$



$$r_{AD} = k_A \left(P_{CO} \cdot C_U^2 - \frac{C_{CO,s} C_{CO,s}}{K_A} \right)$$

At equilibrium $r_{AD} = 0$

$$P_{CO} \cdot C_U^2 = \frac{C_{CO,s} C_{CO,s}}{K_A}$$

Assuming ~~$C_{CO,s} = C_{CO}$~~ $C_{CO,s} = C_{CO}$

$$P_{CO} \cdot C_U^2 = \frac{C_{CO,s}^2}{K_A}$$

$$C_{CO,s}^2 = K_A P_{CO} C_U^2$$

$$C_{CO,s} = (K_A P_{CO})^{1/2} C_U$$

site balance

$$C_t = C_{CO,s} + C_{CO} + C_U$$

$$= 2C_{CO,s} + C_U$$

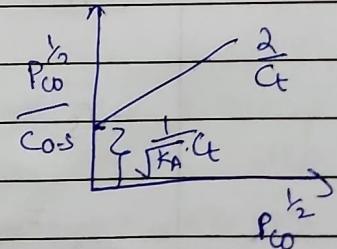
$$C_U = 2C_{CO,s}$$

$$C_{CO,s} = (K_A P_{CO})^{1/2} (C_t - 2C_{CO,s})$$

$$C_{CO,s} = \frac{(K_A \cdot P_{CO})^{1/2} C_t}{1 + 2(K_A \cdot P_{CO})^{1/2}}$$

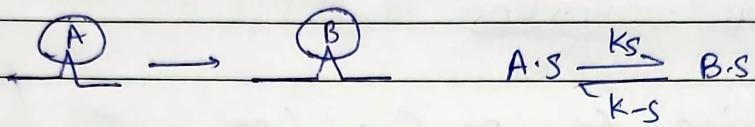
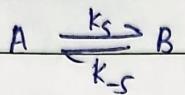
$$\frac{P_{CO}^{1/2}}{C_{CO,s}} = \frac{1}{(K_A)^{1/2} C_t} + \frac{2 P_{CO}^{1/2}}{C_t}$$

$$y \quad c \quad mx$$



Langmuir isotherm
for dissociative adsorption

Surface reaction:



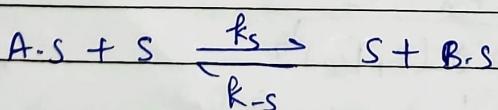
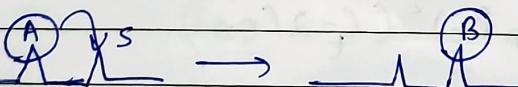
$$r_s = k_s C_{A \cdot S} - k_s C_{B \cdot S}$$

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

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

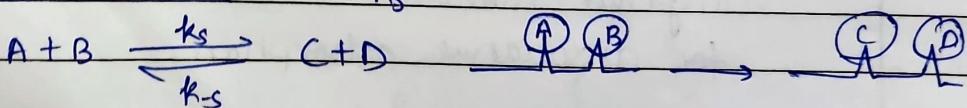
$$k_s = \frac{k_s}{k_s} = \text{equilibrium constant for } \alpha ?$$

Dual site:



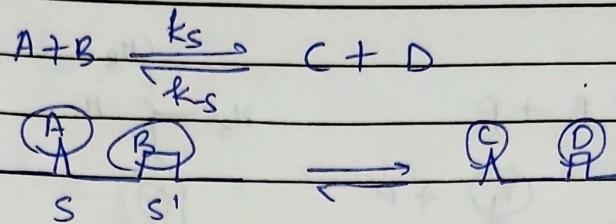
$$r_s = k_s C_{A \cdot S} \cdot C_B - k_s C_{B \cdot S} C_A$$

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



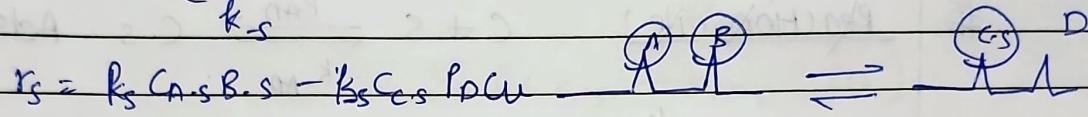
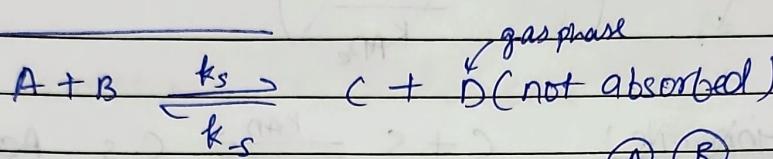
$$r_s = k_s C_{A \cdot S} \cdot C_{B \cdot S} - k_s C_{C \cdot S} C_{D \cdot S}$$

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

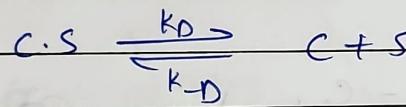


$$r_s = k_s c_{A,s} c_{B,s'} - k_s c_{C,s} c_{D,s'}$$

$$= k_s (c_{A,s} c_{B,s'} - \frac{c_{C,s} c_{D,s'}}{k_s})$$



$$= k_s (c_{A,s} c_{B,s} - \frac{c_{C,s} p_{CO_2}}{k_s}) \rightarrow \text{partial pressure of } D$$



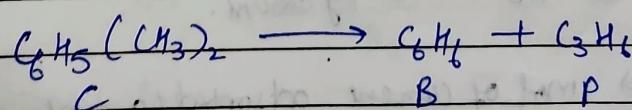
$$r_D = k_D (c_{C,s} - \frac{p_C(w)}{K_{DC}}) = k_D (c_{C,s} - K_{AD} c_{P(w)})$$

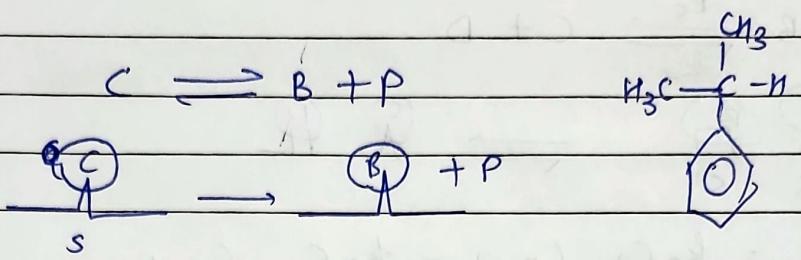
$$r_D = -r_{APC}$$

$$K_D = \frac{1}{K_{AD}}$$

synthesizing rate law mechanism and rate limiting step:-

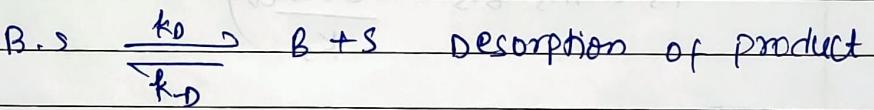
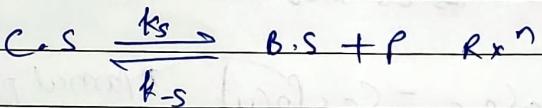
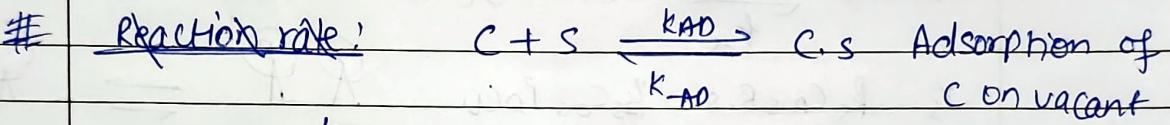
Developing rate law of cumene disproportionation rxn





Absorption rate:

$$r_{AD} = k_{AD} \left(C_{c,s} - \frac{f_{B,S} P_p}{K_{AD,c}} \right)$$



$$r_{AD,c} = k_{AD} \left(P_c C_s - \frac{C_{B,S}}{K_{AD,c}} \right) \quad \text{--- (1)}$$

$$r_s = k_s \left(C_{c,s} - \frac{C_{B,S} \cdot P_p}{k_s} \right) \quad \text{--- (2)}$$

$$r_{D_B} = k_D \left(C_{B,S} - \frac{P_c C_s}{K_{D_B}} \right) \quad \text{--- (3)}$$

$$\text{AT equilibrium} \quad -r_c = r_{AD} = r_s = r_{D_B}$$

$$K_{AD,B} = \frac{1}{K_{D_B}}$$

unit of $r_{AD} = \text{mol/g catalyst}$

$C_{c,s}$ unit $\rightarrow \text{mol of cumene adsorbed/g catalyst}$

$$k_A = (R P_c S)^{\frac{1}{2}} / (\text{atm hr})^{\frac{1}{2}}$$

$$k_A = A^{-1} / s^{-1}$$

$$K_{ADC} = \frac{k_A}{k_D} = \frac{\text{atm.nrt}}{\text{hr}^{-1}} \Rightarrow \text{atm}^{\frac{1}{2}} / \text{KPa}^{-\frac{1}{2}}$$

Assuming adsorption as rate limiting.

$$\text{surface rxn: } r_s > k_A (C_{CS} - \frac{C_{BS} P_p}{K_s})$$

$$\text{desorption } r_D > k_D (C_{BS} - \frac{P_p C_U}{K_{AD_B}})$$

$$= k_D (C_{BS} - K_{AD_B} P_p C_U)$$

$$r_{AD} \ll r_s, r_D$$

$$k_A \ll r_s, r_D$$

compared to r_s and r_D

$$\frac{r_{AD}}{k_A} \gg \frac{r_s}{k_s}, \frac{r_D}{k_D}$$

from eqⁿ(1)

$$P_c(C_A) = \frac{C_{CS}}{K_{ADC}}$$

$$\frac{r_s}{k_s} = C_{CS} - \frac{C_{BS} P_p}{K_s} \approx 0$$

$$C_{CS} = \frac{C_{BS} P_p}{K_s} \xrightarrow{\text{from eq}^n(2)} \quad (4)$$



$$\text{from eq}^n(3) \text{ as } \frac{r_D}{k_D} \approx 0$$

$$C_{BS} = K_{AD_B} P_p C_U \quad (5)$$

putting C_{BS} in eqⁿ(4)

$$C_{CS} = \frac{K_{AD_B} P_p C_U}{K_s}$$

site balance

$$C_t = C_U + C_{CS} + C_{BS}$$

$$C_t = C_U + \frac{k_{AD_B} P_B P_p}{k_s} C_U + k_{AD_B} P_B \cdot C_U$$

$$C_U = \frac{C_t}{1 + \frac{k_{AD_B} P_B P_p}{k_s} + k_{AD_B} P_B}$$

$$r_{AD} = k_{AD} \left(P_C C_U - \frac{k_{AD_B} P_B (C_U \cdot P_p)}{k_s k_{AD_C}} \right)$$

$$= k_{AD} \left(P_C - \frac{k_{AD_B} P_B P_p}{k_{AD_C} k_s} \right) C_U$$

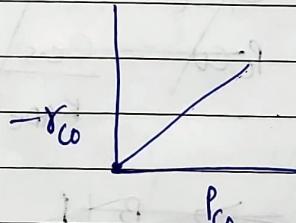
$$-r_C = r_{AD} = k_{AD} \left(P_C - \frac{k_{AD_B} P_B P_p}{k_{AD_C} k_s} \right) \frac{C_t}{\left(1 + \frac{k_{AD_B} P_B P_p}{k_s} + k_{AD_B} P_B \right)}$$

At initial condition:

$$P_B = P_p = 0 \quad \{ \text{As no product} \}$$

$$-r_{C_0} = r_{AD} = k_{AD_C} P_{C_0} C_t$$

$$= k P_{C_0}$$



If the surface reaction is rate limiting
 $k_s \ll k_A, k_D$

$$\frac{r_{AD}}{k_A} \approx 0 \quad \text{and} \quad \frac{r_D}{k_D} \approx 0$$

$$P_C C_U = \frac{C_{CS}}{k_{AD_C}} \quad \text{and} \quad C_{BS} = k_{AD_B} P_B C_U$$

$$\frac{P_C C_{BS}}{k_{AD_B} P_B} = \frac{C_{CS}}{k_{AD_C}}$$

$$r_s = k_s \left(C_{CS} - \frac{C_B \cdot s P_p}{k_s} \right)$$

$$= k_s \left(K_{ADC} P_c C_w - \frac{K_{ADB} P_B P_p C_w}{k_s} \right)$$

$$= k_s \left(K_{ADC} P_c - \frac{K_{ADB} P_B P_p}{k_s} \right) C_w$$

from site balance

$$C_t = C_{BS} + \cancel{C_{CS}} + C_w$$

$$C_t = (K_{ADC} P_c + 1) C_w$$

~~$$\frac{C_t}{K_{ADB} P_B + 1}$$~~

~~$$r_s = k_s \left(K_{ADC} P_c - \frac{K_{ADB} P_B P_p}{k_s} \right) C_w$$~~

At initial state

$$P_p = 0$$

$$C_t = (K_{ADC} P_c + K_{ADB} P_B + 1) C_w$$

$$C_w = \frac{C_t}{K_{ADC} P_c + K_{ADB} P_B + 1}$$

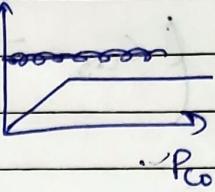
$$P_p = 0$$

$$r_s = r_s = k_s \left(K_{ADC} P_c - \frac{K_{ADB} P_B P_p}{k_s} \right) \frac{C_t}{(K_{ADC} P_c + K_{ADB} P_B + 1)}$$

At initial state $P_p \geq 0$, ~~$P_B \geq 0$~~ $P_B = 0$

$$r_s = r_s = k_s \left(K_{ADC} P_{c_0} \right) \frac{C_t}{(K_{ADC} P_{c_0} + 1)} \Rightarrow r_s = k_s \frac{P_{c_0} C_t}{P_{c_0}}$$

$$r_s = \frac{k_s C_t K_{AD_c} P_{CO}}{1 + K_{AD_c} P_{CO}}$$



$$-r_{CO} = r_s = \frac{K_p P_{CO}}{1 + K_{AD_c} P_{CO}}$$

At low P_{CO} , $K_{AD_c} P_{CO} \ll 1$

then $-r_{CO} = K_p P_{CO}$

At high concn of P_{CO} , $K_{AD_c} P_{CO} \gg 1$

then $-r_{CO} = \frac{K}{K_{AD_c}} = \text{constant}$

Assuming desorption as rate determining step

$$k_d \ll K_{AD}, k_s$$

so, $\frac{r_{AD}}{K_{AD}} \approx 0$ and $\frac{r_s}{k_s} \approx 0$

$$P_{CO} = \frac{C_{CO}}{K_{AD_c}} \text{ and } C_{CO} = \frac{C_{B,S} P_p}{k_s} \Rightarrow C_{B,S} = \frac{k_s C_{CO} P_p}{P_p} = \frac{k_{AD_c} P_c C_{CO}}{P_p}$$

$$r_D = k_D \left(C_{B,S} - \frac{P_{CO}}{K_{DB}} \right)$$

$$r_D = k_D \left(\frac{K_{AD_c} P_{CO} \times k_s}{P_p} - \frac{P_{CO}}{K_{DB}} \right)$$

$$C_t = C_u + C_{CO} + C_{B,S} \Rightarrow C_u + K_{AD_c} P_c C_u + \frac{k_s K_{AD_c} P_c}{P_p}$$

$$= C_u \frac{1 + K_{AD_c} P_c}{P_p}$$

$$r_D = k_D \left(\frac{K_{AD_c} P_c K_S}{P_p} - \frac{P_B}{K_{DB}} \right) c_t$$

$$r_D = k_D \left(\frac{K_{AD_c} P_c K_S}{P_p} - \frac{P_B}{K_{DB}} \right) \frac{c_t}{(1 + K_{AD_c} P_c + K_S K_{AD_c} P_c)} \quad \text{--- (1)}$$

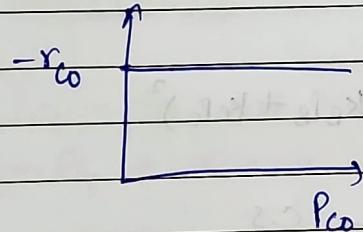
$$r_D = k_D \left(\frac{K_{AD_c} P_c K_S}{P_p} - \frac{P_B P_p}{K_{DB}} \right) \frac{c_t}{(P_p + K_{AD_c} P_c + K_S K_{AD_c} P_c)} \quad \text{--- (2)}$$

At initial

$$P_p = 0, P_B = 0$$

$$-r_{CO} = r_D = k_D \left(K_{AD_c} P_c K_S \right) - c_t \frac{K_S K_{AD_c} P_c}{K_S K_{AD_c} P_c}$$

$$-r_{CO} = r_D = k_D c_t$$



Algorithm for determining reaction mechanism and rate limiting step:

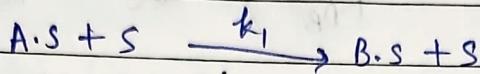
1. Select a mechanism
2. Assume a rate limiting step.
3. Derive the rate law by the rate expression of different steps of the mechanism and by site balance.
4. Compare with the experimental data.

Irreversible surface reaction limited rate law:

1. single site A.s $\xrightarrow{k_1} B.s$ (reaction is $A \rightarrow B$)

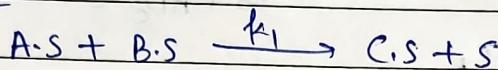
$$-\dot{r}_A = \frac{k_1 P_A}{1 + k_A P_A + k_B P_B}$$

2. Dual site:

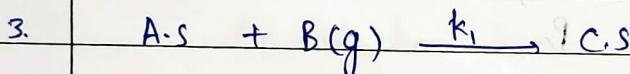


$$-\dot{r}_A = \frac{k_1 P_A}{(1 + k_A P_A + k_B P_B)^2}$$

or

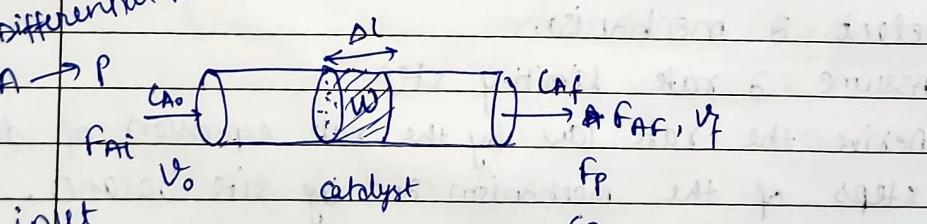


$$-\dot{r}_A = \frac{k_1 P_A P_B}{(1 + k_A P_A + k_B P_B + k_C P_C)^2}$$



$$-\dot{r}_A = \frac{k_1 P_A P_B}{1 + k_A P_A + k_C P_C} \quad \begin{matrix} \text{Eley - Riedel} \\ \text{kinetics} \end{matrix}$$

(Differential Reactor)



weight of catalyst = w

inlet reactant (A) molar flow rate / time = F_{A0}

F_{Af} = outlet Reaction molar flow rate (moles/time)

\dot{r}_A = rate of the reaction (moles/gm of cat. sec)

v_0, v_f = volumetric flow rate of A cm^3/s initial and final
 c_{A_0} = initial concⁿ of A mol/cc
 c_A = final concⁿ of B mol/cc
 c_p = product concⁿ.

* The criteria for being a differential reactor:

- 1) The catalyst amount is very small
- 2) The reactant conversion to product is very low (hence the reactor can be considered as gradientless)
- 3) The heat change due to the reaction is negligible (the reactor is considered isothermal)

Mole balance of A:

$$\text{flow in} - \text{flow out} + \text{rate of formation} = \text{rate of accu.}^0$$

$$F_{A_0} - F_{Af} + \underbrace{r_A \times w}_{\frac{\text{Rate of Rxn}}{\text{mass of cat}}} = 0$$

$$\frac{\text{Rate of Rxn} \times \text{mass of cat.}}{\text{mass of cat.}}$$

$$-r_A = \frac{F_{A_0} - F_{Af}}{w} \quad (1)$$

$$\frac{F_{A_0} - F_{Af}}{F_{A_0}} = x_A$$

$$-r_A = \frac{v_0 c_{A_0} - v_f c_{Af}}{w}$$

$$v c_A = \frac{\text{cc}}{\text{s}} \frac{\text{mol}}{\text{cc}} = \frac{\text{mol}}{\text{s}} = F$$

in terms of product:

$$-r_A = \frac{F_{A_0} x_A}{w} = \frac{F_p}{w}$$

x_A = conversion

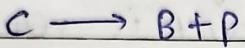
F_p = molar flow rate of product P

1.15 L ac

$$-r_A = \frac{V_0 C_{A0} - V_f C_A}{W}$$

$$= \frac{V_0 (C_{A0} - C_A)}{W} = \frac{V_0 (P_p)}{W} \quad \left\{ \begin{array}{l} V_0 \approx V_f \\ \text{as conversion} \\ \text{is very low} \end{array} \right.$$

$$-r_A = f\left(\frac{C_{A0} + C_A}{2}\right) = f(C_{A0}) \approx f(C_{A0}) \quad \text{when } C_{A0} \approx C_A$$



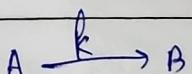
Run no.	P_c	P_B	P_p	$-r_A$	
1	0.5	1	1		product
2	1	1	0		inhibited
3	2	1	0		data
4	1	0	0		
5	2	0	0		pure feed
6	1.5	0	0		data

ideal batch Reactor, the design eqn for heterogeneous catalytic reaction:

$$\begin{aligned} -r_A &= \frac{1}{W} \frac{dN_A}{dt} \\ &= \frac{1}{W} \frac{d(N_{A0} X_A)}{dt} \quad \begin{array}{l} \text{amount of} \\ \text{converted} \end{array} \quad \frac{dN_A}{dt} = \frac{d(N_{A0} X_A)}{dt} \end{aligned}$$

$$= \frac{N_{A0}}{W} \frac{dx_A}{dt}$$

$$\boxed{-r_A W = -N_{A0} \frac{dx_A}{dt}}$$



$$-r_A = \frac{k P_A}{(1 + k_A P_A + k_B P_B)} \approx k P_A \quad \left\{ \begin{array}{l} \text{as } k_A, k_B \rightarrow \text{very small} \\ \text{as temp } \uparrow \end{array} \right.$$

Adsorption equilibrium constant k_A, k_B

Estimation of rate law parameters:



$$-r_A = \frac{k P_A P_B}{k_A P_A + k_B P_B} \quad k, k_A, k_B$$

$$\frac{P_A P_B}{-r_A} = \frac{1}{k} + \frac{k_A P_A}{k} + \frac{k_B P_B}{k}$$

This is a linear rate eqn. which can be solved to estimate parameters

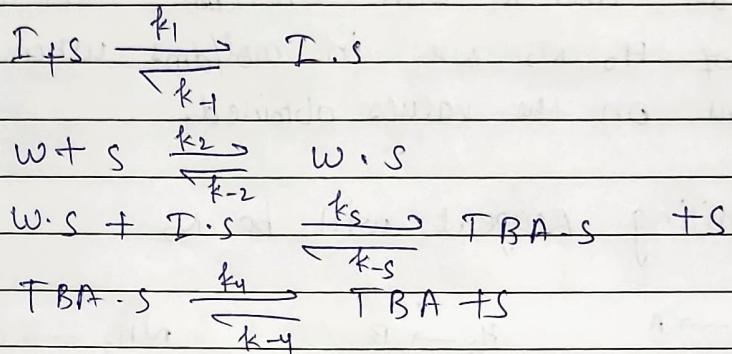
$$-r_A = \left(-\frac{dc_A}{dt} \right)_0 = k c_{A_0}^{\alpha} c_{B_0}^{\beta} \text{ initial rate}$$

$$\ln \left(-\frac{dc_A}{dt} \right)_0 = \ln k + \alpha \ln c_{A_0} + \beta \ln c_{B_0}$$
$$y = a_0 + a_1 x_1 + a_2 x_2$$

catalyst deactivation:

- 1) sintering / ageing
- 2) fouling / coking
- 3) poisoning

1) Tertiary butyl alcohol (TBA) was produced by liquid phase hydration (W) of iso-butene (I) over a solid catalyst. The Rxn mechanism is believed to be



For

$$r_1 = k_1 (C_I \cdot W - C_{I \cdot S}) \quad k_1 = \frac{k_1}{k_{-1}}$$

$$r_2 = k_2 (C_W \cdot W - C_{W \cdot S}) \quad k_2 = \frac{k_2}{k_{-2}}$$

$$r_3 = k_s (C_{W \cdot S} C_{I \cdot S} - C_{T B A \cdot S} C_W) \quad k_s = \frac{k_s}{k_{-s}}$$

$$r_4 = k_4 (C_{T B A \cdot S} - P_{T B A} \cdot C_{T B A}) \quad k_4 = \frac{k_4}{k_{-4}}$$

Surface reaction is rate limiting

$$k_s \ll k_1, k_2, k_4$$

$$\text{So, } \frac{r_3}{k_s} \gg \frac{r_1}{k_1}, \frac{r_2}{k_2}, \frac{r_4}{k_4}$$

$$\frac{r_1}{k_1} = 0 \Rightarrow C_I \cdot W = \frac{C_{I \cdot S}}{k_1}$$

$$\frac{r_2}{k_2} = 0 \Rightarrow C_W \cdot W = \frac{C_{W \cdot S}}{k_2}$$

$$\frac{r_4}{k_4} \geq 0 \Rightarrow C_{TBA,S} = \frac{P_{TBA} \cdot Cu}{k_4}$$

$$r_s = k_s \left(k_2 P_w \cdot Cu \times k_1 P_I \cdot Cu - \frac{k_4 \cancel{P_{TBA}} \cdot Cu^2}{k_4 k_s} \right)$$

$$r_s = k_s \left(k_2 P_w k_1 P_I - \frac{P_{TBA}}{k_4 k_s} \right) Cu^2$$

site balance:

$$C_t = C_{E,S} + C_{W,S} + C_{TBA,S} + Cu$$

$$Cu = k_1 P_I Cu + k_2 P_w Cu + \frac{P_{TBA} \cdot Cu}{k_4} + Cu$$

$$\frac{Cu}{k_1 P_I + k_2 P_w + \frac{P_{TBA}}{k_4} + 1} = Cu$$

$$r_s = k_s \left(k_2 P_w k_1 P_I - \frac{P_{TBA}}{k_4 k_s} \right) \left(\frac{C_t^2}{\left(1 + k_1 P_I + k_2 P_w + \frac{P_{TBA}}{k_4} \right)^2} \right)$$

At $t = 0$

$$P_{TBA} = 0$$

$$r_0 = k_s \left(k_2 C_w k_1 C_I \right) \frac{C_t^2}{\left(1 + k_1 C_I + k_2 C_w \right)^2}$$

Q

The reaction is

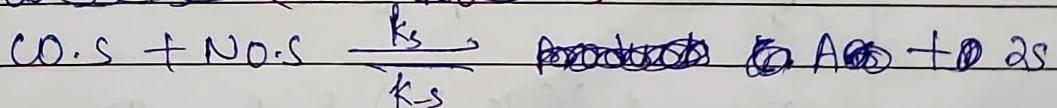
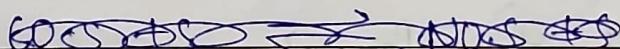
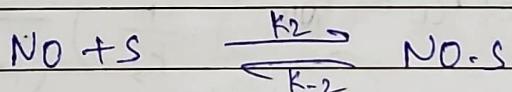
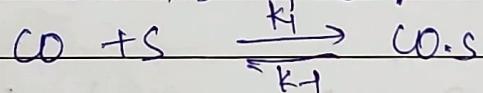


The rate expression is:

$$-r_{NO} = \frac{k_1 P_{NO} P_{CO}}{(1 + K_1 P_{NO} + K_2 P_{CO})^2}$$

Based on your experience, suggest the rate limiting step and derive the rate law which match the above

Irreversible, surface $R \times n$, dual site



$$r_1 = k_1 \left(P_{CO} w - \frac{C_{CO \cdot S}}{K_1} \right)$$

$$r_2 = k_2 \left(P_{NO} w - \frac{C_{NO \cdot S}}{K_2} \right)$$

$$r_s = k_s \left(C_{CO \cdot S} \cdot C_{NO \cdot S} - \frac{P_A w}{K_s} \right)$$

$$k_1, k_2 \gg g_k$$

$$\frac{r_s}{k_s} \gg \frac{r_1}{k_1}, \frac{r_2}{k_2}$$

$$\frac{r_1}{K_1} \geq 0 \quad \text{and} \quad \frac{r_2}{K_2} \geq 0$$

$$C_{O_2} = k_1 P_{CO} C_U \quad \text{and} \quad C_{NO} = k_2 P_{NO} C_U$$

$$r_s = k_s \left(K_1 P_{CO} K_2 P_{NO} - \frac{P_A}{K_s} \right) C_U^2$$

site balance

$$C_t = C_{O_2} + C_{NO} + C_U$$

$$\frac{C_t}{K_1 P_{CO} + K_2 P_{NO} + 1} = C_U$$

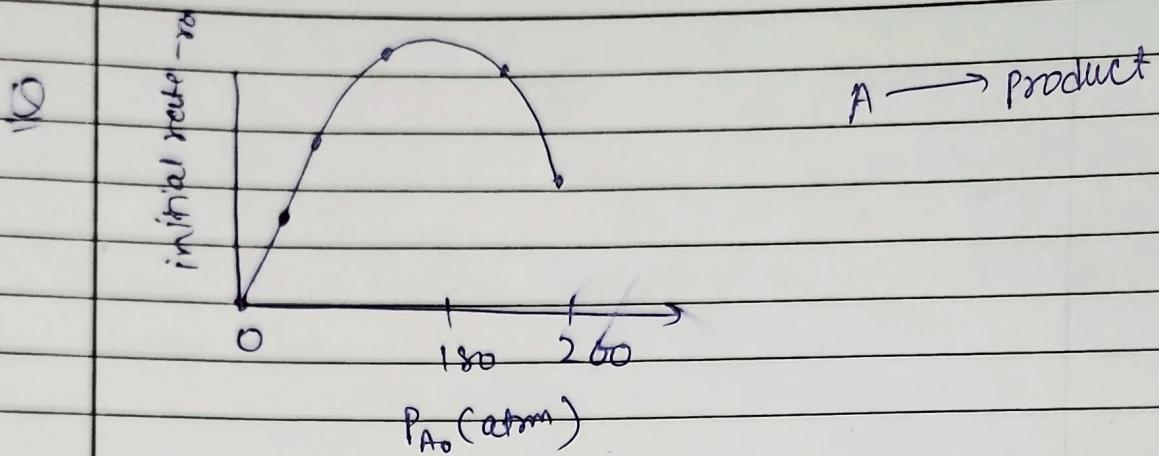
$$r_s = k_s \left(K_1 P_{CO} K_2 P_{NO} - \frac{P_A}{K_s} \right) \frac{C_t^2}{(1 + K_1 P_{CO} + K_2 P_{NO})^2}$$

$$r_s \text{ at } t=0, P_A=0$$

$$r_s = \frac{k_s^2 (K_1 K_2) P_{CO} P_{NO}}{(1 + K_1 P_{CO} + K_2 P_{NO})^2}$$

$$\text{so, } r_s = \frac{K_1 P_{NO} P_{CO}}{(1 + K_1 P_{CO} + K_2 P_{NO})^2}$$

— / —



$$-r_A = \frac{kP_A}{(1+kP_A)^2}$$

when P_A is small, then $1 \gg k_A P_A$, then the denominator is becoming 1, therefore at low P_A $-r_A = kP_A$, which is straight line.

At high P_A , $1 \ll k_A P_A$, then

$$-r_A = \frac{kP_A}{k_A^2 P_A^2} = \frac{k}{P_A}$$

$$-r_{A0}' = \frac{kP_{A0}}{(1+k_1 P_{A0})^2}$$

$$\frac{P_{A0}}{r_{A0}} = \frac{(1+k_1 P_{A0})^2}{k}$$

$$\sqrt{\frac{P_{A0}}{-r_{A0}}} = 1 + k_1 P_{A0}$$