ALGORITHM FOR DETERMINING THE REACTION MECHANISM AND RATE LIMITING STEP

- ✓ Select a mechanism
- ✓ Assume a rate limiting step
- ✓ Derive the rate law by the rate expression of different steps of the mechanism and by site balance
- ✓ Compare with the experimental data

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

IRREVERSIBLE SURFACE REACTION LIMITED RATE LAW

1. <u>Single site</u> $A.S \rightarrow B.S,$ $-r_A = \dfrac{kP_A}{1+K_AP_A+K_BP_B}$

k is the rate constant and K_A and K_B are the adsorption equilibrium constants of A and B respectively

2. <u>Dual site</u> $A.S + S \rightarrow B.S + S,$ $-r_A = \dfrac{kP_A}{(1+K_AP_A+K_BP_B)^2}$

$A.S + B.S \rightarrow C.S + S,$ $-r_A = \dfrac{kP_AP_B}{(1+K_AP_A+K_BP_B+K_CP_C)^2}$

3. <u>Eley Rideal Kinetics</u>

$A.S + B\ (g) \rightarrow C.S$ $-r_A = \dfrac{kP_AP_B}{(1+K_AP_A+K_CP_C)}$

DATA FROM A DIFFERENTIAL REACTOR

- A differential reactor is used to determine rate of the reaction as a function of concentration or partial pressure of reactant.

- It is tube containing a very small amount of catalyst in the form of a thin wafer or disc.
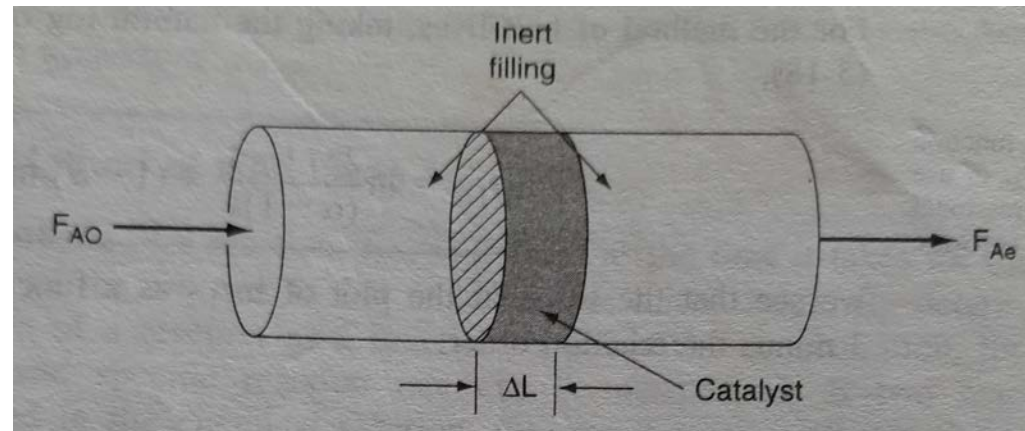
Characteristics of a differential reactor:

➢ The conversion of the reactant in the catalyst bed is extremely small, so the inlet and outlet concentrations are nearly the same

➢ The reactor is assumed to be gradientless, and the rate of the reaction is uniform throughout the reactor.

➢ As the conversion is very low, so the heat change during the reaction is also negligible, hence the reactor is assumed to be isothermal.

Conditions of a differential reactor:

✓ Reactants should not bypass the catalyst bed, i.e., channeling must not occur.

✓ Catalyst life should be long in order to maintain the same rate of the reaction for a sufficiently long time

MOLE BALANCE OF A DIFFERENTIAL REACTOR

The volumetric flow rate through the catalyst bed is monitored. Entering and exiting concentrations are also monitored in this reactor.
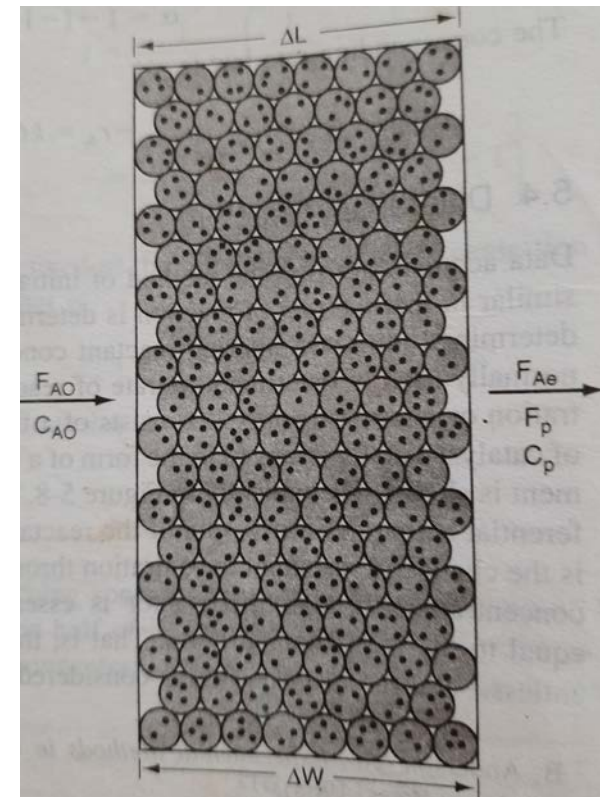
w = Weight of the catalyst

F_{A_0} and F_{A_f} = Inlet and outlet reactant(A) molar flow rates respectively

r_A (mol/g of catalyst.s) = Rate of the reaction

v_0 and v_f = Volumetric flow rates of reactants initially and finally respectively

C_{A_0} and C_A = Initial and final concentration of reactant

C_p = Product concentration

A steady state mole balance on reactant A gives,

Flow rate in − Flow rate out + Rate of generation = Rate of accumulation $\overset{0}{\nearrow}$

$$F_{A_0} - F_{A_f} + \frac{rate\ of\ reaction}{mass\ of\ catalyst} \times mass\ of\ catalyst = 0$$

$$F_{A_0} - F_{A_f} + (r_A).w = 0$$

$$-r_A = \frac{F_{A_0} - F_{A_f}}{w}$$ This is the mole balance equation

In terms of concentration, $-r_A = \dfrac{C_{A_0} v_0 - C_A v_f}{w}$

In terms of product conversion or flow rate of products, $-r_A = \dfrac{F_{A_0} x_A}{w} = \dfrac{F_p}{w}$

x_A = conversion of reactant to product

F_p = molar flow rate of product

When stoichiometric coefficients of A and P are equal, then $F_{A_0} x_A = F_p$

For constant volumetric flow,

$$-r_A = \frac{v_0 (C_{A_0} - C_A)}{w} = \frac{v_0 C_p}{w}$$ here, the rate can be determined by measuring product concentration.

For very little catalyst weight and large volumetric flow of A, $(C_{A_0} - C_A)$ is very small.

$$\therefore -r_A = f(C_{Ab}), \quad C_{Ab} = \frac{C_{A_0} + C_A}{2}$$

$\therefore$ rate is a function of average reactant concentration within the catalyst bed.

However, very little conversion is assumed for differential reactor,

$$C_{Ab} \cong C_{A_0}$$

$$\therefore -r_A = f(C_{A_0})$$

For construction of rate equation for a reaction done in a differential reactor, a series of data is taken. The data can be arranged in a tabular form as below:

For reaction $C \rightarrow B + P$

Run no.	P_C	P_P	P_B	$-r_A$
1	0.5	1	1	$-r_{A1}$
2	1	1	1	$-r_{A2}$
3	2	1	1	$-r_{A3}$
4	1	0	0	$-r_{A4}$
5	2	0	0	$-r_{A5}$

The reaction is carried out at different P_C. The first three runs are done with some product mixed with the reactant. The rates of the reaction determined are called product inhibited data. Here the contribution of concentration of products should be taken into account while calculation of rate of the reaction. Other two sets, run 4 and 5 do not have the product mixed with the reactant feed. The rates of the reaction calculated are called pure feed data.

All the design equations for ideal catalytic or fluid-solid reactions can be obtained from their homogeneous reactors analogues, by substituting reactor volume V (for homogeneous) with the catalyst weight w (for heterogeneous).

The reactor volume for heterogeneous reactor is calculated by

$V = \dfrac{w}{\rho_B}$, ρ_B is bulk density of the catalyst.

For an ideal batch reactor, the differential form of design equation for a heterogeneous reaction is

$$-r_A = \frac{1}{w}\frac{dN_A}{dt} = \frac{1}{w}\frac{(dN_{A_0}X_A)}{dt} = \frac{N_{A_0}}{w}\frac{dX_A}{dt}$$

$$-r_A \cdot w = N_{A_0}\frac{dx_A}{dt}$$