CRE-II

unit-3

~~Solid Catalyzed Reactions~~

catalyst -

A substance that enhances the rate of a chemical reaction and is recovered at the end of the reaction without change in its mass and chemical composition is called a catalyst.

Heterogeneous catalyst reactions occur at the fluid-solid interface.

porous catalyst -

A catalyst which has a large area resulting from pores is called as a porous catalyst.

most catalyst solids have surface areas in the 5 to 1000 m^2/g range.

characteristics of solid catalysts

there are two important characteristics of solid catalysts:

i) activity - It is a measure of the accelerating effect that a catalyst has on the rate of a given reaction.

) specificity (or selectivity) - It refers to a property of a catalyst ~~has on the rate~~ to speed up the main reaction in the presence of several side reactions.

Characteristics of catalysed reaction:

1- A catalyst remains unchanged in its amount and chemical composition at the end of the reaction.

2- A small amount of a catalyst is often sufficient to catalyse a reaction.

3- A catalyst does not change the state/position of chemical equilibrium.

4- A catalyst is usually specific in nature.

5- A catalysed reaction generally has a lower activation energy than non-catalysed reaction. The catalysed reaction proceeds at a faster rate.

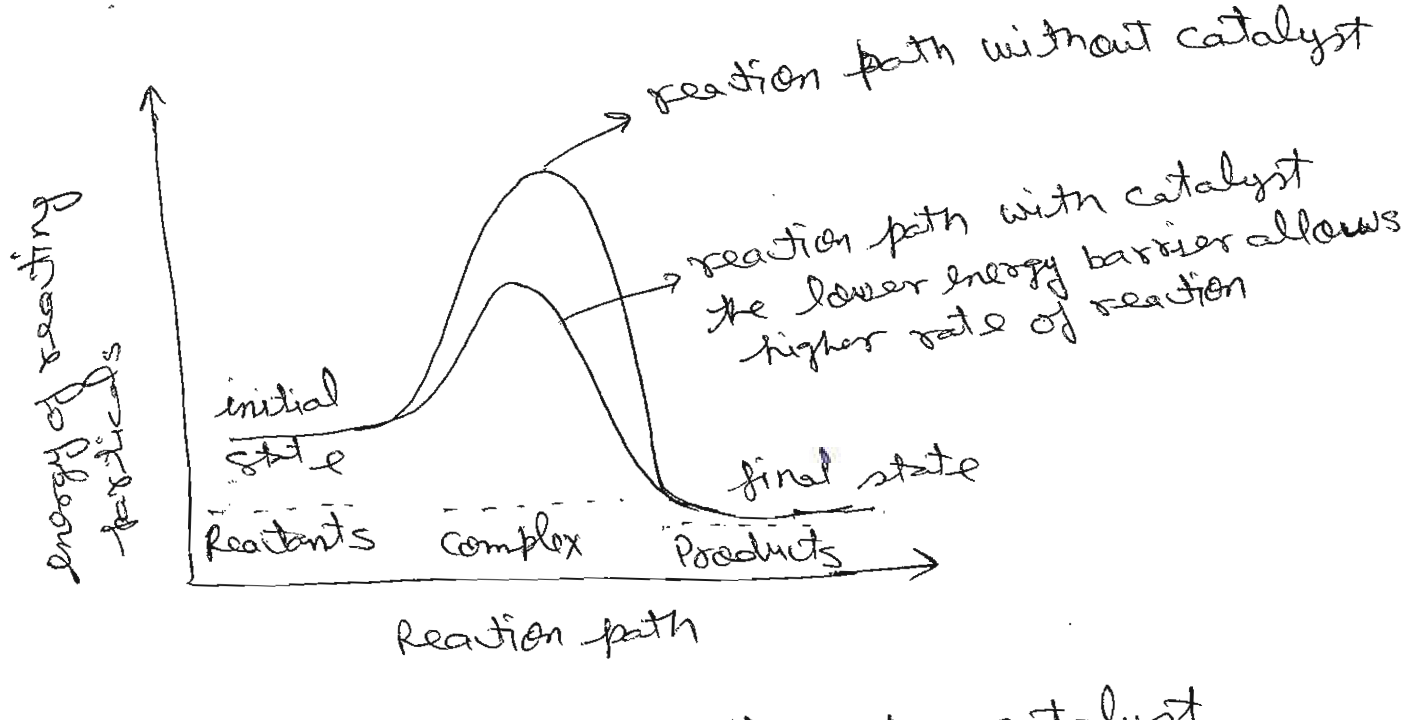


fig - Representation of the action of a catalyst.

Physical properties of solid catalysts

(1) Surface area and Porosity -

The specific surface area of a catalyst or support (in m^2/g) is determined by measuring the volume of gas, usually N_2, needed to provide a monomolecular layer according to the Brunauer - Emmett - Teller (BET) method.

The total surface area of a porous material is given by the sum of the internal and external surface ~~ar~~ areas.

(2) Particle Size and Dispersion

The surface area of active metals dispersed on a support deserves particular consideration since the metal surface area and particle size determine the catalytic properties of supported metal catalysts.

The metal dispersion (D)

$$D = \frac{N_S}{N_T}$$

where N_S - number of metal atoms exposed at the surface

N_T - the total number of metal atoms in a given amount of catalyst.

Dispersion is directly related to particle size and

~~Average crystallite size distributions can be determined independently from X-ray diffraction.~~

(3) Structure and Morphology

X-ray diffraction (XRD) is a routine technique for the identification of phases present in a catalyst. It is based on the comparison of the observed set of reflections of the catalyst sample with those of pure reference phases.

(4) Local Environment of elements

Nuclear spectroscopic methods provide information on the local environment of several selected elements.

Catalyst selection

1- Catalyst selection is a very important activity.

2- It is a significant expenditure.

3- It has a major impaction :
   - Plant efficiency
   - Plant rate
   - Achievement of desired turnaround schedule

4- The major factors influencing catalyst selection include gas temperature and potential contaminants such as halogenated and sulphur and particulate.

5- Selecting Key Performance Criteria

(i) Activity - want high conversion through close approach to equilibrium.

(ii) Pressure drop - low pressure drop improves efficiency & ~~plate~~ plant rate.

(iii) Strength - Want zero breakage during loading and to sustain high plant rate through stable pressure drop with time.

Catalyst Poisoning

1- A substance that reduces the effitiveness of a catalyst in a chemical reaction.

2. In theory, because catalyst are not consumed in chemical reaction, they can be used repeatedly over an indefinite period of time.

3- In pratice, poisons which come from the reacting substances or products of the reaction itself, accumulate on the surface on ~~the surface~~ of solid catalysts and cause their effectiveness to decrease.

4. For this reaction, when the effectiveness of a catalyst has reached a certain low level, steps are taken to remove the poison or replenish the active catalyst ~~has reached a certain~~ component that may have reacted with poison.

e.g

A catalytic converter for an automobile can be poisoned if the vehicle is operated on gasoline containing lead additives. Fuel cells running on hydrogen must use very pure reactants, free of sulfur and carbon compounds.

Mechanism of Solid catalysed reactions

The steps involved in solid catalysed fluid-phase reactions (in converting the reactants into products) are as follows:

1. external or surface diffusion step -

Diffusion of the reactant A from the bulk fluid phase to the external surface of the catalyst through the fluid film.

2- the pore diffusion step.

Diffusion of the reactant from the pore mouth into the catalyst pores.

3- Adsorption of reactant A onto the catalyst surface (external & pore surfaces).

4- chemical reaction of the adsorbed reactant on the surface of the catalyst (e.g $A \rightarrow R$) to form product (surface reaction).

5- Desorption of the products (e.g R) from the surface.

6- Reverse pore diffusion.

Diffusion of the desorbed products from the interior of the catalyst (pores) to the pore mouth at the external surface, i.e. to the ~~su~~ external surface.

7- Reverse external - diffusion -

Diffusion of the products from the external surface into the bulk fluid phase through the fluid film surrounding the catalyst.

diffusion steps → steps 1, 2, 6 & 7.

reaction steps → steps 3, 4 & 5.

Deactivating Catalysts.

Activity of catalysts normally decreases with time.

The life of any catalyst generally depends on type of reactions as well as reaction conditions.

For any catalystic process, the life of catalyst is a major economic factor.

To regenerate or replace deactivated catalysts, the process need to be shutdown and consequently production is disrupted.

Therefore, deactivation of catalysts increase the cost of production significantly.

A catalyst can be deactivated in three ways

1. Poisoning
2. Fouling
3. Sintering or phase transformation

1 - Poisoning - If the catalyst surface is slowly modified by chemisorption on the active sites by materials which are not easily removed, then the process is frequently called poisoning.

Restoration of activity, where possible is called reactivation.

If the adsorption is reversible then a change in operating conditions may be sufficient to reactivate the catalyst.

If the adsorption is not reversible, then we have permanent poisoning.

2- Fouling - If deactivation is rapid and caused by a deposition and a physical blocking of the surface this process is often termed fouling.

Removal of this solid is termed regeneration.

Carbon deposition during catalystic cracking is a common example of fouling:

$$C_{10}H_{22} \rightarrow C_5H_{12} + C_4H_{10} + C\downarrow \text{ on catalyst}$$

3. Sintering or phase transformation -

Because of local high temperature, support of catalyst itself may undergo structural modification or sintering causing a reduction in specific surface area or change in chemical nature of catalyst agent so that it becomes catalytically inactive.

Hence, poisoning & fouling are dependent on concentration of reactant or products or impurities. On the other hand, sintering & phase transformation may be assumed to be independent of fluid phase composition. This is also ~~thef~~ therefore known as independent deactivation.

Steps to reduce deactivation -

Following steps can be taken to reduce the possibility of deactivation of catalysts:

a - Removal of poison material form feed.
b - Use of hydrogen which reduces coking
c - Removal of hot spot by proper design of reactor / process Control to prevent any thermal deactivation.

Mechanisms of catalyst Deactivation

The deactivation of a catalysts can occur by different mechanism

1. Parallel deactivation -

the reactant (A) may produce a side product which deposits on and deactivates the surface. This is called parallel deactivation.

Deposition depends on reactant concentration.

$$\begin{tikzcd}[row sep=small] & R \\ A \arrow[ur] \arrow[dr] & \\ & P\downarrow \end{tikzcd} \qquad \text{or} \qquad A \longrightarrow R + P\downarrow$$

2. Series deactivation -

the reaction product (R) may decompose or react further to produce a material which the deposits on and deactivates the surface. This is called series deactivation.

In this case, deposition depends on product concentration

$$A \longrightarrow R \longrightarrow P\downarrow$$

3 - Side-by-side ~~Reaction~~ deactivation -

An impurity in the feed (P) may deposit on and deactivates the surface. This is called side-by-side deactivation.

Deposition depends on concentration of impurities in the feed.

$$A \longrightarrow R$$
$$P \longrightarrow P\downarrow$$

4- Independent deactivation -

This catalyst decay involves the structural modification or sintering of the catalyst surface caused by exposure of the catalyst to extreme condition such as high temp.

This type of decay is dependent on the time that the catalyst spends in the high temperature environment, & since it is unaffected by the materials in the gas stream.

The Rate & Performance Equations -

The activity of a catalyst pellet at any time is defined as

$$a = \frac{\text{rate at which the pellet converts reactant A}}{\text{rate of reaction of A } \cancel{\text{wh}} \text{ with a fresh pellet}}$$

$$a = \frac{-r'_A}{-r'_{A0}}$$

$$\left(\begin{array}{c}\text{reaction}\\ \text{rate}\end{array}\right) = f_1\left(\begin{array}{c}\text{main stream}\\ \text{temperature}\end{array}\right)\cdot f_3\left(\begin{array}{c}\text{main stream}\\ \text{Concentration}\end{array}\right)\cdot f_5\left(\begin{array}{c}\text{present activity}\\ \text{of the catalyst}\\ \text{pellet}\end{array}\right)$$

$$\left(\begin{array}{c}\text{deactivation}\\ \text{rate}\end{array}\right) = f_2\left(\begin{array}{c}\text{main stream}\\ \text{temperature}\end{array}\right)\cdot f_4\left(\begin{array}{c}\text{main stream}\\ \text{Concentration}\end{array}\right)\cdot f_6\left(\begin{array}{c}\text{present state}\\ \text{of the catalyst}\\ \text{pellet}\end{array}\right)$$

for n^{th} order reaction,

$$-r'_A = k' C_A^n a$$

where a - present activity of the catalyst pellet.

Arrhenius temperature dependency, & isothermal conditions.

$$-r_A' = K_0' e^{-E/RT} C_A^n \cdot a$$

for deactivation which in dependent on the ~~temp~~ concentration of gas-phase species.

$$-\frac{da}{dt} = K_d C_i^m a^d = K_{do} e^{-E_d/RT} \cdot C_i^m \cdot a^d$$

d - order of deactivation

m - measures the concentration dependency

E_d - activation energy or temperature dependency of the deactivation.

i = A (reactant), R (product), P (3rd substance)

For parallel deactivation

$$\begin{tikzcd} A \arrow[r] \arrow[dr] & R \\ & P\downarrow \end{tikzcd}$$

$$\left.\begin{aligned} -r_A' &= K' C_A^n a \\ -\frac{da}{dt} &= K_d C_A^m a^d \end{aligned}\right.\begin{aligned} &\text{– Reaction rate} \\ &\text{– Deactivation rate} \end{aligned}$$

For series deactivation

$$A \longrightarrow R \longrightarrow P\downarrow$$

$$\left.\begin{aligned} -r_A' &= K' C_A^n a \\ -\frac{da}{dt} &= K_d C_R^m a^d \end{aligned}\right\}$$

For side-be side deactivation

$A \rightarrow R$

$P \rightarrow P\downarrow$

$$\left.\begin{aligned} -r_A' &= k' C_A^n a \\ -\frac{da}{dt} &= k_d C_P^m a^d \end{aligned}\right\}$$

For independent deactivation
(concentration independent)

$$\left.\begin{aligned} -r_A' &= k' C_A^n a \\ -\frac{da}{dt} &= k_d a^d \end{aligned}\right\}$$

In certain reaction, such as isomerization & cracking, deactivation may be caused both by reactant & product

$A \rightarrow R$

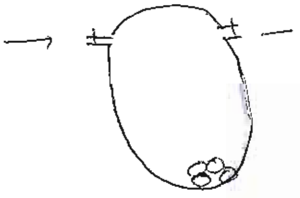
$A \rightarrow P\downarrow$

$R \rightarrow P\downarrow$

$$-\frac{da}{dt} = k_d (C_A + C_R)^m a^d$$

The Rate Equation from Experiment

Batch Solid - for ~~f~~ slow deactivation



Batch for both solid & fluid

Plug flow for fluid

Flow of solids - for fast deactivation

Solids ~ plug flow

Fluid - plug flow

fig - Slow deactivation may use a batch of Solid in experimentation

Fast deactivation requires a flow of solids.

~~Bea~~ Because of the ease of experimentation batch-solids devices are much preferred, however, they can only be used when deactivation is slow enough.

Batch - Solids: Determining the rate for independent Deactivation

for Ist order reaction & first-order deactivation & Concentration independent

Based on unit mass of solid in fluid-solid systems

$$-r'_A = k' C_A a \quad \text{with } \varepsilon_A = 0 \qquad \text{— ①}$$

$$-\frac{da}{dt} = k_d a \qquad \text{— ②}$$

Batch-solids, Batch Fluid -

$$-r_A = -\frac{dC_A}{dt} = \frac{W}{V}\left(-\frac{1}{W}\frac{dN_A}{dt}\right) = \frac{W}{V}(-r'_A)$$

we know

$$(-r_A)V = (-r_A)W$$

$$-\frac{dC_A}{dt} = \frac{W}{V}k' C_A a \quad — ③$$

$$-\frac{da}{dt} = k_d a \quad — ②$$

by integration $\int \frac{da}{a} = -k_d \int dt$

$$\ln a = -k_d t + \ln a_0$$

(a_0 - constant)

$$\ln \frac{a}{a_0} = -k_d t$$

$$a = a_0 e^{-k_d t} \quad — ④$$

for unit initial activity, or $a_0 = 1$

$$a = e^{-k_d t} \quad — ⑤$$

put in ③

$$-\frac{dC_A}{dt} = \frac{W}{V}k' C_A \cdot e^{-k_d t}$$

~~dC_A~~

$$-\frac{dC_A}{C_A} = \frac{W}{V} K' e^{-K_d t}\, dt$$

by integration

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \frac{W}{V} K' \int_0^t e^{-K_d t}$$

$$\ln \frac{C_{A0}}{C_A} = \frac{W K'}{V K_d}\left(1 - e^{-K_d t}\right) \quad \text{——} ⑥$$

At infinite time, the concentration of reactant in an irreversible reaction does not drop to zero.

$$\ln \frac{C_{A0}}{C_{A\infty}} = \frac{W K'}{V K_d} \quad \text{——} ⑦$$

from ⑥ & ⑦

$$\ln \frac{C_{A0}}{C_A} = \ln \frac{C_{A0}}{C_{A\infty}} - \frac{W K'}{V K_d} e^{-K_d t}$$

$$\ln \frac{C_A}{C_{A\infty}} = \frac{W K'}{V K_d} e^{-K_d t}$$

taking log on both side

$$\boxed{\ln \ln \frac{C_A}{C_{A0}} = \ln \frac{W K'}{V K_d} - K_d t} \quad \text{——} ⑧$$

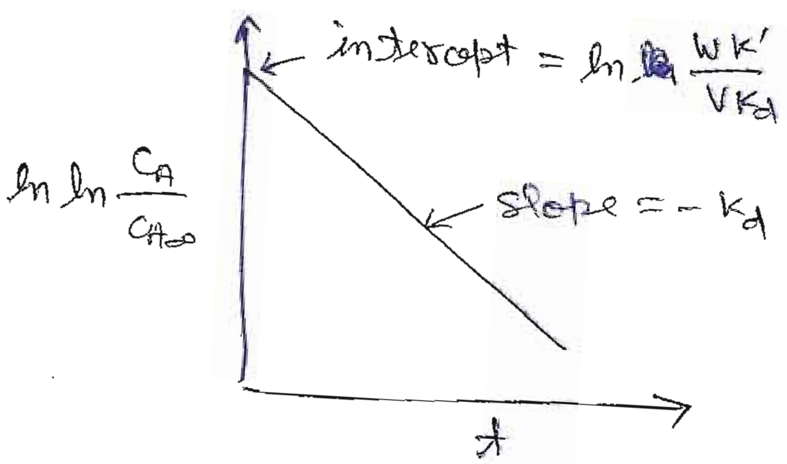


fig - Kinetic expressions for batch-solid, batch-fluid reactor.

Batch-solid, Mixed Constant Flow of fluid

$$-r_A' = K' C_A a$$

for mixed flow, space time

$$\tau' = \frac{W C_{A0}}{F_{A0}} = \frac{W}{v} = \frac{C_{A0} - C_A}{(-r_A')} \qquad — ⑧$$

$$\tau' = \frac{C_{A0} - C_A}{K' C_A a} \Rightarrow K' a \tau' C_A = C_{A0} - C_A$$

$$\Rightarrow C_A (K' a \tau' + 1) = C_{A0}$$

$$\frac{C_{A0}}{C_A} = 1 + K' a \tau' \qquad — ⑩$$

from equ ⑤ $a = e^{-K_d t}$ put in ⑩

$$\frac{C_{A0}}{C_A} = 1 + K' e^{-K_d t} \tau' \qquad — ⑪$$

$$\frac{C_{A0}}{C_A} - 1 = K'\tau' e^{-K_d t}$$

taking log on both side

$$\boxed{\ln\left(\frac{C_{A0}}{C_A} - 1\right) = \ln(K'\tau') - K_d t} \quad \text{— ⑫}$$

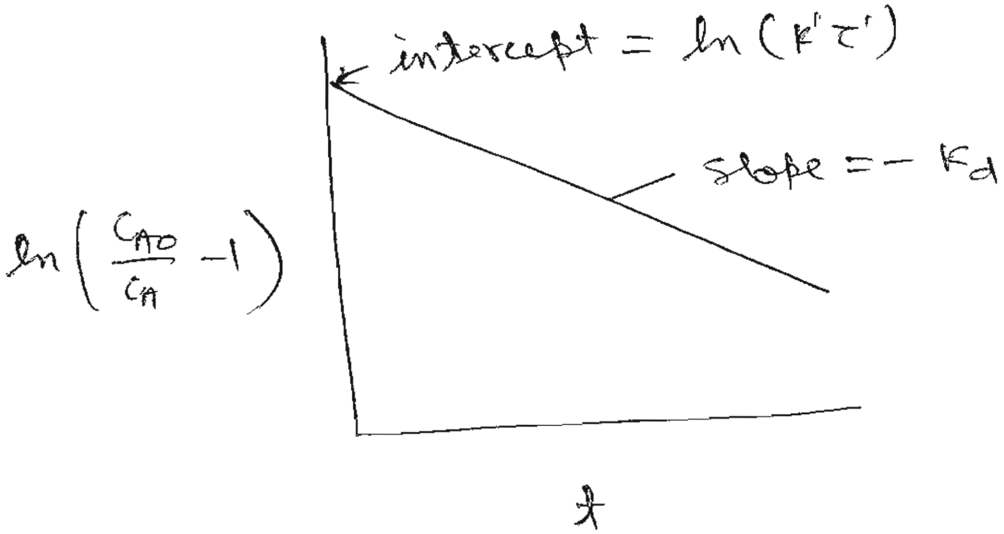


fig - kinetic expression for a batch of solids & steady-state mixed flow of fluids.

<u>Batch solid, mixed changing flow of fluid (to keep C_A fixed)</u>

For steady flow in a mixed reactor

for eqn ⑪

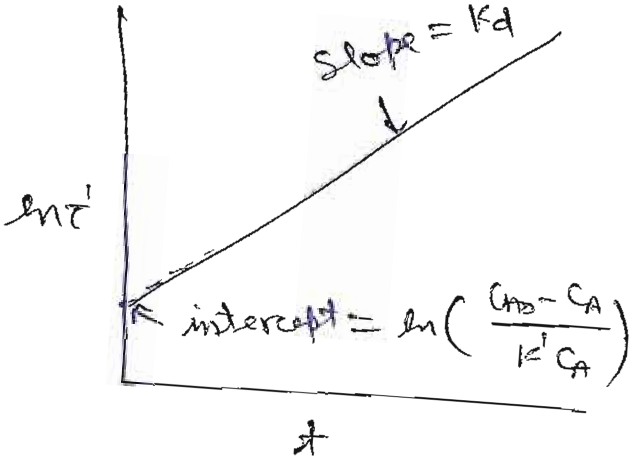
$$\frac{C_{A0}}{C_A} = 1 + K' e^{-K_d t} \tau' \quad \text{—— ⑪}$$

To keep C_A constant the flow rate must be slowly changed with time.

$$C_{A0} = C_A + k' e^{-k_d t} \tau' C_A$$

$$C_{A0} - C_A = k' e^{-k_d t} \tau' C_A$$

$$\frac{C_{A0} - C_A}{k' C_A} = \tau' e^{-k_d t}$$



taking log on both side

$$\boxed{\ln \tau' = k_d t + \ln\left(\frac{C_{A0} - C_A}{k' C_A}\right)} \quad — ⑬$$

Batch-solid, Plug Constant Flow of fluid -

for plug flow

$$\frac{W}{F_{A0}} = \int \frac{dX_A}{-r'_A} = \int \frac{dX_A}{k' a C_A} = \frac{1}{k' a} \int \frac{dX_A}{C_A}$$

$$= -\frac{1}{k' a} \int \frac{dC_A}{C_{A0} \cdot C_A}$$

$$dX_A = -\frac{dC_A}{C_{A0}}$$

$$\frac{W}{F_{A0}} = \frac{1}{k' a C_{A0}} \ln \frac{C_{A0}}{C_A} \quad — ⑭$$

$$\tau' = \frac{W C_{A0}}{F_{A0}} = \frac{1}{k' a} \ln \frac{C_{A0}}{C_A}$$

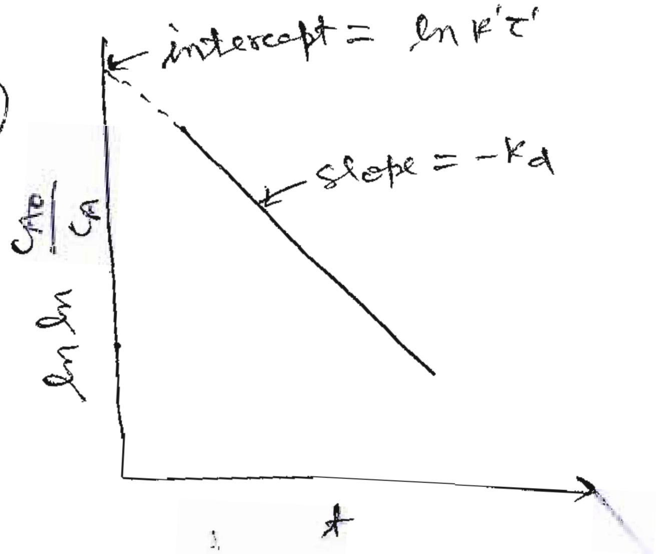
from ⑤ $a = e^{-k_d t}$

$$\tau' = \frac{1}{k' e^{-k_d t}} \ln \frac{C_{A0}}{C_A} \quad \text{—— (15)}$$

$$\ln \frac{C_{A0}}{C_A} = \tau' k' \, e^{-k_d t}$$

taking log on both side

$$\boxed{\ln \ln \frac{C_{A0}}{C_A} = \ln \tau' k' - k_d t} \quad \text{—— (16)}$$



Batch-solid, Plug changing Flow of fluid (to keep C_A fixed)

for equ ⑮

$$\tau' = e^{k_d t} \cdot \frac{1}{k'} \ln \frac{C_{A0}}{C_A}$$

taking log

$$\ln \tau' = k_d t + \ln \left(\frac{1}{k'} \ln \frac{C_{A0}}{C_A} \right) \quad \text{—— (17)}$$