14CH604: CHEMICAL REACTION ENGINEERING – II

APRIL 2018

1. A). The fluid elements travel in different directions and therefore their ages are different. The distribution of residence times expressed in terms of mean, variance and skewness.

    B) Macro fluid contains number of micro fluid elements. each macro molecule approximated as a globule. Each macro molecule may behave like a batch reactor. higher conversions possible with micro fluids.

    C). is a measure of extent of surface reaction rate influenced by the pore diffusion resistance.

    D). these are foreign or unwanted substance present in feed mixture which inhibits the activity of a catalyst

    E). The reaction which occurs in single step are called single reactions. All elementary reactions are single step reactions.

    The reactions which occur in two or more steps are called multiple reactions like series and parallel reactions.

    F). It is an equilibrium relationship between concentration of solute adsorbed on adsorbent surface and concentration of solute in fluid medium at constant temperature.

    G) The mechanism which offer higher resistance or the slowest step is called rate controlling step or mechanism.

    H) Adsorption by strong chemical bonds which irreversible.

    I) A know quantity of tracer injected in one shot at time t=0

    J) For exothermic reactions, conversion decreases with temperature whereas conversion increases with temperature in case of endothermic reaction.

    K) The porous catalyst offers more surface area than non porous catalyst. The pore volume is measured using helium mercury method.

    L) Ideal reactors assumes uniform and infinite mixing in case of CSTR, flat velocity profile in case of tubular reactors. Non ideal reactors are real reactors in which dead zones, channeling, bypassing and short circuiting of fluid generally observed.

2. A)4M The equilibrium composition, as governed by the equilibrium constant, changes with temperature, and from thermodynamics the rate of change is given by
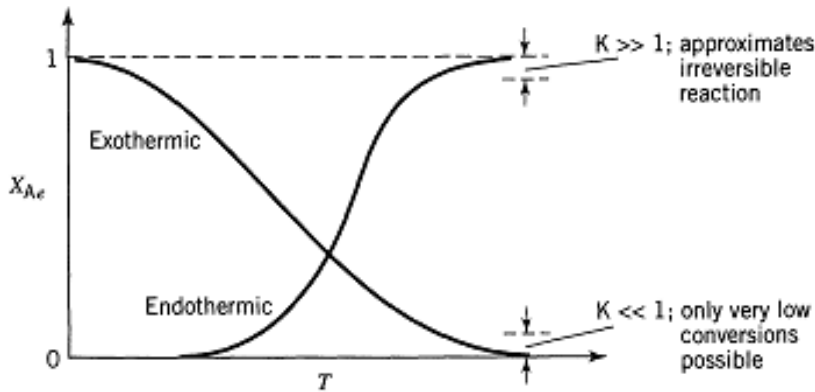
$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{R T^2}$$

$$\boxed{\ln \frac{K_2}{K_1} = -\frac{\Delta H_r}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

When heat of reaction is function of temperature

$$\ln \frac{K_2}{K_1} = \frac{1}{R}\int_{T_1}^{T_2}\frac{\Delta H_r}{T^2}\,dT$$

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^{T}\nabla C_p\,dT$$

$$\mathbf{R}\ln\frac{K_2}{K_1} = \nabla\alpha\ln\frac{T_2}{T_1} + \frac{\nabla\beta}{2}(T_2 - T_1) + \frac{\nabla\gamma}{6}(T_2^2 - T_1^2)$$

$$+ \left(-\Delta H_{r0} + \nabla\alpha T_0 + \frac{\nabla\beta}{2}T_0^2 + \frac{\nabla\gamma}{3}T_0^3\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

2M

1. The thermodynamic equilibrium constant is unaffected by the pressure of the system, by the presence or absence of inerts, or by the kinetics of the reaction, but is affected by the temperature of the system.

2. Though the thermodynamic equilibrium constant is unaffected by pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.

3. For an increase in temperature, equilibrium conversion rises for endothermic reactions and drops for exothermic reactions.

4. For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction.

5. A decrease in inerts for all reactions acts in the way that an increase in pressure acts for gas reactions

B). 2m: Definition of adiabatic operation, diagram
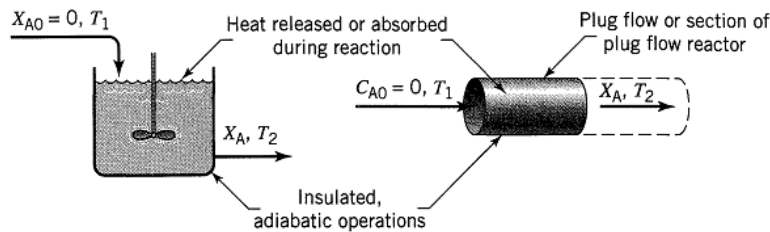
$\mathbf{C'_p}, \mathbf{C''_p}$ = Mean specific heat of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

$\mathbf{H'}, \mathbf{H''}$ = enthalpy of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

ΔH_{ri} = heat of reaction per mole of entering reacting A, and at temperature T_i.

4M: Balance equations

Enthalpy of entering feed:

$$\mathbf{H'_1} = \mathbf{C'_p}\,(T_1 - T_1) = 0 \text{ J/mol A}$$

Enthalpy of leaving stream:

$$\mathbf{H''_2}X_A + \mathbf{H'_2}(1 - X_A) = \mathbf{C''_p}\,(T_2 - T_1)X_A + \mathbf{C'_p}(T_2 - T_1)(1 - X_A) \text{ J/mol A}$$

Energy absorbed by reaction:

$$\Delta H_{r1} X_A \text{ J/mol A}$$

Replacing these quantities in the energy balance,

$$\text{input} = \text{output} + \text{accumulation} + \text{disappearance by reaction}$$

we obtain at steady state

$$0 = [\mathbf{C''_p}\,(T_2 - T_1)\,X_A + \mathbf{C'_p}\,(T_2 - T_1)(1 - X_A)] + \Delta H_{r1} X_A$$

2M : Final expressions

By rearranging,

$$X_A = \frac{\mathbf{C'_p}\,(T_2 - T_1)}{-\Delta H_{r1} - (\mathbf{C''_p} - \mathbf{C'_p})\,(T_2 - T_1)} = \frac{\mathbf{C'_p}\Delta T}{-\Delta H_{r1} - (\mathbf{C''_p} - \mathbf{C'_p})\Delta T}$$

$$X_A = \frac{\mathbf{C'_p}\Delta T}{-\Delta H_{r2}} = \left(\frac{\text{heat needed to raise feed stream to } T_2}{\text{heat released by reaction at } T_2} \right)$$

3. A) 3M: We define the optimum temperature progression to be that progression which minimizes V/F_{A0} for a given conversion of reactant. This optimum may be an isothermal or it may be a changing temperature: in time for a batch reactor, along the length of a plug flow reactor, or from stage to stage for a series of mixed flow reactors. It is important to know this progression because it is the ideal which we try to approach with a real system. It also allows us to estimate how far any real system departs from this ideal.

3M
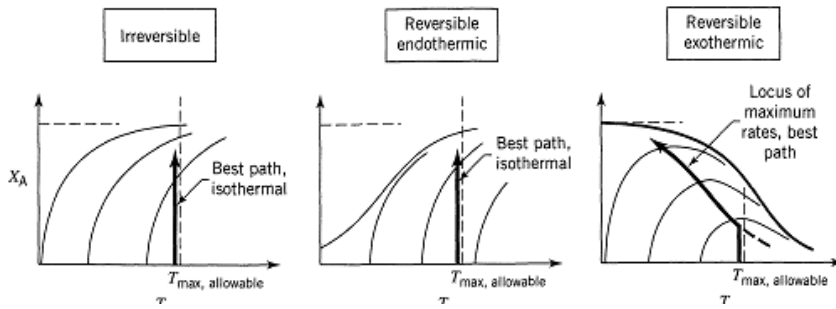
B) Formula

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_r}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

4. **The Pulse Experiment**

Let us find the E curve for a vessel of volume V m^3 through which flows v m^3/s of fluid. For this instantaneously introduce M units of tracer (kg or moles) into the fluid entering the vessel, and record the concentration-time of tracer leaving the vessel. This is the C- curve. From the material balance for the vessel we find
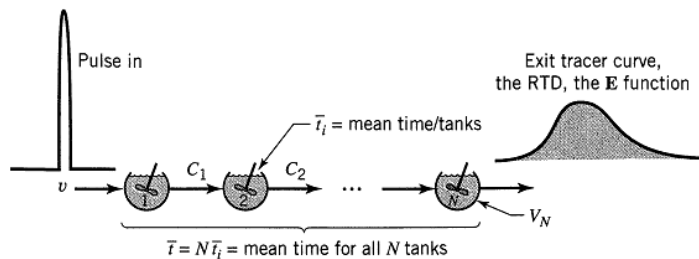
$$\begin{pmatrix}\text{Area under the}\\ C_{\text{pulse}} \text{ curve}\end{pmatrix}: \quad A = \int_0^\infty C\,dt \cong \sum_i C_i \Delta t_i = \frac{M}{v} \quad \left[\frac{\text{kg}\cdot\text{s}}{\text{m}^3}\right]$$

$$\begin{pmatrix}\text{Mean of the}\\ C_{\text{pulse}} \text{ curve}\end{pmatrix}: \quad \bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} \cong \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v} \quad [s]$$

$$E = \frac{C_{\text{pulse}}}{M/v}$$
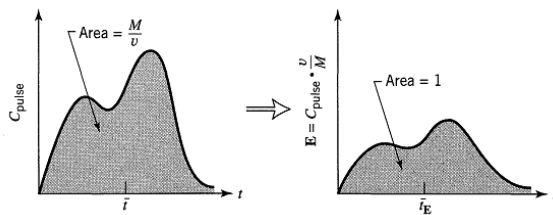
Tanks in series model

2M

At any time t after the tracer is introduced make a material balance, thus

$$\begin{pmatrix} \text{rate of disappearance} \\ \text{of tracer} \end{pmatrix} = \begin{pmatrix} \text{input} \\ \text{rate} \end{pmatrix} - \begin{pmatrix} \text{output} \\ \text{rate} \end{pmatrix}$$

In symbols this expression becomes

$$V_1 \frac{dC_1}{dt} = 0 - vC_1 \qquad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

where C_1 is the concentration of tracer in tank "1." Separating and integrating then gives

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\frac{1}{\bar{t}_1} \int_0^t dt$$

or

$$\frac{C_1}{C_0} = e^{-t/\bar{t}_1}$$

4M

For the second tank where C_1 enters, C_2 leaves, a material balance gives

$$V_2 \frac{dC_2}{dt} = v \cdot \underbrace{\frac{C_0}{\bar{t}_1} e^{-t/\bar{t}_1}}_{C_1} - vC_2 \qquad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

$$\boxed{\begin{aligned}
& \bar{t}\, \mathbf{E} = \left(\frac{t}{\bar{t}} \right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/\bar{t}} && \cdots \bar{t} = N\bar{t}_i \cdots \sigma^2 = \frac{\bar{t}^2}{N} \\[2mm]
& \bar{t}_i\, \mathbf{E} = \left(\frac{t}{\bar{t}_i} \right)^{N-1} \frac{1}{(N-1)!} e^{-t/\bar{t}_i} && \cdots \bar{t}_i = \frac{\bar{t}}{N} \cdots \sigma^2 = N\bar{t}_i^2 \\[2mm]
& \mathbf{E}_{\theta i} = \bar{t}_i\, \mathbf{E} = \frac{\theta_i^{N-1}}{(N-1)!} e^{-\theta_i} && \cdots \sigma_{\theta i}^2 = N \\[2mm]
& \mathbf{E}_\theta = (N\bar{t}_i)\, \mathbf{E} = N \frac{(N\theta)^{N-1}}{(N-1)!} e^{-N\theta} \cdots \sigma_\theta^2 = \frac{1}{N}
\end{aligned}}$$

5. .

$$\bar{t} = \frac{\int_0^\infty tC\, dt}{\int_0^\infty C\, dt} \cong \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v}$$

t	0	10	20	30	40	50	60	70
tC	0	380	800	1200	1560	1850	2160	2450
E	0.013	0.015	0.015	0.015	0.015	0.014	0.0136	0.013
$t-\bar{t}$	-34.61	-24.61	-14.61	-4.61	5.39	15.39	25.39	35.39
$(t-\bar{t})^2 E$	15.57	8.48	3.2	0.32	0.43	3.31	8.75	16.28

The variance $\sigma^2 = \int_0^\infty (t - \bar{t})^2 E\, dt = 390.33$

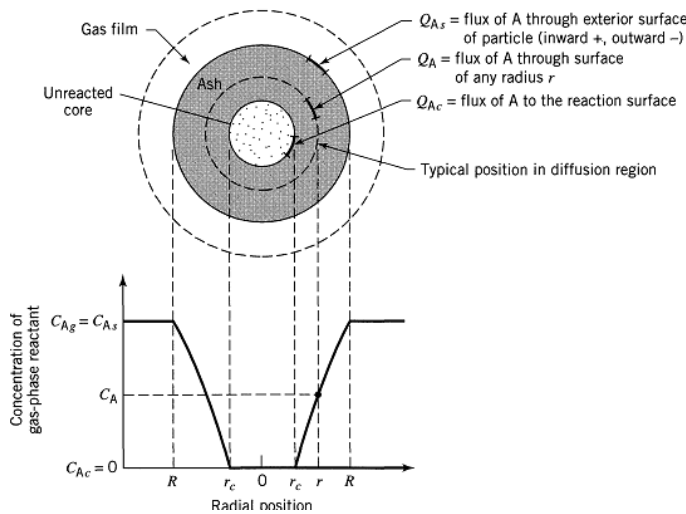The number of tanks arranged in series, $N = \dfrac{\bar{t}^2}{\sigma^2} = 3.07$

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k\bar{t}_i)^N} = \frac{1}{\left(1 + \dfrac{k\bar{t}}{N}\right)^N}$$

Mean residence time = 34.61 min
Conversion using MFR = 63.4%
PFR = 82.3%, TIS MODEL: 74.6%

6. diagram and balance equation-2+3m

The rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{constant}$$

$$Q_A = \mathscr{D}_e \frac{dC_A}{dr}$$

$$-\frac{dN_A}{dt} = 4\pi r^2 \mathscr{D}_e \frac{dC_A}{dr} = \text{constant}$$

Integration and result -4m

Integrating across the ash layer form R to r_c, we obtain

$$-\frac{dN_A}{dt} \int_R^{r_c} \frac{dr}{r^2} = 4\pi \mathscr{D}_e \int_{C_{Ag}=C_{As}}^{C_{Ac}=0} dC_A$$

or

$$-\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R}\right) = 4\pi \mathscr{D}_e C_{Ag}$$

$$-\rho_B \int_{r_c=R}^{r_c} \left(\frac{1}{r_c} - \frac{1}{R}\right) r_c^2 \, dr_c = b\mathscr{D}_e C_{Ag} \int_0^t dt$$

$$t = \frac{\rho_B R^2}{6b\mathscr{D}_e C_{Ag}} \left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3\right]$$

Complete conversion (2M), expression in term of conversion(2M)

For the complete conversion of a particle, $r_c = 0$, and the time required is

$$\tau = \frac{\rho_B R^2}{6b\mathscr{D}_e C_{Ag}}$$

$$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3$$

which in terms of fractional conversion, as given in Eq. 10, becomes

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$$

7. A)
   3x2=6m
   Film diffusion control

$$\frac{t}{\tau} = X_B$$

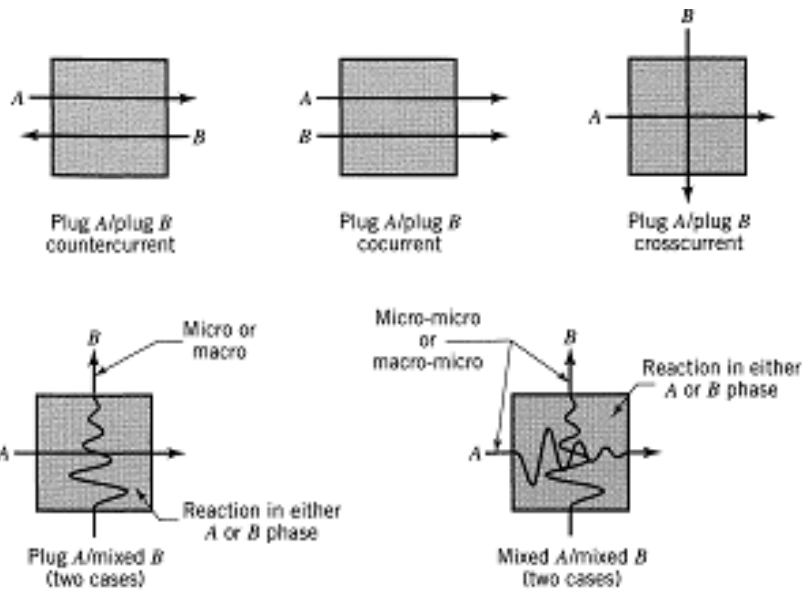Ash layer diffusion control

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$$
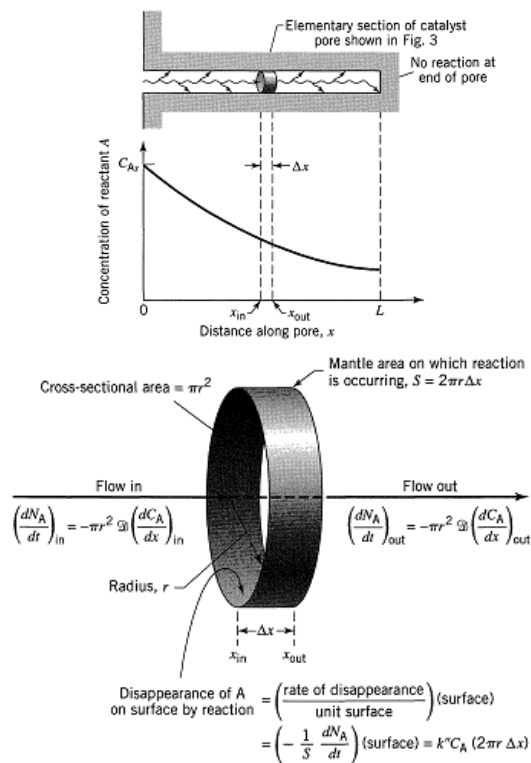
Chemical reaction control

$$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$$

For the given data, it is a chemical reaction controlled reaction.
B) Diagrams and description

Plug A/plug B
countercurrent

Plug A/plug B
cocurrent

Plug A/plug B
crosscurrent

Plug A/mixed B
(two cases)

Mixed A/mixed B
(two cases)

8. .

diagrams and element analysis-2M

Elementary section of catalyst pore shown in Fig. 3

No reaction at end of pore

c_{A_s}

Δx

x_{in} x_{out} L

Distance along pore, x

Concentration of reactant A

Cross-sectional area $= \pi r^2$

Mantle area on which reaction is occurring, $S = 2\pi r \Delta x$

Flow in

$$\left(\frac{dN_A}{dt}\right)_{in} = -\pi r^2 \mathscr{D}\left(\frac{dC_A}{dx}\right)_{in}$$

Flow out

$$\left(\frac{dN_A}{dt}\right)_{out} = -\pi r^2 \mathscr{D}\left(\frac{dC_A}{dx}\right)_{out}$$

Radius, r

Δx

x_{in} x_{out}

Disappearance of A on surface by reaction $= \left(\dfrac{\text{rate of disappearance}}{\text{unit surface}}\right)$ (surface)

$= \left(-\dfrac{1}{S}\dfrac{dN_A}{dt}\right)$ (surface) $= k''C_A\,(2\pi r\,\Delta x)$

3M: MOLAR BALANCE

output - input + disappearance by reaction = 0

$$-\pi r^2 \mathscr{D}\left(\frac{dC_A}{dx}\right)_{out} + \pi r^2 \mathscr{D}\left(\frac{dC_A}{dx}\right)_{in} + k''C_A(2\pi r\Delta x) = 0$$

2M   Simplification

$$\frac{d^2C_A}{dx^2} - \frac{2k''}{\mathscr{D}r}C_A = 0$$

$$\frac{d^2C_A}{dx^2} - \frac{k}{\mathscr{D}}C_A = 0$$

$$C_A = M_1e^{mx} + M_2e^{-mx}$$

$$m = \sqrt{\frac{k}{\mathscr{D}}} = \sqrt{\frac{2k''}{\mathscr{D}r}}$$

$$M_1 = \frac{C_{As}e^{-mL}}{e^{mL} + e^{-mL}}, \qquad M_2 = \frac{C_{As}e^{mL}}{e^{mL} + e^{-mL}}$$

3M   Solution

$$\frac{C_A}{C_{As}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL}$$

2M   Definition and answer

$$\text{Effectiveness factor, } \mathscr{E} = \frac{(\text{actual mean reaction rate within pore})}{(\text{rate if not slowed by pore diffusion})}$$

$$= \frac{\bar{r}_{A,\text{ with diffusion}}}{r_{A,\text{ without diffusion resistance}}} \qquad\qquad \mathscr{E}_{\text{first order}} = \frac{\overline{C}_A}{C_{As}} = \frac{\tanh mL}{mL}$$

9. A) 2M→ Catalyst description

In a thermodynamically feasible chemical reaction, when addition of a small amount a chemical substance increases the rate of attainment of chemical equilibrium but the substance itself does not undergo any chemical change, then the reaction is called a catalytic reaction. The substance that enhances the reaction rate is called a catalyst. Catalysts work by providing alternative mechanism involving a different transition state of lower energy.
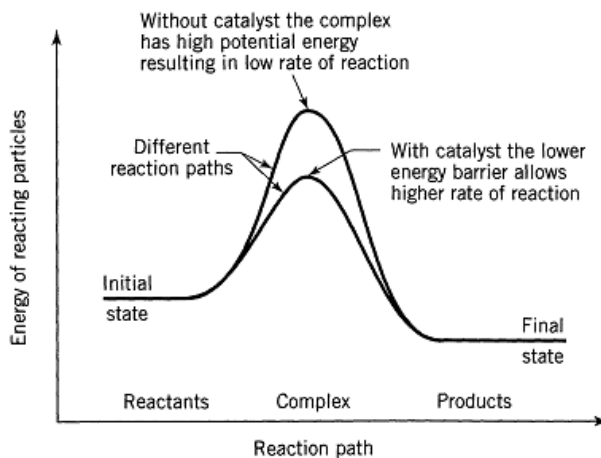
2M→ Catalyst deactivation

It is defined as decreasing catalyst activity or efficiency due to inert materials present in reaction mixture or presents of poisons and inhibitors.

B) Single mechanism (1M)

A + X → A.X   Adsorption of A on catalyst surface
A.X + B → C.X   Surface reaction
C.X → C + X   Desorption of Product C
3M

Step 1. A molecule is adsorbed onto the surface and is attached to an active site.

Step 2. It then reacts either with another molecule on an adjacent site (dual-site mechanism), with one coming from the main gas stream (single-site mechanism), or it simply decomposes while on the site (single-site mechanism).

Step 3. Products are desorbed from the surface, which then frees the site.

Net rate expressions for individual steps
1M
Total site balance
2M Simplification

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