Lecture # 32 CHE331A

Catalysis

- **Non-isothermal reactors**

- **Non-ideal reactors**

- **Catalysis**

- **Kinetics of Catalytic Reactions**

- **Diffusion and Reaction in porous catalysts**

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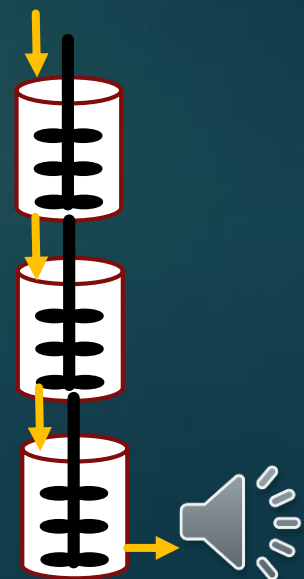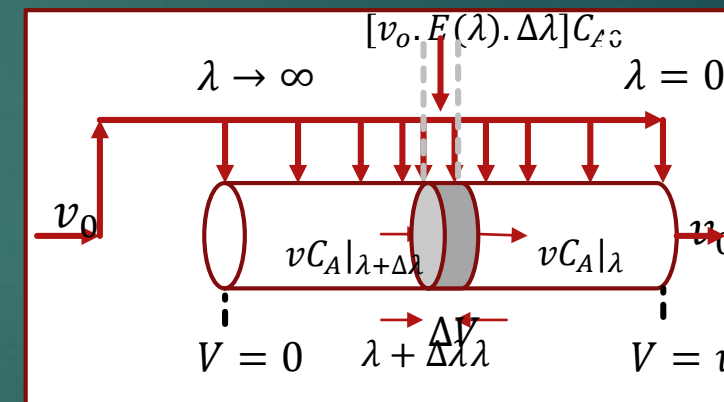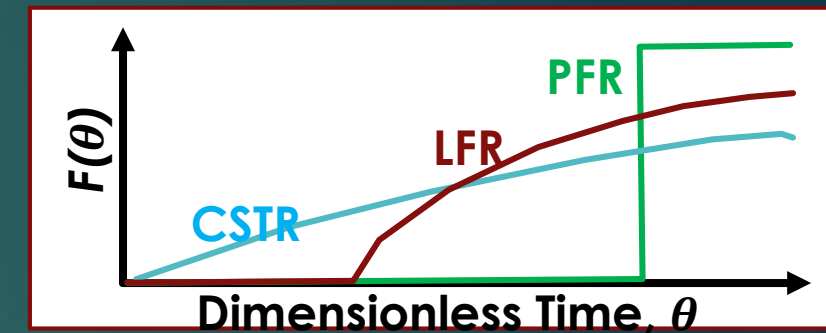# Previously, non-ideal reactors

▶ Residence time distribution
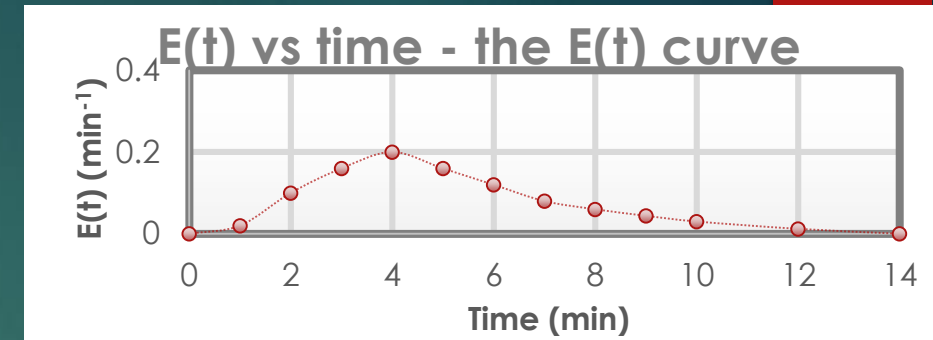
  ○ Tracer input studies

  ○ Construction of E(t) and F(t) versus t curves

  ○ Application of RTD to ideal reactors

▶ Models to describe Real reactors

  ○ Zero parameter models

  ○ One parameter models

▶ Tanks-In-Series Model – a one parameter model

▶ Application to Reactor Design and Analysis

A large percentage of chemical process use catalysts

▶ Some of the uses of catalysis are:

- inorganic chemicals (e.g., NH_3 and H_2SO_4)

- organic chemical (e.g, hydrogenation and polymerization)

- petroleum technology (e.g., cracking and reforming)

- production of synthetic fuels (e.g., coal liquefaction and gasification)

- pollution control (e.g., automotive, industrial)

- energy conversion (fuel cells)

▶ In India, the chemical industry is the 6th largest in the world and accounts for about 2.1% of the GDP, employing about 5 million people

Catalysts affect the rate of a reaction

► But remained unchanged after the catalytic cycle

► It can accelerate or slow a particular reaction step and hence the formation of a particular species

► It does not affect the equilibrium; just the approach/rate to achieve it

► Depending on the phase of the catalyst and the reactants/products, the catalysts can be homogeneous or heterogeneous

► Homogeneous when all are in the same phase and heterogeneous when the catalyst is in a different phase

► Considering only heterogeneous catalysts in this course

A heterogeneous catalytic reaction occurs at or near the fluid-solid interface

▶ Principles of heterogeneous catalytic reactions are also applicable to non-catalytic fluid-solid reactions

▶ Solid-catalysts come in different shapes and sizes

▶ Cylinders, spheres, plates, hollow cylinders, and others

▶ Since fluid-solid interface is important a large interfacial area is beneficial for achieving significant rates

▶ High interfacial areas are provided by porous material, e.g., a silica-alumina cracking catalyst has the following

▶ Pore volume of 0.6 cm^3/g-cat, average pore radius of 4 nm and surface area of 300 m^2/g-cat

Heterogeneous catalysis - contd

▶ Sometimes the pore are so small and uniform that the catalysts act as molecular sieves

▶ Often the catalysts contains small particles of active material dispersed over a less active material called a support

▶ Unsupported catalysts also exists

▶ Some catalysts don't maintain their original activity

▶ They deactivate due to (i) change in active site, (ii) deposit of a foreign substance on the active site, or other reasons

▶ For a heterogeneous catalytic reaction to occur, at least one of the reactants must adsorb on to the surface

Adsorption are of 2 types depending on the specific process that the species undergoes

| Process	Physical (Physisorption)	Chemical (Chemisorption)
Forces of attraction	van der Waals	chemical bonds (rearrangement of atoms)
Heat of adsorption	2-6 kcal (usually of the same order of magnitude as liquefaction heat)	>15 kcal exception: endothermic adsorption
Activation	no activation energy	activation required
Temp range	near saturation (misleading if material highly porous)	higher than saturation
Selective	No	Yes
Layers of adsorbates	multiple	mono

Chemisorption is the one that affects the reaction rate

▶ Suggested that reactions occur only at certain "active" sites or centers and are not catalyzed over the entire solid surface
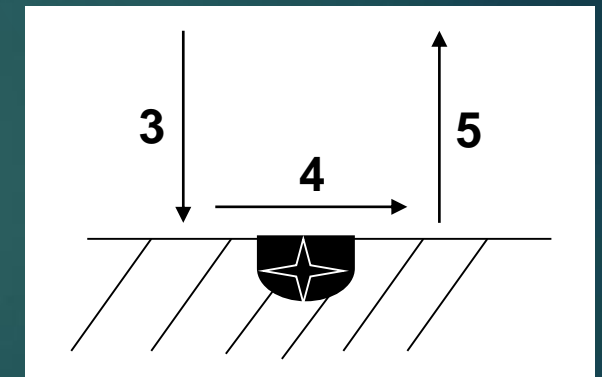
▶ Steps taken by a reactant molecule (1 to 7) shown

Steps 3, 4, 5 are taking place on an active site

A spherical catalyst particle with pores
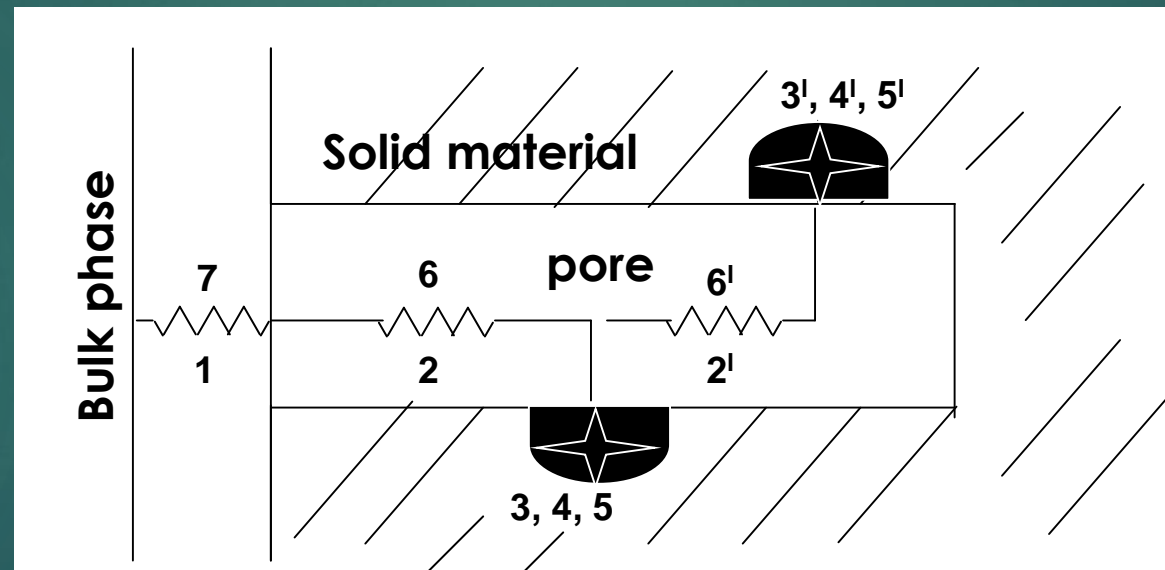
A porous catalyst showing a single hypothetical pore

- Depiction of an active site
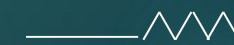
- Transport resistance

Combination of physical and chemical steps occur in a heterogeneous catalytic reaction

As per the figure given in the previous overhead, the steps are:

1. Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet – external diffusion

2. Diffusion of reactant(s) from pore mouth through the catalyst pores to the active sites (not there for non-porous catalysts) – internal diffusion

3. Adsorption of species A on to the surface of the active site

4. Reaction at active site – surface reaction (single/multiple steps)

5. Desorption of products from the active site

6. Diffusion of products from the interior to external surface (not there for non-porous catalysts)

7. Mass transfer of the products from the external surface to the bulk liquid

Adsorption (step 3) is a necessary step – Adsorption isotherm, which is used to find conc of surface species

▶ Adsorption of A on a vacant site S on the surface can be represented as

$$A + S \rightleftharpoons A.S,$$ where $A.S$ is the adsorbed species; e.g., A can be CO

▶ The conc of total surface sites S, C_t (mol/g-cat), is a constant and given by:
$$C_t = C_S + C_{A.S}$$ (site balance)

○ where C_S = conc of vacant sites and $C_{A.S}$ = conc of sites occupied by A

▶ The adsorption of A can be treated as an elementary reaction and

○ rate of attachment/adsorption (formation of A.S) is: $r_{AS,1} = k_A P_A C_S$ and

○ rate of detachment/desorption (disappearance of A.S) is: $r_{AS,2} = -k_{-A} C_{A.S}$

Gas phase concentration of A and concentration of adsorbed A are related by the Langmuir isotherm

▶ Net rate of adsorption of A is: $r_{AS} = k_A \left(P_A C_S - \frac{C_{A.S}}{K_A} \right)$ where $K_A = {k_A}/{k_{-A}}$

    ○ K_A is the equilibrium constant for adsorption of A

    ○ C_S is not readily observable

▶ Using quasi-equilibrium approach: $r_{AS} = 0$ and $C_{A.S} = K_A P_A C_S$

▶ Using site balance $C_t = C_S + C_{A.S}$ we have $C_{A.S} = K_A P_A (C_t - C_{A.S})$

▶ Re-arranging we have: $C_{A.S} = \frac{K_A P_A C_t}{1 + K_A P_A}$

▶ The equation relates $C_{A.S}$ to P_A (an measurable quantity) and is called the Langmuir isotherm for (mono)molecular adsorption

The Langmuir Isotherm can be obtained for dissociative adsorption too

▶ For dissociative adsorption: $A.B + S + S \rightleftharpoons A.S + B.S$, e.g., A.B is CO

▶ $r_{ABS} = k_A \left(P_{AB} C_S^2 - \dfrac{C_{A.S} C_{B.S}}{K_A} \right) = k_A \left(P_{AB} C_S^2 - \dfrac{C_{A.S}^2}{K_A} \right)$ since $C_{A.S} = C_{B.S}$

▶ Similarly: $C_{AS} = C_S (K_A P_{AB})^{1/2}$ $C_t = C_S + 2C_{A.S}$ and $C_S = \dfrac{C_t}{1 + 2(K_A P_{AB})^{1/2}}$

▶ Thus, $C_{A.S} = \dfrac{C_t (K_A P_{AB})^{1/2}}{1 + 2(K_A P_{AB})^{1/2}} \rightarrow$ the Langmuir Isotherm for dissociative adsorption

▶ Other types of adsorption exists, e.g., $A + B + S + S \rightleftharpoons A.S + B.S$

▶ The validity of the models or determination of constants can be determined by plotting measurable properties and checking for linearity:

  ○ $P_A / C_{A.S}$ vs P_A for molecular adsorption OR $(P_{A.B})^{1/2} / C_{A.S}$ vs $(P_A)^{1/2}$ for above

  ○ Constants can also be determined from slope and intercept