Chemical Reaction Engineering - II

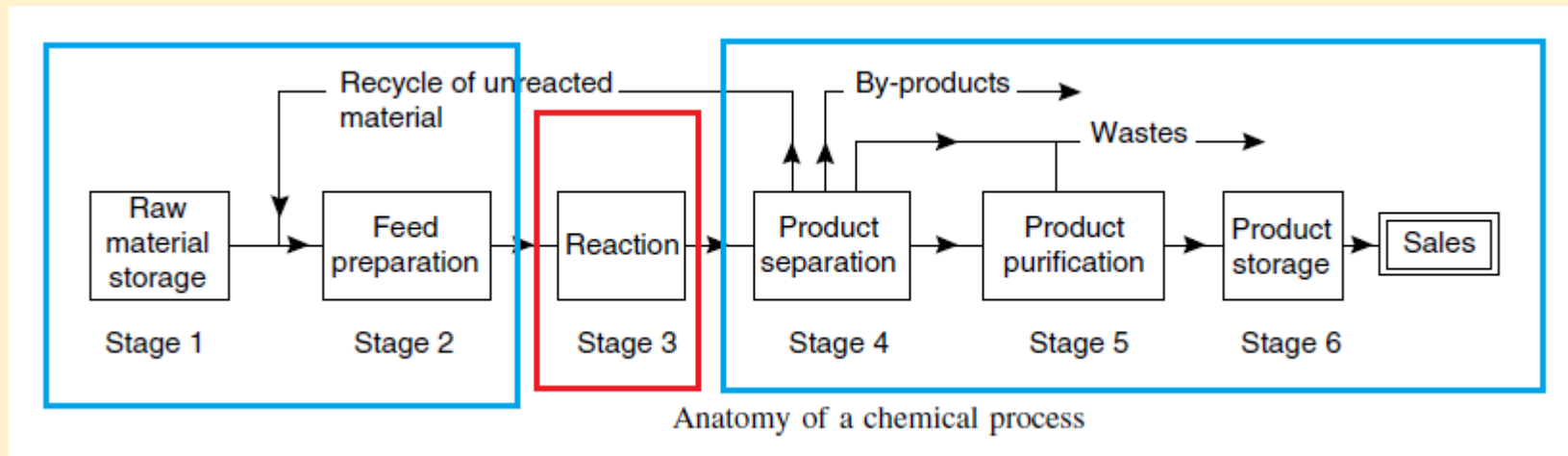## CHE-S402

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Introduction

- Any chemical industrial process can be characterized in terms of three major components – **pre-reaction, reaction, post-reaction**

Anatomy of a chemical process

- The first and last components usually comprise of **physical operations** (mixing, vaporization, absorption, adsorption, distillation, extraction etc)

- The middle component comprise of the actual **chemical reaction** that leads to the formation of the desired chemical product

- The **reaction** can be of any type, **single or multiple**, involving **more than one phase** and can be performed in **reactors of various designs**

- There are two courses on Chemical Reaction Engineering in our syllabus –

  Chemical Reaction Engineering- I (CHE-S304)

  Chemical Reaction Engineering – II (CHE-S402)

In the first course (CHE-S304), all the basic aspects of reaction engineering was covered, such as reaction kinetics, how to find a rate law based on laboratory experimental data, design of ideal reactors, effect of kinetics on reactor design, how heat transfer affects reactor design and finally study of non-ideal reactors

The ultimate objective of the study of reaction engineering is the design of chemical reactors


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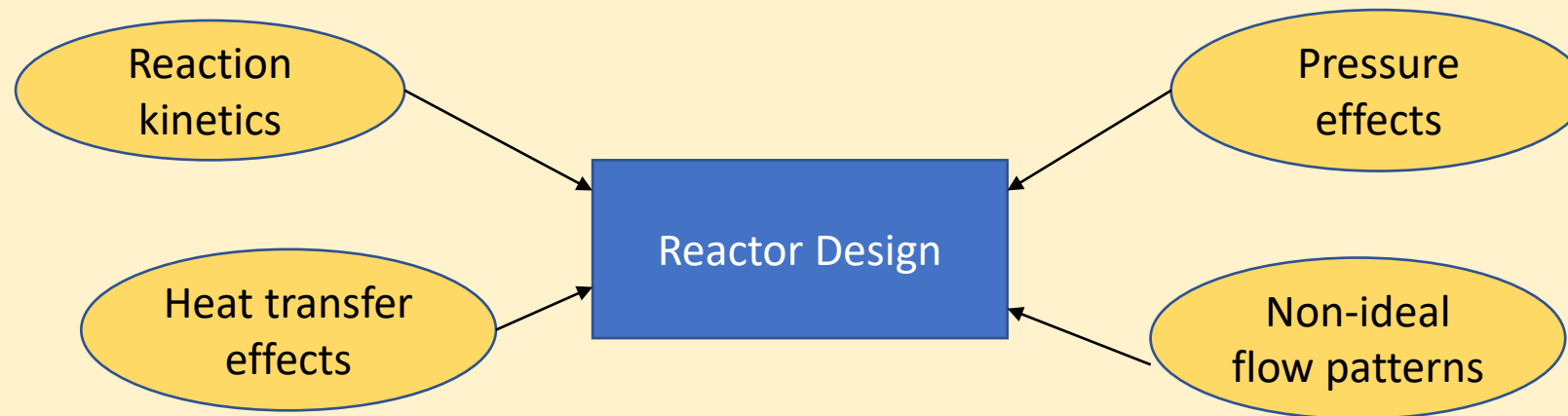
In this course, development of reaction rates and reactor design were all done for **homogeneous systems**

In the second course, CHE-S402, we build on the basics learnt in the first course, and will deal primarily with **heterogeneous systems**

- **Reactions involving more than one phase are termed as heterogenous.** Such reactions may be either **catalytic** or **non-catalytic**

- In a **catalytic reaction**, the catalyst is usually in the solid phase and the reactants and products may be gases or liquids
    - Example: production of benzene (gas) from cyclohexane (gas) using a Pt-Al_2O_3 catalyst (solid)
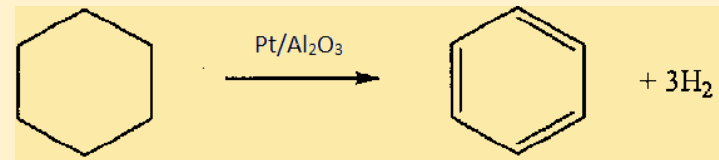

(Catalytic reactions can also be homogeneous when the catalyst, reactants and products are all in one phase)

- In a **non-catalytic heterogenous reaction**, the reactants or products are present in more then one phase
    - Example: $ZnS(s) + \frac{3}{2}O_2(g) \rightarrow ZnO(s) + SO_2(g)$
    $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

[Unlike a steady state operation of gas-solid catalytic reactors, non-catalytic gas-solid reactions are intrinsically dynamic]

- Heterogenous systems have two complicating factors that must be accounted for –
  - (a) the complication of the rate expression
  - (b) the complication of the contacting patterns of the multiphase systems

- The phase boundaries inherent in the heterogenous systems require that
  (1) transport processes (mass and heat transfer) as well as

  (2) intrinsic reaction rate must be accounted for in reactor design
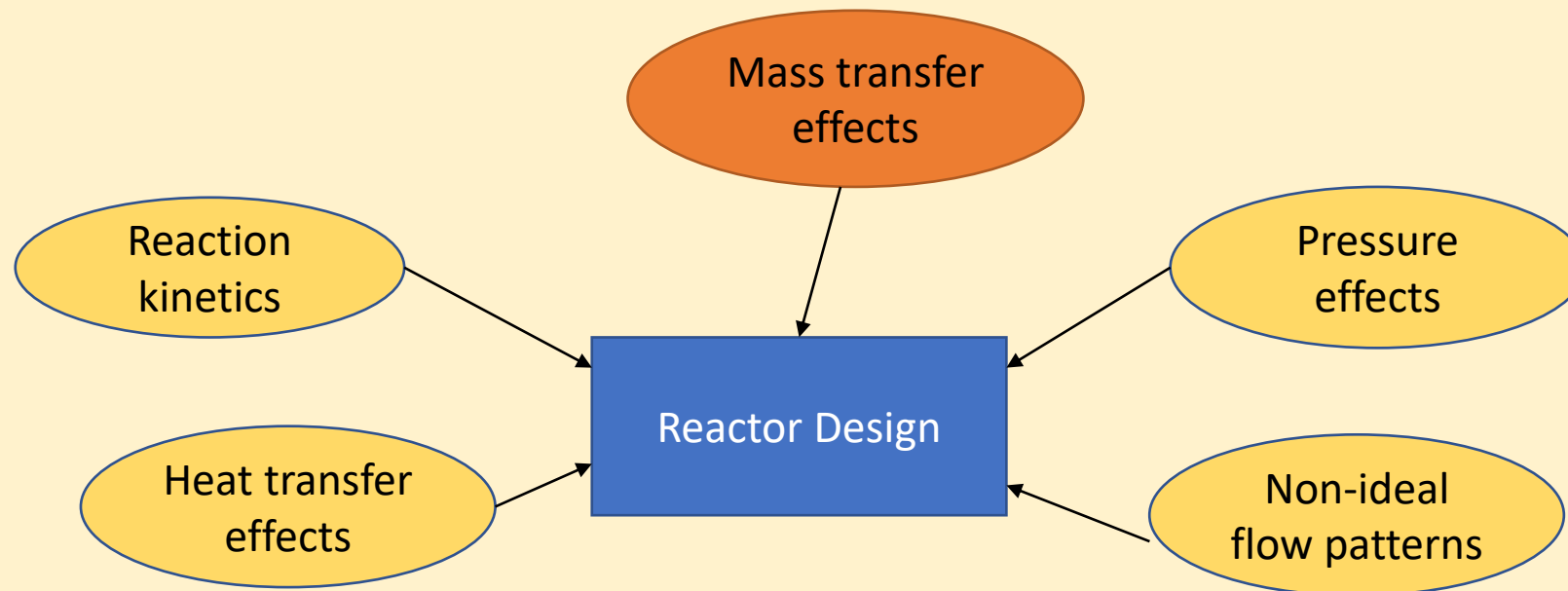
- For a gas-solid reaction, the different steps involved are - movement of the gaseous reactant from the bulk to the solid surface through the gas film, reaction at the solid surface, the reverse movement of the gaseous product from the solid to the bulk gas through the gas film

- The rate of reaction is thus influenced by both mass transfer and reaction kinetics
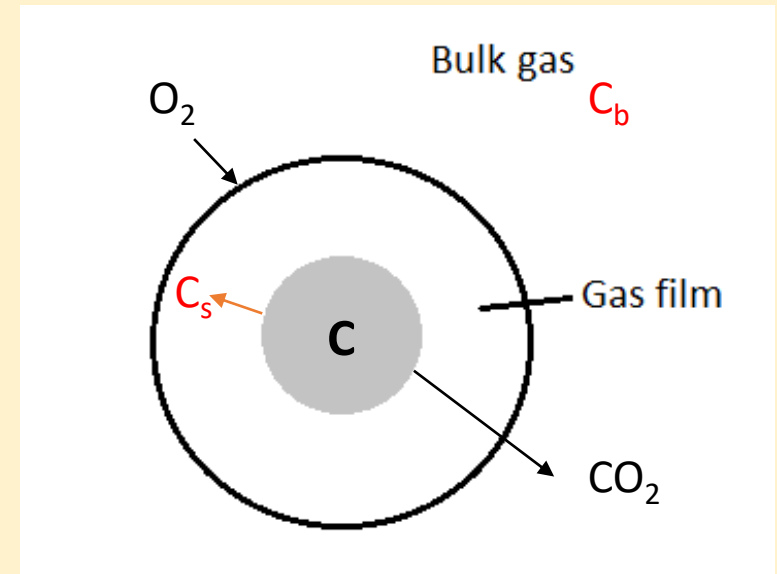
For eg., $C + O_2 \rightarrow CO_2$

Three steps involved are : i) mass transfer of O_2 from bulk to the surface

                               ii) reaction at C surface

                               iii) diffusion of CO_2 from the surface to the bulk

The resistance of mass transfer in the gas film results in the concentration on solid surface (C_s) being lower than the bulk concentration (C_b)

As the surface concentration (C_s) is difficult to determine, the **global rate** is determined in terms of the bulk concentration (C_b)

Let us consider a **gas phase catalytic reaction on a non-porous solid catalyst**: $A(g) \rightarrow B(g)$

Rate of transport of A from bulk gas phase to the solid catalyst surface, $r_p = k_m a_m (C_b - C_s)$

(k_m = mass transfer coefficient, a_m = external area per unit mass of catalyst)

Rate of reaction at the catalyst surface, $r_R = kC_s$ (k = reaction rate constant per unit mass of catalyst)

At steady state the two rates are equal.

Therefore, $k_m a_m (C_b - C_s) = kC_s$

As $C_s < C_b$, mass transfer resistance reduces the rate of reaction

or, $k_m a_m C_b - k_m a_m C_s = kC_s$

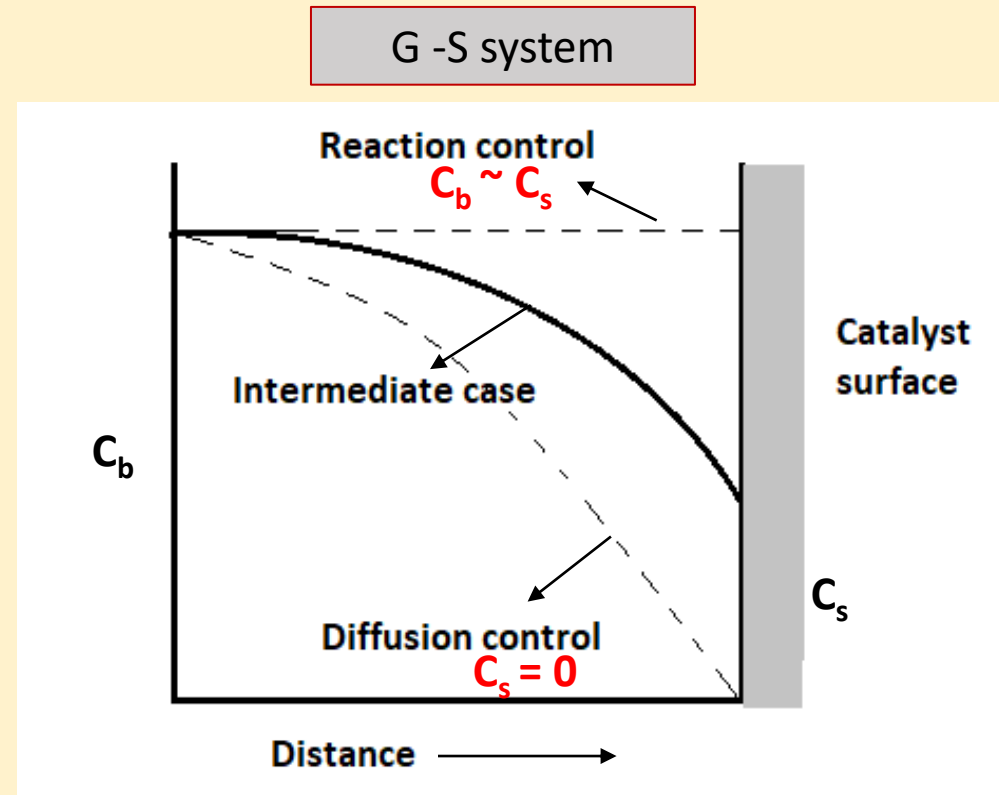or, $C_s = \dfrac{k_m a_m}{k_m a_m + k} C_b$

or, **reaction rate**, $r = \dfrac{kk_m a_m}{k_m a_m + k} C_b$

or, $\boxed{r = \dfrac{1}{\dfrac{1}{k} + \dfrac{1}{k_m a_m}} C_b}$

This is the **global rate**, r.
Also called **overall rate** or
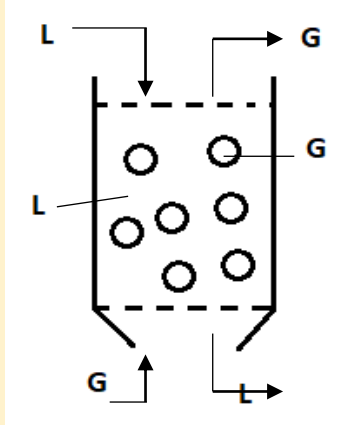**observed rate** or **measured rate**

$r = \dfrac{C_b}{\Sigma resistances}$ The effects of reaction and mass transfer are additive as seen in the resistance term in the denominator
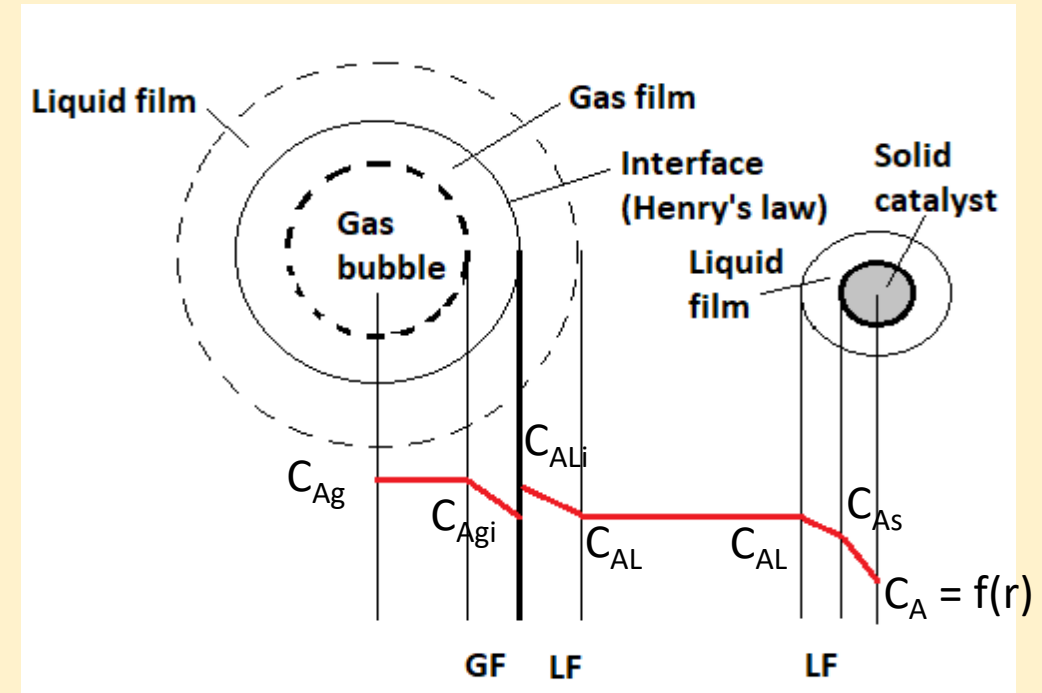

G -S system

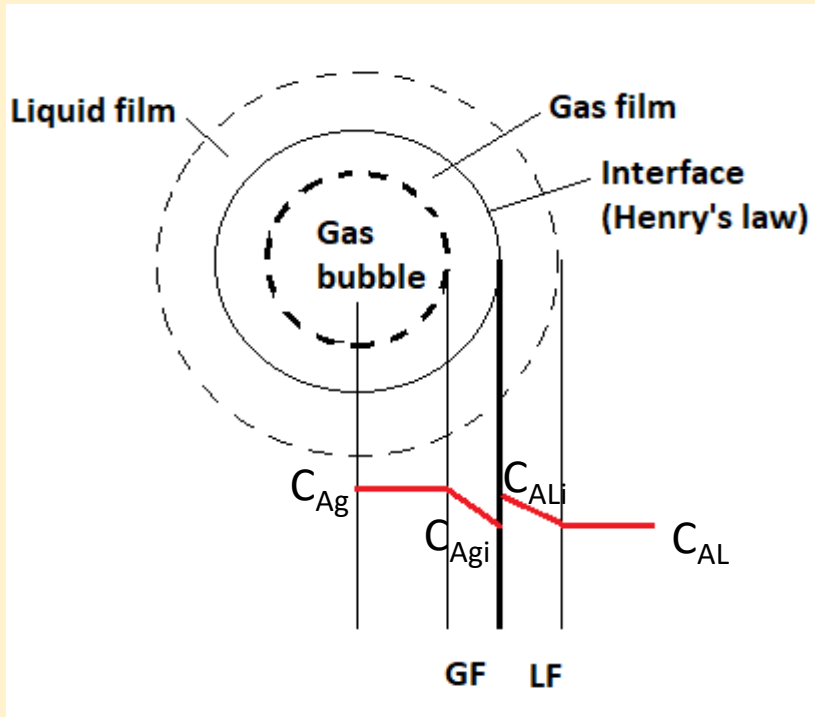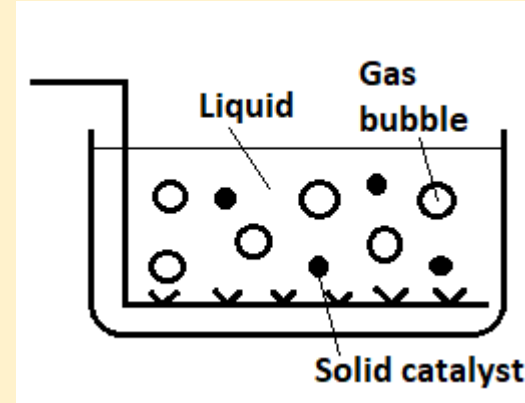Reaction control
$C_b \sim C_s$

Intermediate case

Catalyst surface

C_b

Diffusion control
$C_s = 0$

C_s

Distance

Other multiphase systems

G - L system (bubble)

G - L - S system (slurry)

Chemical Reaction Engineering, O. Levenspiel

- To get an **overall rate expession**, the individual steps are written first (they are equivalent forms) and then the overall rate determined after eliminating the unknown terms

- The rate of reaction are often expressed in the following ways:

Based on total reactor volume

$$-r_A = -\frac{1}{V_r}\frac{dN_A}{dt} = \frac{mol\ of\ A\ reacted}{(volume\ of\ reactor)(time)}, \left[\frac{mols\ reacted}{m^3 reactor.s}\right]$$

Based on weight of catalyst pellets

$$-r_A' = -\frac{1}{W}\frac{dN_A}{dt} = \frac{mol\ of\ A\ reacted}{(mass\ of\ catalyst)(time)}, \left[\frac{mols\ reacted}{kg\ catalyst.s}\right]$$

Based on catalyst surface area

$$-r_A'' = -\frac{1}{S}\frac{dN_A}{dt} = \frac{mol\ of\ A\ reacted}{(interfacial\ surface\ area\ of\ catalyst)(time)}$$

$$\left[\frac{mols\ reacted}{m^2 catalyst\ surface.s}\right]$$

$$\frac{mol\ of\ A\ reacted}{time} = (-r_A)V_r = (-r_A')W = (-r_A'')S$$

If the steps are in series (as discussed), $r_{overall} = r_1 = r_2 = r_3$

If the steps are in parallel, $r_{overall} = r_1 + r_2 + r_3$

- Now going back to the overall (global) rate determined earlier

$$r = \frac{1}{\frac{1}{k} + \frac{1}{k_m a_m}} C_b$$

The mass transfer resistance term mentioned above is known as the *external mass transfer resistance* or *external diffusion resistance*

- As the catalytic reaction takes place at the fluid-solid interface, a large interfacial area is required for a significant reaction rate

- This area is often provided by the **inner porous structure** of the solid catalyst

- The **reaction takes place inside the pores** of a porous catalyst instead of the external catalyst surface (which has limited surface area)

- As the reactant has to be **transported from the mouth of the catalyst pores** on the external surface to the **catalytic surface in the pore**, there is another diffusional resistance involved

- This resistance is called the *internal mass transfer resistance* or *internal diffusion resistance*

- The **overall reaction rate of a heterogenous reaction** will be influenced by the **external and/or internal diffusion resistance and/or the kinetic resistance**

- The largest resistance or the slowest step would be the rate controlling step of the reaction
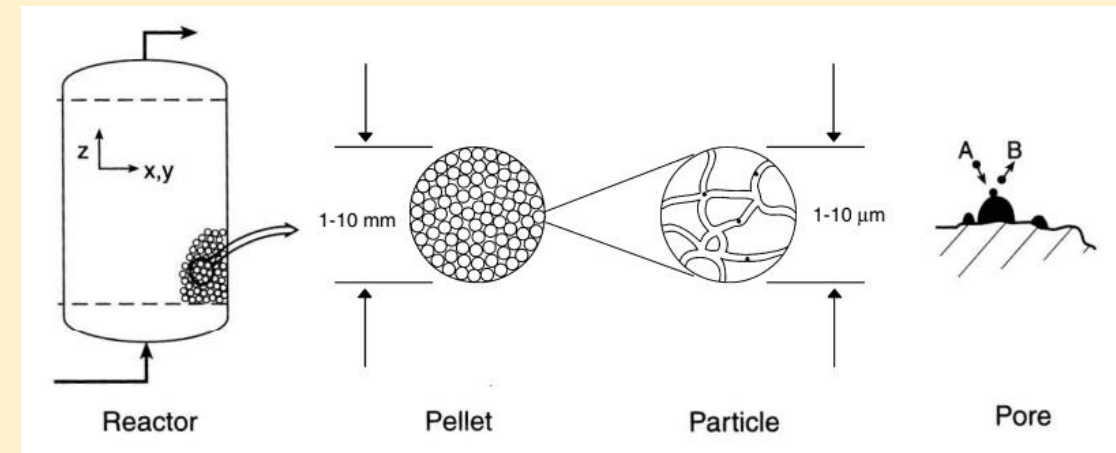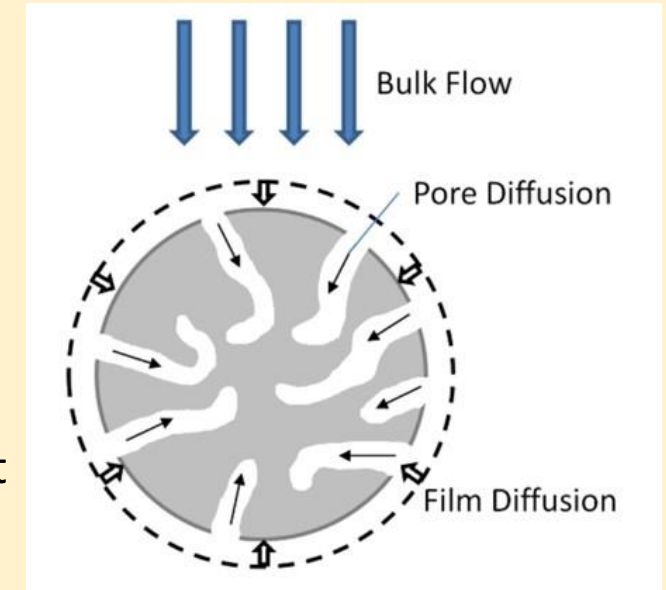
- Apart from mass transfer resistances, **heat transfer resistances** also have an **effect on the overall reaction rate** of an heterogenous reaction

- For an **exothermic reaction** taking place in the inner pores of a solid catalyst, the **temperature at the inner pores may be higher than that at the pellet surface**

  Example: Oxidation of SO_2 with air is carried out using a Pt catalyst. Bulk temperature is 465^oC. Actual temperature on the catalyst surface is 15^oC above, i.e., 480^oC. The rate calculated at this temperature is 31% higher than the rate calculated at the bulk temperature.

- **High temperature** in the pores is caused by **exothermic reaction along with heat transfer resistance**

- **Rate of reaction** will be **higher in the pores due to increased temperature**, but **mass transfer resistance leads to lower reactant concentration inside the pores, resulting in decreased reaction rate**

- The global rate gives a balance of the two effects

- For an **exothermic** reaction the **diffusion and thermal resistances have an opposite effect** on the rate

Syllabus

- Introduction to heterogenous processes

- Catalysis – definition and general characteristics

- Adsorption – physical and chemical adsorption; adsorption isotherms

- Solid catalyst – preparation and characterization

- Rate equations for fluid-solid reactions (kinetic models) – Langmuir- Hinshelwood, Eley-Ridel models

- Heterogenous Data Analysis

- Internal Transport Processes – Reaction and Diffusion in porous catalysts

- External Transport Processes in heterogenous reactions

- Deactivation

- Fluid-particle reaction kinetics (non-catalytic)

- Fluid-fluid reaction kinetics

Recommended Books

- *Chemical Engineering Kinetics*, J. M. Smith, 3rd Edition, Mc Graw Hill International Edition
- *Elements of Chemical Reaction Engineering*, H.S. Fogler, 4th Edition, Prentice Hall India
- *Chemical Reaction Engineering*, O. Levenspiel, 3rd Edition, Wiley and Sons

Relevant NPTEL courses

- *Chemical Reaction Engineering II*, Prof. Ganesh Vishwanathan, IIT Bombay (https://nptel.ac.in/courses/103/101/103101141/)
- *Chemical Reaction Engineering 2 (Heterogenous Reactors),* Prof. K. Krishnaiah, IIT Madras (https://nptel.ac.in/courses/103/106/103106117/)
- *Chemical Reaction Engineering* , Prof. Jayant M Modak, IISc Bangalore (https://nptel.ac.in/courses/103/108/103108097/)
- *Chemical Reaction Engineering II*, Prof. A.K.Suresh, Prof. G. Vishwanathan, Prof. S. M. Mahajani, IIT Bombay (https://nptel.ac.in/courses/103/101/103101008/)
- *Catalyst Science and Technology*, Dr. Mahuya De, IIT Guwahati (https://nptel.ac.in/courses/103/103/103103026/)
- *Heterogenous Catalysis and Catalytic Processes,* Prof. K. K. Pant, IIT Delhi (https://nptel.ac.in/courses/103/102/103102012/)