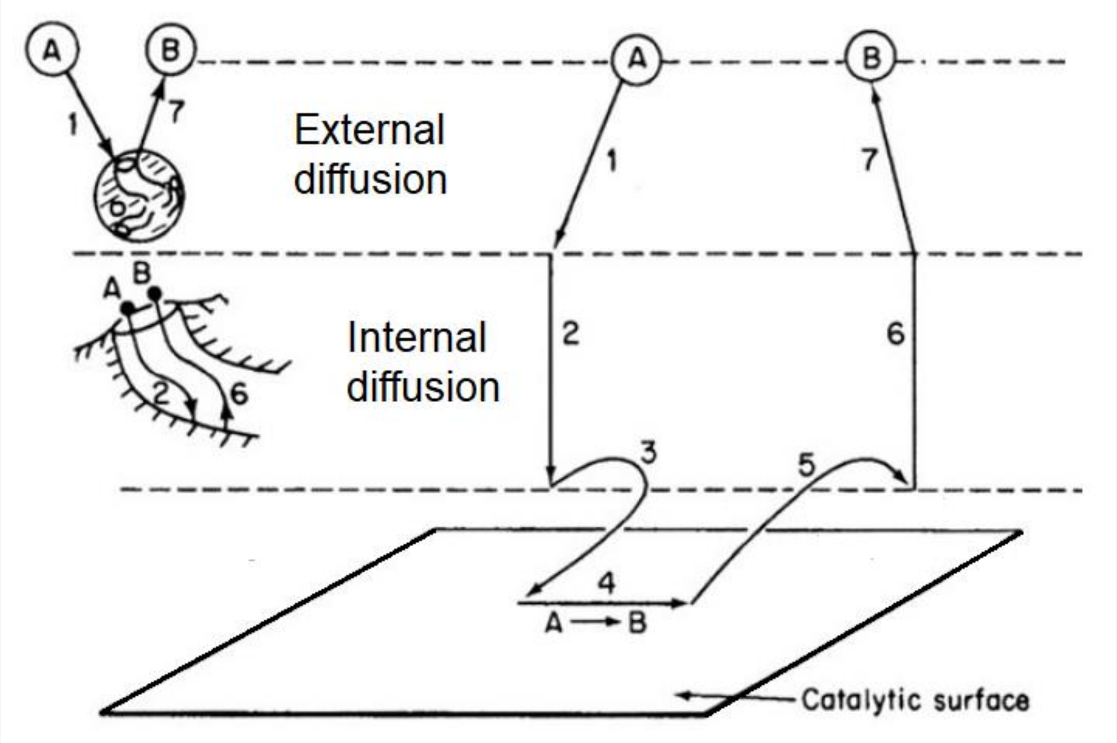
Rate equations for fluid-solid reactions (kinetic models)

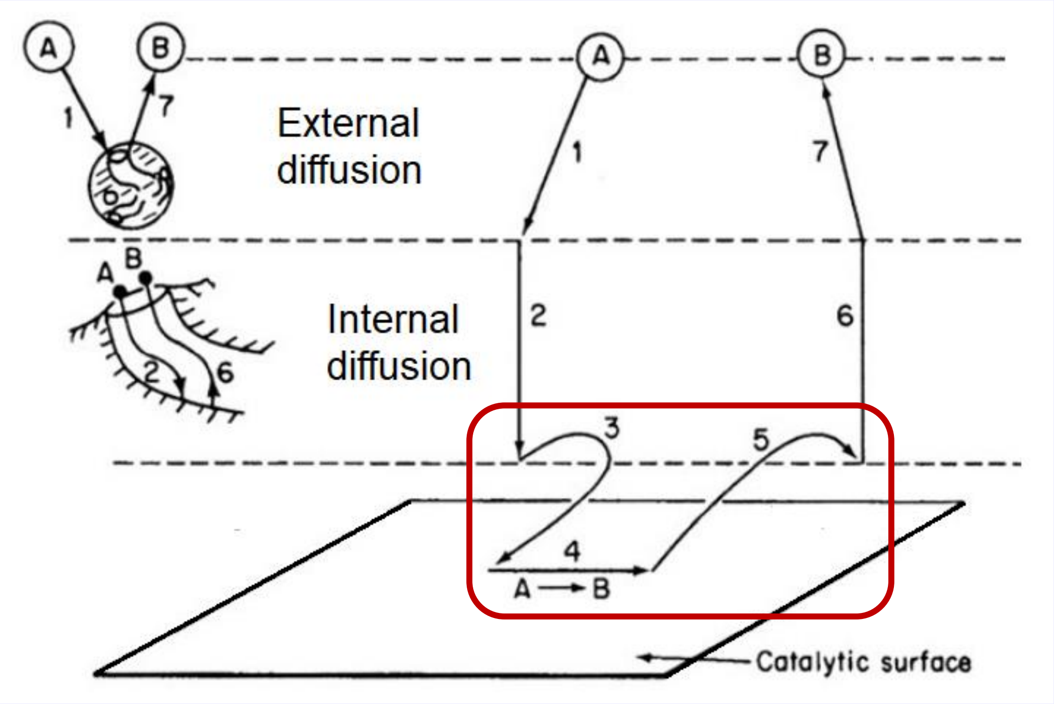
Book: *Elements of Chemical Reaction Engineering*, H.S. Fogler, 4th Edition (Chapter 10)

The overall process by which heterogenous catalytic reactions proceed can be broken down into a sequence of individual steps –

1) Mass transfer of reactant A from the bulk fluid to the external surface of the catalyst pellet
2) Diffusion of the reactant A from the pore mouth to the internal catalytic surface through the catalyst pore
3) Adsorption of reactant A onto the catalyst surface
4) Reaction on the surface of the catalyst $A \rightarrow B$
5) Desorption of the product B from the catalyst surface
6) Diffusion of the product B from the interior of the pellet to the pore mouth at the external surface
7) Mass transfer of the product B from the external pellet surface to the bulk fluid



The overall reaction rate is equal to the rate of the slowest step in the mechanism



- When the **diffusion steps** (1,2,6 and 7) are **very fast** compared to the reaction steps (3,4 and 5), the concentrations near the active site are indistinguishable from those in the bulk fluid
- In such cases, **transport or diffusion steps do not affect the overall rate of the reaction**
- However, if the **reaction steps** (3,4 and 5) are **vey fast** compared to the diffusion steps, **mass transfer affects the reaction rate**
- When **diffusion from the bulk fluid to the catalyst surface** or to the mouth of the catalyst pore affects the rate (external diffusion), **changing the flow conditions past the catalyst changes the overall reaction rate**
- In porous catalysts, **diffusion within the catalyst pore** (internal diffusion) may limit the rate of reaction

In this chapter, only the steps of **adsorption, surface reaction and desorption** are considered

It is assumed that the diffusion steps (1,2,6 and 7) are so fast that the **overall rate is not affected by mass transfer in any manner**

- One of the essential requirements for reactor design is the **availability of a rate expression for the reaction**
- One of the jobs of a chemical engineer, therefore, is to carry out experiments, and then analyse rate data to develop a correct rate law
- As rate laws for a heterogenous catalytic system rarely follow the power law model (where rate for the reaction $A + B \rightarrow C$ is $-r_A = kC_AC_B$), they are more difficult to formulate
- **Development of a rate model is done** from **data collected from a reactor** where the **external and internal diffusion does not affect the rate**
- The **rate developed under such conditions** is known as the ***intrinsic rate***

Let us now see how conditions can be set up where external and internal diffusional effects are negligible

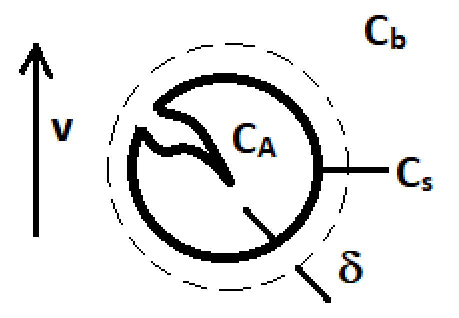
External diffusion

- The rate of transfer from the bulk to the surface of the catalyst is given by $\boldsymbol{r_p = k_m a_m (C_b - C_s)}$
- It is seen that the mass transfer coefficient, $\boldsymbol{k_m}$ is inversely proportional to the boundary layer thickness, $\boldsymbol{\delta}$

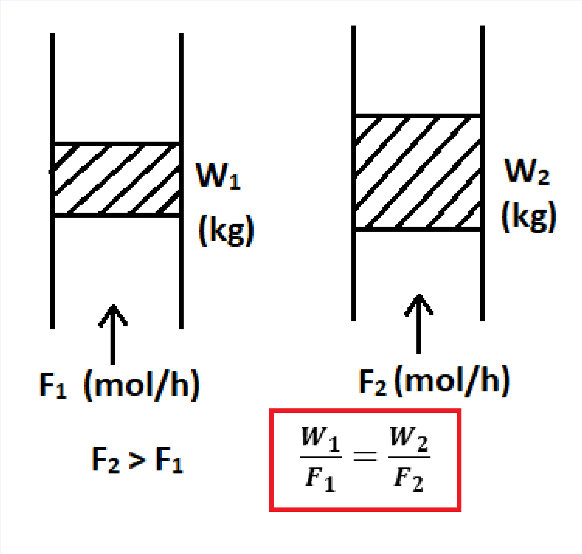
$$\boldsymbol{k_m = \frac{D_{AB}}{\delta}}$$

where D_{AB} is the diffusivity

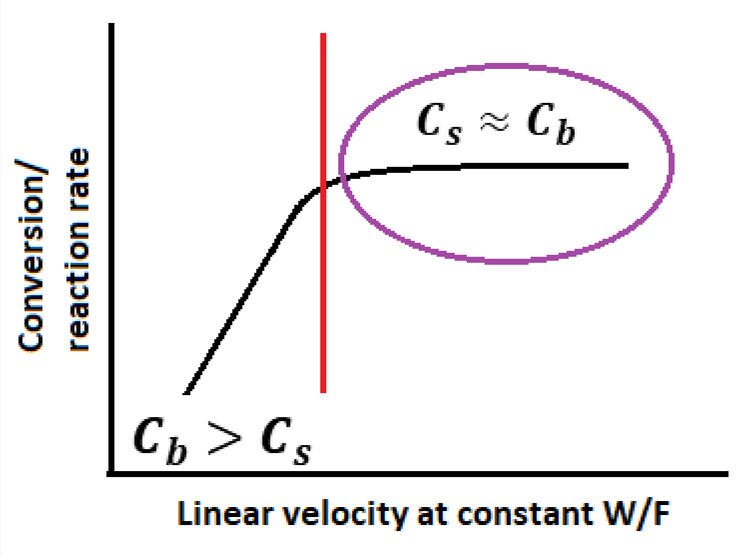
- If $\boldsymbol{\delta}$ is large, $\boldsymbol{k_m}$ is small ($\because\ \boldsymbol{k_m} = \frac{\boldsymbol{D_{AB}}}{\boldsymbol{\delta}}$) which slows the rate of transfer and makes it rate limiting
- As the velocity across the pellet is increased, the boundary layer thickness reduces ($\boldsymbol{\delta}$) and mass transfer rate is increased
- At sufficiently large velocities, this thickness, $\boldsymbol{\delta}$ is so small, that $\boldsymbol{C_s} \approx \boldsymbol{C_b}$ and there is no mass transfer resistance



- In order to determine the condition where the external mass transfer resistance becomes negligible, the reactor is operated with <u>different weights of catalyst</u> (W) and <u>different molar flow rates</u> (F_{Ao}) such that their ratio ($\frac{W}{F_{Ao}}$) is constant $\left[\frac{W}{F_{Ao}} = \int \frac{dX_A}{(-r_A)}\right]$
- As different molar flow rates (F) are used, the velocity (v) also changes since $v = \frac{F\times M}{\rho\times A}$

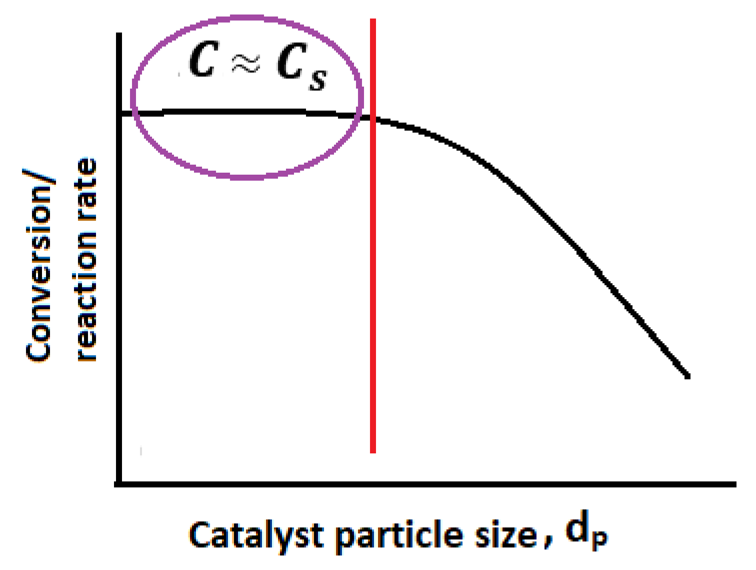


- A plot of reaction rates versus linear velocity shows an initial portion where $reaction\ rate \propto linear\ velocity$, after which it plateaus out. This <u>plateau region</u> is the section where $\boldsymbol{C_s} \approx \boldsymbol{C_b}$
- A reactor is then **operated** in **these** $\frac{W}{F_{Ao}}$ **conditions** (shown by the purple region) **where it is devoid of mass transfer limitations**, and can be used to estimate intrinsic kinetics



Internal diffusion

- Since the reactants need to diffuse from the mouth to the interior of the pore in the catalyst, the size of the catalyst pellet becomes important during reaction
- For large pellets, the time taken to diffuse inside is much larger than the time taken for reaction
- Often the reactant is consumed near the exterior surface of the pellet and the catalyst near the centre is wasted
- Gases diffuse in and out quickly in a smaller pellet



- In order to determine the condition where the internal mass transfer resistance becomes negligible, the reactor is operated under identical conditions $(T, P, \frac{W}{F_{Ao}})$ with catalysts of different sizes (d_p)
- A plot of reaction rate versus catalyst particle size shows that initially the rate remains constant as particle size increases and then there is a decrease in rate with increase in particle size
- The reaction rate is affected by internal diffusion as the catalyst particle size increases
- Operating the reactor with small pellets (shown by the purple region) help to get rid of internal mass transfer limitations
- Smaller pellets, however, have the problem of pressure drop

Therefore, the **pellet size** and the **external fluid velocity** are chosen for reactors such that there is no external or internal diffusion limitations. Data from such reactors can then be used to determine the intrinsic rates