

# CHAPTER 7

## MASS TRANSFER EFFECTS IN CHEMICAL REACTIONS

S. Pushpavanam

Chemical Engineering Department, Indian Institute of Technology Madras  
Chennai 600036, India

Catalysts are substances which accelerate the reaction without being consumed. Thermodynamics helps us determine whether a reaction is possible or not. The free energy change of a reaction gives information on the feasibility of a reaction. One calculates the free energy change, and if it is negative one can decide a reaction is possible i.e., can occur. The free energy change does not reveal any information on the kinetics or the rate of the reaction. Hence whether the reaction occurs fast or slow, cannot be inferred from thermodynamics.

Sometimes the reaction of interest occurs slowly. Hence in order for sufficient quantity of the product to be manufactured one may have to wait for a very long time. Catalysts can be used to speed up reactions. A catalyst is a substance which affects the rate of the reaction but does not get consumed. Catalysts change the reaction rates by offering a different path or mechanism for the reaction. Catalysts change the speed of reaction. However, they do not affect the equilibrium.

Homogeneous catalysts are substances which are in the same phase as the reactants. In a heterogeneous catalytic process the catalyst is in a different phase than the reactants. Consequently in these systems there is more than one phase. Most common catalysts are in the solid phase while the reactants are in the liquid or gaseous state. Examples of systems where the reactant is in the gaseous state are, manufacture of ammonia from nitrogen and hydrogen over an Fe catalyst, oxidation of sulfur dioxide to sulfur trioxide over vanadium pentoxide catalyst etc. Sometimes the reactants can be present in both the liquid and gaseous form as in hydro-desulphurisation of petroleum fractions. This reaction is carried out over a Co-Mo catalyst (solid phase), and diesel or the petroleum fraction is allowed to trickle over the catalyst surface as a thin film. Hydrogen gas necessary for the hydrodesulfurisation flows over the liquid film. Such systems are in general called multiphase reactors since more than two phases are involved. Heterogeneous catalysts are usually preferred since, the product mixture in the fluid phase can be easily separated from the solid catalysts. In many cases the catalysts are valuable and their reuse is necessary. Catalytic reactions occur at the fluid-solid interface.

Since reactions occur near the interface a large area is helpful in attaining a high rate. This is ensured by using a porous structure for supporting the catalyst. The carrier solid has many fine pores. The surfaces of these pores which are almost cylindrical in shape provides the area for the reaction. The surface area of these pores is large. A typical catalyst has a pore volume of  $0.6 \text{ cm}^3/\text{g}$  and an average pore radius of 4 nm. Surface area is  $300 \text{ m}^2/\text{g}$ . This is the surface area available for the active catalyst to be deposited.

A catalyst that has a large area resulting from pores is a porous catalyst. Raney Ni is used in hydrogenation of vegetable and animal oils, Pt on  $\text{Al}_2\text{O}_3$  catalyst is used for reforming of naphtha, Fe is the catalyst in  $\text{NH}_3$  synthesis. The pores are sometimes very small, so that they admit only small molecules and prevent large ones from entering. Materials like this are called molecular sieves. They can be natural like clay or zeolites or synthetic like aluminosilicates. These act to improve selectivity by allowing only some molecules to enter the catalyst particle.

Not all catalysts need the extended surface of a porous structure. Some are sufficiently active, that the effort to get a porous catalyst would be wasted. These are called monolithic catalysts. One example is Pt-gauge used in  $\text{NH}_3$  oxidation for nitric acid manufacture. This kind of catalyst is used when heat removal is a major factor. Different processes with similar goals can result in different catalysts. Thus for example for catalytic oxidation of automobile exhausts, Ford uses monolithic catalysts, while GM uses porous catalysts. Both use Pt as the active catalyst.

Porous catalysts contain minute particles of an active material dispersed over a less active substance called support. The active material is a pure metal or metal alloy. These are called supported catalysts. Unsupported catalysts contain major amount of promoters which increase the activity.

Examples of supported Catalysts are:

- (i) Pt on  $\text{Al}_2\text{O}_3$  in petroleum refining,
- (ii)  $\text{V}_2\text{O}_5$  on silica.

Unsupported catalysts:

- (i) promoted iron in  $\text{NH}_3$  synthesis
- (ii) Pt gauge use in  $\text{NH}_3$  oxidation.

The activity of the catalyst usually decreases with time. This is called deactivation. This can happen due to various reasons. For example a change in the surface crystal structure can cause this. Alternatively a foreign material can be deposited on the active surface. This is called poisoning or fouling and this also renders the catalyst inactive. Deactivation can be fast as in the catalytic cracking of naphtha where carbonaceous material or coke deposits on the catalyst surfaces. In other cases it is very slow. A schematic of a packed bed reactor with a regular packing of catalyst particles is shown in Fig1. The reacting fluids flow through the inter-particle spaces in the bed and diffuses through the pores inside each particle. The reactions occur in the pores of each particle.

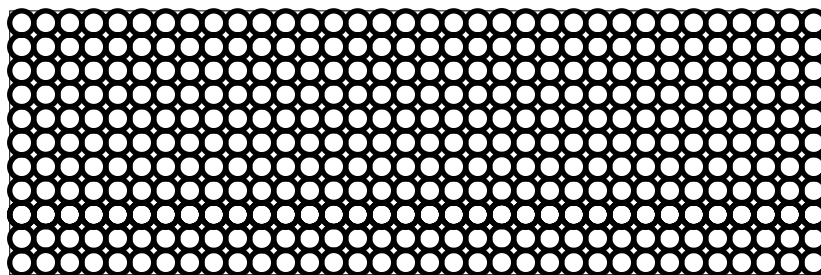


Fig.1 A packed bed reactor with spherical catalyst particles arranged regularly

Consider a catalytic gas-solid reaction. This reaction occurs through a mechanism where in at least one or all reactants must be attached to the surface. This is called adsorption. This can be by physical adsorption, which is similar to condensation. This process is exothermic and the heat of adsorption is small about 5 kcal/g mol. In this the forces of attraction between the gas molecules and the solid surfaces are weak. Amount of gas adsorbed decreases as the temperature increases. Once the temperature exceeds the critical temperature only small amounts of adsorbed material remain on the surface.

Chemical reactions are affected by chemisorption. Here the adsorbed atoms or molecules are held to the surface by valence forces as those which occur in bonded atoms of molecules. This is highly exothermic (100 kcal/g mol) when compared to physisorption. If chemisorption occurs for a catalytic reaction, the temperature for the reaction is decided by the temperature range over which chemisorption occurs.

Reaction is visualised as occurring over active sites. These are points on the catalyst surface that can form strong chemical bonds with an adsorbed atom/molecule.

~~Catalytic packed bed reactors are depicted below:-~~

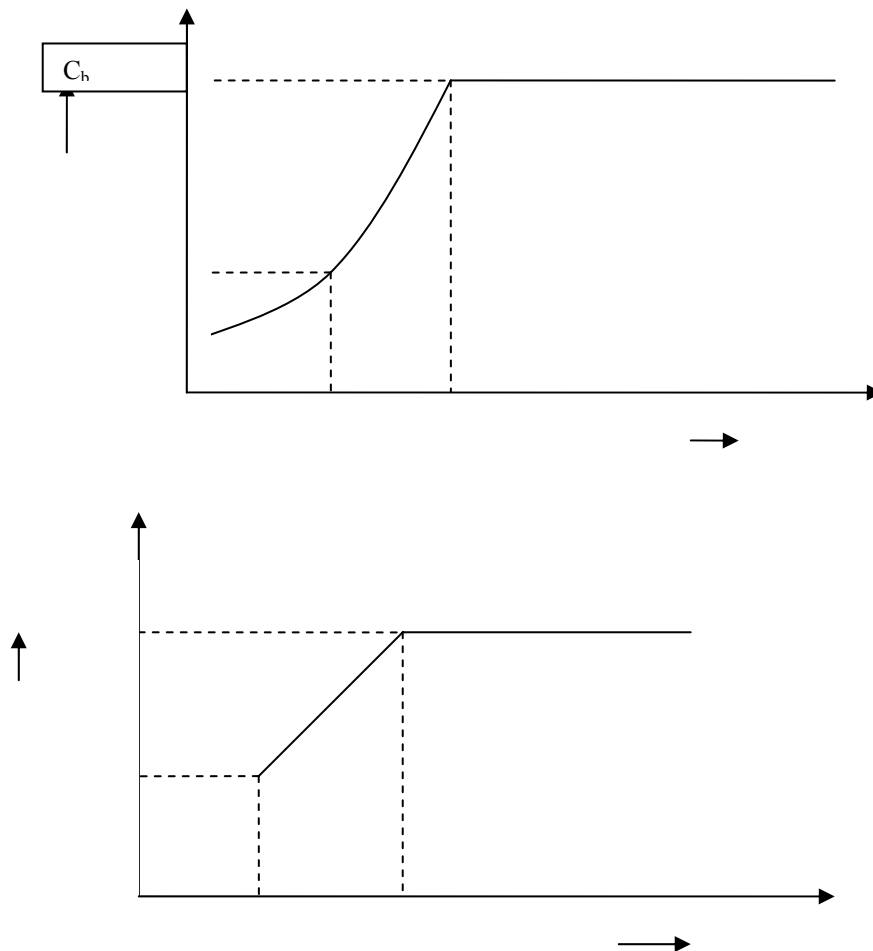
The different steps in a catalytic gas-solid reaction are:

- (i) Diffusion of gas from bulk to catalyst surface (external mass transfer step)
- (ii) Diffusion of gas through pores of catalyst (internal mass transfer step)
- (iii) Adsorption of gas at the site of catalyst
- (iv) Surface reaction at the catalyst surface
- (v) Desorption of product gas from catalyst site
- (vi) Diffusion of products through pores( internal mass transfer step)
- (vii) Diffusion of products from surface to bulk ( external mass transfer step)

As a result of these steps there is a concentration profile which exists in the pellet. This is depicted in Fig 7.2a. In this figure, the qualitative variation of concentration of the reactant near a pellet of radius  $R_p$  is shown. The concentration in the bulk phase is  $C_b$ . This exists till one comes to within a thickness of  $\delta$  around the pellet. The concentration drops from  $C_b$  to  $C_s$  the surface value at the radial position  $R_p$ . The external mass transfer resistance is assumed to be concentrated across this layer of thickness  $\delta$ . Concentration can be viewed as a potential and due to the external mass transfer resistance there is a drop in the concentration from  $C_b$  to  $C_s$ . Similarly the concentration also varies inside the pellet. Thus there is a decrease in the reactant concentration values as one moves towards the pellet center.

If the diffusion steps or mass transfer steps 1, 2, 6, 7 are very fast, this implies that there is no resistance for the mass transfer from bulk to the particle surface and from particle surface to the active site in the pore. Consequently the concentration near all catalyst sites is the same as that of bulk. Under these conditions the mass transfer steps do not affect the reaction rate. One can calculate the reaction rate from the reaction mechanism assuming that the concentration at the catalyst site is the same as that in the bulk.

Fig. 7.2 Concentration profiles for different mass transfer effects a) internal and external mass transfer resistance is significant b) internal mass transfer resistance is negligible and external mass transfer resistance is significant.



If diffusion from the bulk gas to the solid surface is slow, then the external mass transfer resistance is high. If one further assumes that the internal particle resistance is low then the concentration profile would be as shown in Fig.7.2b. The external mass transfer resistance depends on the flow conditions that prevail in the reactor. Thus increasing the flow rate of the reactants—conditions can help to reduce the external mass transfer resistance.

If internal diffusion effects are significant and there is no external mass transfer resistance then the concentration profile would vary across the pellet.

In what follows it is assumed that there are no mass transfer resistances as a first case (**section 7.1**). On the basis of this assumption the reaction rate can be found for an assumed mechanism. The validity of the assumed mechanism can be verified by comparing with experimental data.

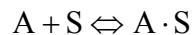
The next case (**section 7.2**) that we analyse would be assuming that only external mass transfer resistances are significant and internal diffusional resistances are negligible. The concept of rate determining step in this context can then be outlined.

The case where only internal diffusional resistance is significant and the external mass transfer resistance is negligible is then considered (**section 7.3**). The focus here would be in particular to examine how these diffusional effects can falsify the kinetics. The situation where both the resistances are significant and the design equation for the reactor under these conditions will be the last case considered in this chapter. (**section 7.4**)

### 7.1 Determination of a mechanism of a surface reaction:

Chemisorption usually occurs in every catalytic reaction. In this step one of the molecules or radicals gets adsorbed on the active site of the catalyst. Let S denote an active site. It denotes an empty site with no molecules adsorbed on it.

A.S denotes a site in which an atom, molecule or a radical A is adsorbed. The reversible reaction



represents the adsorption process. The following terms are **now** defined .

$C_t$  = molar concentration of active sites per gram of catalyst,

= Number of vacant sites divided by Avogadro number per unit mass of catalyst.

$C_v$  = molar concentration of vacant sites per gram.

$S_a$  = surface area per unit mass of catalyst.

Since all the catalytic sites are either vacant or have an A or a B adsorbed on it we can use a mass balance of the sites. This yields

$$C_t = C_v + C_{A.S} + C_{B.S}$$

Adsorption of a gas on a catalyst is hence a crucial step in the reaction process. This process is represented in the form of adsorption isotherms. These isotherms depict the amount of gas adsorbed as a function of pressure at a fixed temperature

A model system or a mechanism is proposed for the adsorption. The isotherm obtained or predicted from the model is compared with experimental data. If the model prediction matches the experimental data to within a reasonable accuracy the model can be assumed to be possibly correct. One cannot conclude that this is the mechanism since there could be other mechanisms which can yield the same quantitative behavior. However if there is a mismatch between the model and the experimental data then one is guaranteed that the model proposed is not correct and he should look for a different model. For example,  $H_2$  can be adsorbed on the site as molecules or as atoms. These two mechanisms can be represented as



**Adsorption as molecules:** Assuming each of the steps to be elementary one obtains

$$\begin{aligned} r_{alt} &= \text{rate of adsorption} \\ &= k_A P_{H_2} \cdot C_v \end{aligned}$$

$$r_{\text{det}} = k_{-A} C_{\text{H}_2 \cdot \text{S}}$$

$$r_{\text{ad}} = r_{\text{alt}} - r_{\text{det}}$$

$$= k_A P_{\text{H}_2} \cdot C_v - k_{-A} C_{\text{H}_2 \cdot \text{S}}$$

$$= k_A \left( P_{\text{H}_2} \cdot C_v - \frac{C_{\text{H}_2 \cdot \text{S}}}{K_A} \right)$$

In general  $k_A$ ,  $k_{-A}$  increase with temperature while  $K_A$  decreases with temperature. Since adsorption alone is considered and no reaction there are only two kinds of sites, vacant sites or those with hydrogen adsorbed on them.

$$C_t = C_v + C_{\text{H}_2 \cdot \text{S}}$$

At equilibrium the net rate of adsorption is zero

$$C_{\text{H}_2 \cdot \text{S}} = K_A C_v P_{\text{H}_2}$$

$$= K_A P_{\text{H}_2} (C_t - C_{\text{H}_2 \cdot \text{S}})$$

$$C_{\text{H}_2 \cdot \text{S}} = \frac{K_A P_{\text{H}_2} C_t}{1 + K_A P_{\text{H}_2}}$$

So a plot of  $\left[ \frac{P_{\text{H}_2}}{C_{\text{H}_2 \cdot \text{S}}} \right]$  vs  $P_{\text{H}_2}$  should be a straight line if the adsorption were to occur by molecules.

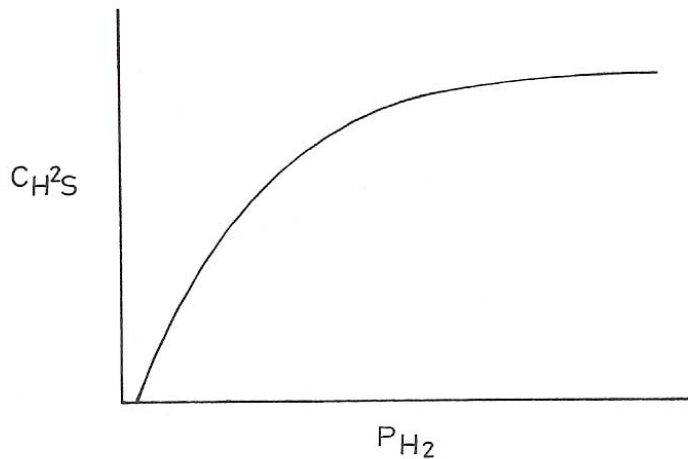
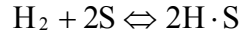


Fig. 7.3. Schematic representation of concentration of adsorbed sites as a function of partial pressure of hydrogen

**Adsorption in the form of atoms:** We now assume that the hydrogen molecule has its atoms adsorbed on two adjacent sites



$$r_{AD} = k_A \left( P_{\text{H}_2} C_v^2 - \frac{C_{\text{H} \cdot \text{S}}^2}{K_A} \right)$$

$$C_{\text{H} \cdot \text{S}} = (K_A P_{\text{H}_2})^{\frac{1}{2}} C_v$$

$$C_t = C_v + C_{\text{H} \cdot \text{S}}$$

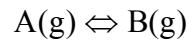
$$= C_{\text{H} \cdot \text{S}} + \frac{C_{\text{H} \cdot \text{S}}}{(K_A P_{\text{H}_2})^{\frac{1}{2}}}$$

$$C_{\text{H} \cdot \text{S}} + \frac{C_t (K_A P_{\text{H}_2})^{\frac{1}{2}}}{1 + (K_A P_{\text{H}_2})^{\frac{1}{2}}}$$

Once again the steps are assumed to be elementary. A schematic depiction at equilibrium of the variation of the concentration of adsorbed sites with partial pressure of hydrogen is shown in Fig.7.3. **The dependence of concentration of adsorbed sites on the partial pressure of hydrogen is qualitatively similar for both hypothesis i.e. hydrogen being adsorbed as atoms or molecules. We can discriminate between the two only by comparing with experimental data.**

Now the focus will be on obtaining an expression for the reaction rate from a mechanism. When there is an internal diffusional resistance the concentration or partial pressure of the reactant varies with the catalytic site. The local value prevailing at a site hence has to be used. For simplicity it is assumed that there are no transport resistances. Consequently the partial pressure of A is equal at all sites. In particular, there are no diffusional resistances, so that there are no concentration gradients. Even if there were these resistances the expression would remain the same but one would have to use the local values of the partial pressure or concentration of the reactant.

Consider the catalytic reaction where we have isomerisation of A,

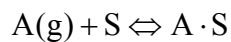


All catalytic reactions occurring on the catalytic site, take place through three main steps,

- (i) adsorption of reactant on site,
- (ii) surface reaction,
- (iii) desorption of products from site.

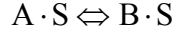
(Shifted to this place from below)

For the moment we assume the reaction occurs by adsorption of A on active site. This is represented by means of the reaction,



Here S represents a vacant site and A · S represents a site on which A is adsorbed

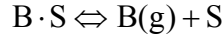
The reaction occurring on the surface is represented as,



The product

formed is in the adsorbed state. This is just one possible mechanism for the formation of a product.

This adsorbed B.S undergoes a desorption step releasing the vacant site,



The rate of adsorption of A is given by,

$$r_{ad} = k_a P_A C_v - k_{-a} C_{A.S}$$

The rate of surface reaction is given by,

$$r_s = k_s C_{A.S} - k_{-s} C_{B.S}$$

The rate of desorption of B is given by,

$$r_d = k_d C_{B.S} - k_{-d} P_B C_v$$

Since the three steps occur in series, at steady-state their rates must be equal, i.e.,

$$r_{ad} = r_s = r_d$$

The rate at which B is produced  $r_B$  is given by,

$$r_B = r_{ad} = r_s = r_d$$

However this by itself is of limited use since these expressions contain quantities like  $C_{A.S}$  and  $C_{B.S}$  and  $C_v$  which cannot be measured. It is necessary to obtain a rate expression which is independent of these quantities. The aim is to determine the reaction rate in terms of measurable quantities. This includes the partial pressures of A, B, and the total concentration of the catalytic sites  $C_T$ . It is hence necessary that one eliminates the unknown concentrations  $C_{A.S}$ ,  $C_{B.S}$  and  $C_v$  and obtain an expression for  $r_B$ .

The concept of a rate determining step can be used to achieve this goal. It is assumed that one of the steps is slow and rate determining compared to the other steps. The other steps are assumed to be relatively fast and hence, at equilibrium. Thus if adsorption is the rate limiting step, then the surface reaction and desorption are assumed to be relatively fast and hence assumed to have attained equilibrium. This together with the total catalytic site balance yields the required equations to determine the kinetics in terms of the measurable quantities.

Since there are only three kinds of sites, vacant sites, sites with A adsorbed, sites with B adsorbed one can write,

$$C_v + C_{A.S} + C_{B.S} = C_T$$

Three different cases will now be discussed: These different cases arise when each of the steps is assumed to be rate determining.

**Case (i) Adsorption as the rate determining step**

When adsorption is rate limiting since the surface reaction is at equilibrium,

$$K_S C_{A.S} = C_{B.S}$$

The desorption step is also at equilibrium. Thus this yields,

$$K_D C_{B.S} = P_B C_v.$$

$$\text{This yields, } C_{BS} = \frac{P_B C_v}{K_D}, C_{AS} = \frac{P_B C_v}{K_D K_S}$$

$$\text{Hence, } C_v = \frac{C_T}{1 + \frac{P_B}{K_D K_S} + \frac{P_B}{K_D}}$$

From this,

$$r_B = k_a C_v P_A - k_{-a} \frac{P_B C_v}{K_D K_S}$$

$$= k_a C_v \left( P_A - \frac{P_B}{K_A K_D K_S} \right)$$

$$= \frac{k_a \left( P_A - \frac{P_B}{K_A K_D K_S} \right) C_T}{1 + P_B \left( \frac{1}{K_D} + \frac{1}{K_D K_S} \right)}$$

$C_T$  is a constant for a particular catalyst and  $P_A, P_B$  are measurable and we now have **the reaction rate in terms of measurable quantities**

**Case(ii) Surface reaction is rate-limiting:**

In this case adsorption and desorption steps are at equilibrium. This yields,

$$K_A P_A C_v = C_{AS}$$

$$K_D C_{BS} = P_B C_v$$

The total site balance yields,

$$C_v \left( 1 + K_A P_A + \frac{P_B}{K_D} \right) = C_T.$$

The rate of reaction,  $r_B$  is now given by

$$r_B = k_a \left( C_{A.S} - \frac{C_{BS}}{K_S} \right)$$

$$= k_a C_v \left( K_A P_A - \frac{P_B}{K_D} \right)$$



$$= k_a C_T \left( \frac{K_A P_A - \frac{P_B}{K_D}}{1 + K_A P_A + \frac{P_B}{K_D}} \right)$$

**Case (iii) Desorption as the rate-limiting step:**

We now have,

$$r_B = k_d \left( C_{B,S} - \frac{P_B C_v}{K_D} \right)$$

Since adsorption and surface reaction are at equilibrium, it can be written as

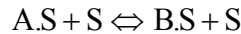
$$K_A P_A C_v = C_{A,S}, K_S C_{A,S} = C_{B,S}$$

Also,  $C_v = (1 + K_A P_A + K_S K_A P_A) = C_T$

$$C_v = \frac{C_T}{(1 + K_A P_A + K_S K_A P_A)}$$

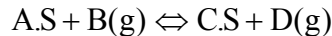
$$r_B = \frac{k_d \left( K_S K_A P_A - \frac{P_B}{K_D} \right) C_T}{(1 + K_A P_A + K_S K_A P_A)}$$

Thus one gets different rate expressions for the three different hypothesis of different rate controlling steps. These expressions have to be tested and validated with experimental data. It is possible to eliminate mechanisms which are wrong and do not fit the data. It may so happen that more than one rate expression fits the experimental data. One can only say which mechanism may fit the data. Each of the steps namely adsorption, reaction and desorption can also occur through different mechanisms. The mechanisms proposed above are not unique. For example the surface reaction can occur as follows,



Here in order for the surface reaction to occur a site on which A is adsorbed needs a vacant site to react with. This will yield a different rate expression for different rate limiting steps.

Mechanisms where reactions occur between two sites are called Langmuir-Hinshelwood mechanism. Sometimes one may have an adsorbed site reacting with a molecule in the gas-phase directly. Thus we could have,



These reactions are said to follow the Rideal-Eliy mechanism.

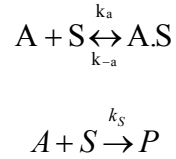
**Pseudo steady state approach:**

It is also possible to determine the kinetics using the pseudo steady-state assumption which is adopted for homogeneous phase reactions

These two approaches can be compared as follows

- (i) Based on assuming a step to be very slow and the rate controlling step and assuming all the others to be very fast and at equilibrium.
- (ii) Based on assuming the net rate of production of the intermediate to be zero i.e., at pseudo steady state.

Consider the isomerisation reaction  $A \rightarrow P$  occurring through the following mechanism



Here,  $r_p = k_s C_{A.S}$ .

The condition  $C_{A.S} + C_v = C_T$  also holds good.

Assuming first step to be very fast and at equilibrium, then,

$$k_a P_A C_v = k_{-a} C_{A.S}$$

$$\text{or, } K_A P_A C_v = C_{A.S}$$

$$\text{Hence, } C_v = \frac{C_T}{1 + K_A P_A}$$

$$\text{and } C_{A.S} = \frac{K_A P_A}{1 + K_A P_A},$$

$$\text{which yields, } r_p = \frac{k_s K_A P_A}{1 + K_A P_A},$$

This is the rate expression for the reaction using the concept of a rate determining step.

One can also assume the net rate of production of the intermediates i.e the adsorbed sites to be zero i.e they are assumed to be at steady-state. This yields,

$$r_{A.S} = k_a P_A C_v - k_{-a} C_{A.S} - k_s C_{A.S}.$$

If this is at pseudo-steady state, then one has,

$$C_{A.S} = \frac{k_a P_A C_v}{k_{-a} + k_s}.$$

$$\text{Also, } C_v \left( 1 + \frac{k_a P_A}{k_{-a} + k_s} \right) = C_T$$

This yields,

$$\begin{aligned}
 r_p &= k_S C_{A,S} \\
 &= \frac{k_S k_a P_A}{k_{-a} + k_S + k_a P_A} \\
 &= \frac{k_S K_a P_A}{1 + K_a P_A + \left(\frac{k_S}{k_{-a}}\right)}
 \end{aligned}$$

Hence when  $k_S \ll k_a$ , identical expressions will be obtained from both approaches. This is consistent since when  $k_S$  is very low then it is the rate determining step. In general, however, the two approaches give rise to different rate expressions.

Since the kinetic expression or the rate equation is available one can use this to design a reactor. In reactor design one is interested in finding how much catalyst is required to achieve a given conversion. Consider a packed bed reactor. This is essentially a tubular reactor which is packed with catalyst pellets. With the weight of the catalyst is the independent variable, hence  $W = 0$  at inlet and it increases as one goes downstream.

$r_A'$  is defined to be the rate of the reaction on a per unit weight basis. A mole balance at steady-state gives (see Fig. 7.4),

$$F_A \Big|_w - F_A \Big|_{w+dw} + r_A' dw = 0$$

$$\text{or, } \frac{dF_A}{dW} = r_A'$$

In terms of conversion,  $F_A = F_{A_0}(1 - x)$

$$F_{A_0} \frac{dx}{dW} = r_A'$$

$$\text{or, } W = \int dW = F_{A_0} \int_0^{x_f} \frac{dx}{(-r_A')}$$

The kinetic expression in terms of concentrations or partial pressures is employed to determine the weight of catalyst required. This design equation is very similar to that of a plug flow reactor sustaining a homogenous chemical reaction. There, since the reaction rate is on a per unit volume basis, one finds the reactor volume whereas in the present case, since the rate is on a per unit mass basis, one finds the mass of the catalyst required. This similarity is to be expected since no mass transfer limitations or diffusional resistances have been taken into account.

These resistances result in a lowering of reactant concentration at the catalytic site. The reaction rate hence has to be evaluated at this low concentration. For typical reactions, rates decrease with decreasing concentration. Hence the actual reaction rate is lower than that evaluated at the bulk concentration. Hence a larger amount of the catalyst is required, for the same amount of conversion than that predicted by earlier equation when mass transfer resistances are included.

## 7.2 External mass transfer resistance:

The case of a chemical reaction occurring on the surface of a non-porous catalyst will be now considered.

Here the catalyst is assumed to be deposited only on the outer surface of the particle which is assumed to be solid i.e., non-porous. Since the particle is non porous there is no internal diffusional resistance. For

simplicity the particle is assumed to be spherical. The reaction occurs over the external surface area of the sphere. If there is no mass transfer resistance the concentration of the gas phase at the interface would be the same as that of the bulk. Hence the rate of the reaction can be evaluated using the bulk concentration value in the reaction rate expression.

However if external mass transfer resistance is significant then there is a concentration gradient outside the catalyst particle. As a result of this the concentration at the particle surface  $C_S$  is lower than that in the bulk  $C_B$ . The rate of the reaction hence has to be evaluated using  $C_S$  and not  $C_B$ . However  $C_S$  is unknown and has to be determined.

It is assumed that the reaction is occurring at steady state. Hence the rate at which the reactant A reaches the surface of the particle must be equal to the rate at which it is consumed by the reaction. This yields

$$-r'_a \cdot A_p = k_m A_p (C_B - C_S).$$

The reaction rate expression on the left is evaluated at the surface concentration which is unknown. This equation is hence an algebraic equation which has to be solved for  $C_S$ . Once  $C_S$  is determined we can find the rate of the reaction by substituting that value in either side of the above equation. In general the reaction rate is a monotonically increasing function of the concentration and so external mass transfer resistance always decreases the reaction rate.

The behavior of the system under two limiting conditions is considered.

- i) Consider the case of extremely high external mass transfer resistance: The high external mass transfer resistance induces a significant drop in the concentration of the reactant. As a result the rate of supply of the reactant to the surface is very slow compared to the reaction rate. Under these conditions the concentration of the reactant at the surface  $C_S$  is negligibly small and can be approximated to be zero. The rate of the reaction under these conditions is then given by the R.H.S of equation and is given by  $k_m C_B$ . Thus the reaction behaves as if it is a first order reaction with the mass transfer coefficient as the reaction rate. Hence under these conditions the mechanism of the reaction does not decide the reaction rate. Irrespective of how complicated the reaction rate expression the reaction behaves as if it is a first order reaction with the mass transfer coefficient as the reaction rate constant. Here the reaction rate is very fast compared to the rate of external mass transfer. Hence at the catalyst site the reactant is consumed as soon as it reaches the site resulting in a low concentration at the site.
- ii) The case of low mass transfer resistance or slow reaction: In this case there is no drop in the concentration of the reactant outside the particle. Here the mass transfer rate is very high compared to the reaction rate. Consequently the concentration at the surface is equal to that of the bulk and one has to evaluate the reaction rate using the bulk concentration values in the reaction rate expression obtained from the actual mechanism. Here the rate is evaluated from the LHS of the equation this using bulk concentration values. Since the reaction is slow it is the rate determining step.

The effect of external mass transfer resistance can be quantified. When this resistance is high, the concentration will drop from the bulk value to an intermediate value at the surface as discussed. This is  $C_A^S$ .

The flux of A to the surface of the pellet is  $k_m (C_A^0 - C_A^S)$ . At steady-state, the amount of A consumed by the reaction is supplied by mass flux. The reaction is assumed to be first order for the sake of simplicity.

$$-r_A = k_m (C_A^0 - C_A^S) = k_r C_A^S$$

When the mass transfer coefficient is very low, the reaction rate is much higher than the rate of mass transfer and external mass transfer is rate controlling. The reactant gets consumed as soon as it reaches the catalytic site. The concentration at the site is hence given by  $k_m C_A^0$ , since here  $C_A^S \ll C_A^0$  and one can approximate  $C_A^S = 0$ .

The reaction rate is hence determined by the mass transfer coefficient. The reaction hence behaves as a first order reaction, with the rate constant being the mass transfer coefficient. Hence even if the reaction has highly complex kinetics when it is mass transfer limited, one can treat it as a first order reaction with rate constant being mass transfer coefficient.

The concept of the rate determining step and how this can be used to diagnose and propose improvements in case a reactor is performing below the expected efficiency will be discussed **now**. Consider a situation where the reaction is designed for 70% conversion but actually yields only 40% conversion. One would like to take appropriate corrective steps to improve this conversion value to the designed value.

Lets assume that the reaction is occurring under conditions where the reaction is the rate determining step. This implies that the reaction is very slow compared to the rate of external mass transfer. Hence the external mass transfer is very fast and so any improvement in this is not going to yield any significant **improvement in the** reaction rate. Consequently in this case one has to increase the reaction rate by increasing the temperature or by using a more active catalyst.

If the reaction were occurring when the external mass transfer is the rate determining step, then here the reaction rate is relatively fast. Hence any increase in temperature will only serve to increase the reaction rate which is already very high. The cause for the loss of efficiency is however the external mass transfer resistance and so one must take initiative to reduce this resistance. This can be reduced for example by increasing the flow rate of the gases since this increases the mass transfer coefficient. It is hence necessary to determine which of the steps are fast or slow so that one can take suitable corrective action in case there is a drop in the performance efficiency.

Consider a solid sphere, such that the catalyst is deposited only on the external surface area  $A_p$ . The reaction hence occurs only on the surface where the concentration is  $C_{AS}$ . This surface concentration cannot be measured. One can measure only the bulk concentration  $C_{A0}$ . The rate of mass transfer to the pellet is

$$A_p k_m (C_{A0} - C_{AS})$$

The rate of reaction is  $k_r C_{AS} A_p$ . Both these expressions contain an unknown  $C_{AS}$ . We exploit the fact that at steady-state these two have to be equal to find  $C_{AS}$ . This is substituted back and one gets the rate expression in terms of  $C_{A0}$ .

$$k_m (C_{A0} - C_{AS}) = k_r C_{AS}$$

or,

$$C_{AS} = \frac{k_m C_{A0}}{k_m + k_r}$$

Hence the reaction rate is

$$\frac{k_m k_r C_{A0}}{k_m + k_r} A_p$$

When  $k_m \gg k_r$ , the reaction rate is the determining and the surface concentration equals bulk concentration and we have,

$$r_A = k_r A_p C_{A0}$$

When  $k_m \ll k_r$ , external mass transfer is rate determining and the surface concentration is almost zero, and we have

$$r_A = k_m A_p C_{A0}$$

So we have mathematically shown what we physically expect. This treatment shows the interplay between the two effects, rate constant and mass transfer coefficient.

### 7.3 Internal diffusional effects:

We will now discuss how internal diffusional resistance changes the concentration of reactant inside a pore. For simplicity we consider a single cylindrical pore of radius 'r' and length L as shown.

The catalyst is deposited on the inner curved surface of the pore (Fig. 7.5). The end at  $x=0$  is exposed to the reactant A at a fixed concentration i.e the bulk concentration or a surface concentration. The end at  $x=L$  is blocked or sealed. Consequently the different species can't go through this face and the flux is zero. We consider an incremental shell of thickness  $dx$ , extending from  $x$  to  $x+dx$ . The mass balance for the species 'A' is given as,

$$\text{in} - \text{out} + \text{generation} = \text{accumulation}$$

$$\text{in} - \text{out} + \text{generation} = 0, \text{ at steady state.}$$

Since the flux is purely by diffusion, we have,

$$-D \left. \frac{dC}{dx} \right|_x A + D \left. \frac{dC}{dx} A \right|_{x+dx} + r_A'' \cdot 2\pi \Delta x r = 0$$

Here  $r_A''$  is the reaction rate per unit surface area. Since  $A = \pi r^2$ , we have,

$$D \frac{d^2C}{dx^2} + r_A'' \cdot \frac{2}{r} = 0$$

This is subject to boundary conditions

$$C_A(x=0) = C_{AS}, \quad \left. \frac{dC_A(L)}{dx} \right| = 0$$

$C_{AS}$  is taken to be the same as the bulk concentration.

The differential equation governs how C depends on x. This dependency is a function of the parameters D, L, r, k,  $C_{AS}$ . We can determine how each parameter individually affects the concentration profile. We can depict this dependency graphically. This would require many curves, each of which determines the functional dependency of C on x. To get a deeper and a more comprehensive insight into the factors affecting the behavior we can render this equation dimensionless. This will help us determine the group of parameters which in turn determines the behaviour of the concentration in the pellet. For this purpose we define the dimensionless variables.

$$C^* = \frac{C_A}{C_{AS}}, \quad x^* = \frac{x}{L}.$$

Thus the dependent and independent variable are both rendered dimensionless. For simplicity we consider a first order reaction. This renders the equation linear and permits an analytical solution. We have,

$$r_A'' = -k'' C_A = \frac{1}{S} \frac{dN_A}{dt},$$

where  $k''$  is the rate constant defined on a per unit area basis. Here  $k''$  has units of  $\text{cm}^3 / (\text{cm}^2 \text{ cat}) \text{ sec}$ .

In terms of dimensionless units,

$$\frac{d^2 C^*}{dx^2} - \frac{2L^2}{rD} k'' C^* = 0$$

$$C^*(0) = 1, C^*(1) = 0$$

We define  $\phi^2 = L^2 \frac{2k''}{rD}$ , the parameter is written as  $\phi^2$ , to indicate that it is positive. **The square is usually used to confirm that it cannot be negative**, The parameter  $\phi$  is called the Thiele Modulus. The differential equation is,

$$\frac{d^2 C^*}{dx^{*2}} - \phi^2 C^* = 0$$

$$C^*(0) = 1, C^*(1) = 0.$$

Hence the dependence of dimensionless concentration on spatial coordinate  $x^*$  depends on only one parameter  $\phi$ . We can hence represent the dependency in a one-parameter family of curves. Hence it is the combination of parameters as it appears in  $\phi^2$  which is important.

Two linearly independent solutions for the differential equation are  $\sinh \phi(x^* - 1)$ ,  $\cosh \phi(x^* - 1)$ . These satisfy the differential equation.

Hence,  $C^* = A \sinh \phi(x^* - 1) + B \cosh \phi(x^* - 1)$ .

Since,  $\frac{dC^*(1)}{dx^*} = 0$ ,

$$A\phi \sinh \phi(x^* - 1) + B\phi \cosh \phi(x^* - 1) = 0$$

$$\Rightarrow A = 0.$$

$$C^* = B \cosh \phi(x^* - 1)$$

$$C^*(0) = 1 \Rightarrow B = \frac{1}{\cosh(1 - \phi)},$$

$$\text{or } C^* = \frac{\cosh \phi(x^* - 1)}{\cosh(-\phi)} = \frac{\cosh \phi(1 - x^*)}{\cosh(\phi)}$$

The variation of  $C^*$  on  $x^*$  for various  $\phi$  is shown in Fig. 7. 6.

For low values of  $\phi$  the concentration every where inside the pore is high. Here the diffusion coefficient is very high as compared to the reaction rate and hence the concentration is uniform across the pore and is almost equal to the surface concentration  $C_s$ . The reaction rate in comparison to the diffusion rate is very low. Hence all the sites through out the pore participate in the reaction. For low values of  $\phi$  the diffusion rate is very high and the reaction rate is very low. The reaction is the rate limiting step. Under these conditions the reaction is unable to consume the A supplied by diffusion. We can hence take the concentration of A to be uniformly equal to the surface concentrations under these conditions. The

concentration of A available at the catalytic site is equal to the surface concentration. The reaction rate can hence be evaluated neglecting the internal diffusion effect. We can calculate the reaction rate using the kinetics, and assuming the reaction rate takes place everywhere in the pore at the surface concentration. The concentration curves for  $\phi = 0$  and 0.1 hence almost coincide and we have a uniform value of concentration for all spatial positions  $x^*$  ( $x/L$ ) (Fig.7.6)

For high  $\phi$ , the concentration drops to a low value near the sealed end of the pore. Consequently a significant fraction of the pore length doesn't have a high enough concentration and doesn't participate in the reaction. To illustrate this we show the concentration dependency on spatial position for  $\phi = 0.25$  and 0.5 in Fig. 7.6. So any expensive catalyst which is deposited away from the pore mouth under these conditions is hence unutilised.

The parameter  $\phi$  can hence be interpreted as the ratio of two rates the reaction rate to diffusion rate. For high values of  $\phi$  the reaction rate is fast and the diffusion rate is slow. Here the internal diffusion rate results in significant concentration gradients. The concentration inside the pore is significantly different from the surface concentration. Hence the reaction rate has to be evaluated at the concentration prevailing at each spatial position inside the pore and not at the surface. The reaction rate consequently inside the pellet will be in general lower than what is present when no diffusional resistance is present. This is true since for most reactions the rate decreases with decrease in concentration.

The effectiveness factor of a catalyst is defined as the ratio of the actual reaction rate to the reaction rate when there are no diffusional resistances. This is defined as,

$$\eta = \frac{\text{Actual reaction rate}}{\text{Reaction rate when no diffusion resistance is present.}}$$

Clearly the numerator is evaluated by taking into account the finite diffusional resistance. Under steady-state conditions, the amount of A consumed by reaction must be equal to the amount of A coming into the pore at  $x = 0$ . This can be established by integrating the differential equation over the length of the pore.

$$D A \frac{d^2 C}{dx^2} = 2\pi r k'' C$$

$$\text{or } D A \frac{d}{dx} \left( \frac{dC}{dx} \right) = 2\pi r k'' C$$

$$\text{or } D A \int_0^L d \left( \frac{dC}{dx} \right) = 2\pi r \int_0^L k'' C dx$$

$$\text{or } D A \left[ \frac{dC(L)}{dx} - \frac{dC(0)}{dx} \right] = 2\pi r \int_0^L k'' C dx$$

From b.c at  $x = L$ ,

$$- D A \frac{dC(0)}{dx} = 2\pi r \int_0^L k'' C dx$$

This equation states that the

amount of A entering at  $x=0$  = amount of A being consumed in the pore by reaction.

Hence,



$$\begin{aligned}
 \eta &= \frac{-D A \frac{dC(0)}{dx}}{2\pi r k'' C_{AS} L} \\
 &= \frac{D \pi r^2 C_{AS}}{2\pi r L k'' C_{AS} L} \frac{dC^*(0)}{dx^*} \\
 &= \frac{1}{\phi^2} \frac{dC^*(0)}{dx^*} \\
 &= \frac{\tanh \phi}{\phi}
 \end{aligned}$$

For low  $\phi$ ,  $\phi \rightarrow 0$ ,  $\eta \rightarrow 1$ .

For high  $\phi$ ,  $\eta \rightarrow 1/\phi$ .

Consequently on a log - log plot the  $\eta$  versus  $\phi$  dependency is as shown in Fig.7.7

For low  $\phi$ , the reaction is rate controlling and internal diffusion is very fast. Consequently the concentration inside the pore is very close to  $C_{AS}$  and the effectiveness factor is close to unity.

For high  $\phi$ , the internal diffusional effects are significant. Here the effectiveness factor is lower than unity, since the concentrations inside the pore are lower than the surface concentrations. This lowers the reaction rate inside the pore. The actual reaction rate in the pore is hence equivalent to that in the pore, assuming the concentration is the surface concentration everywhere times the effectiveness factor.

#### Diffusional resistance in a catalyst pellet:

So far we have considered the concentration profile in a single cylindrical pore, caused by a finite internal diffusional resistance. Catalytic reactions take place in packed beds which are filled by catalyst pellets. A catalytic pellet consists of a random network of cylindrical pores. In addition to this, the pores may have varying cross-sectional area. Also inside the pellet they are randomly distributed and oriented (Fig. 7.8).

As a consequence of the random network the molecules have to take a tortuous path to go from one point to another. They cannot go directly from A to B, as the crow flies. Besides when considering the flow of gas molecules of A through a surface, only the portions of surface intersected by the pores contribute to the flow. The other portions of the surface are impermeable and do not allow any A to flow across them.

To incorporate these non-idealities, one uses an effective diffusivity,  $D_e$  to model the flux. This is different from the molecular diffusivity 'D'. Here we consider  $-D_e \nabla C$  to represent the flux.

We consider a spherical porous catalyst particle. We want to determine how concentration varies with position 'r' inside the pellet.

We consider a thin spherical shell of thickness  $dr$  from  $r$  to  $r+dr$ (Fig. 7.9)

The mass balance of the species A is given as,

$$\text{in} - \text{out} + \text{generation} = \text{accumulation}$$

$$-D_e \frac{dC}{dr} 4\pi r^2 \Big|_r + D_e \frac{dC}{dr} 4\pi r^2 \Big|_{r+dr} + r_A'' S \cdot 4\pi r^2 dr = 0$$

Here  $r_A''$  is the reaction rate per unit surface area of catalyst surface and S is the surface area per unit volume of the catalyst.

One might think the flow of A is occurring towards the center. Hence the in term corresponds to the surface at 'r+dr'. Here the flux is in the '-r' direction and is hence  $D_e \frac{dC}{dr} \Big|_{r+dr}$ . Similarly the out term is at the surface 'r'. This is again in the negative r direction and is  $D_e \frac{dC}{dr} \Big|_r$ . Since this is an out term it is associated with a negative sign and we recover the equation.

The differential equation governing the concentration profile is,

$$\frac{D_e}{r^2} \frac{d}{dr} \left( r^2 \frac{dC}{dr} \right) + r_A'' S = 0$$

This is subject to boundary conditions,

$$C_A(r = R) = C_A^S$$

$$C_A(r = 0) = \text{finite.}$$

For the n<sup>th</sup> order reaction,

$$r_A'' = K'' C_A^n$$

Here the '' is used to indicate that the reaction rate and is determined on a per unit surface area basis. Its units are hence (cm<sup>2</sup>)/cm<sup>2</sup> cat moles<sup>n-1</sup> sec .

The variation of the concentration C<sub>A</sub> on spatial coordinate r hence depends on the parameters C<sub>AS</sub>, D<sub>e</sub>, R, k'', and S. Rather than study the effects of these parameters individually on the concentration profile, we look for a compact way to represent the dependency of C on r. We achieve this by rendering the equation dimensionless. There is only one dependent variable C<sub>A</sub> and one independent variable, r. This is made dimensionless choosing the scales C<sub>AS</sub> and R. Define,

$$C = \frac{C_A}{C_{AS}} \text{ and } s = \frac{r}{R}$$

We then obtain,

$$\frac{1}{s^2} \frac{d}{ds} \left( s^2 \frac{dC}{ds} \right) - \frac{k'' C_{AS}^{n-1} R^2}{D_e} S C^n = 0$$

$$C(s = 1) = 1$$

$$C(s = 0) = \text{bounded}$$

We defined,

$$\phi^2 = \frac{k'' C_{AS}^{n-1} R^2 S}{D_e}$$

The parameter  $\phi$  is called the Thiele Modulus and it clearly depends on the surface concentration C<sub>AS</sub>. The second order equation is,

$$\frac{d^2C}{ds^2} + \frac{2}{s} \frac{dC}{ds} - \phi^2 C = 0$$

This is an equation with variable coefficients, which yields  $C(S)$ . We define a new variable  $Y(S)=C(S) \cdot S$ . The new variable  $Y$  is determined by,

$$\frac{d^2Y}{ds^2} - \phi^2 Y = 0$$

subject to,

$$Y(s) = 1 \text{ at } s = 1$$

$$Y(0) = 0$$

This has a solution of the form,

$$Y(s) = A \sinh(\phi s) + B \cosh(\phi s)$$

$$Y(0) = 0 \quad \Rightarrow B = 0$$

$$Y(1) = 1 \quad \Rightarrow A = \frac{1}{\sinh \phi}$$

$$\text{This yields, } Y(s) = \frac{\sinh(\phi s)}{\sinh \phi}$$

$$\text{and } C(s) = \frac{1}{s} \frac{\sinh(\phi s)}{\sinh \phi}$$

The dependence of  $C(s)$  on  $s$  for various  $\phi$  is shown in Fig.7.10, Hence for higher values of  $\phi$ , the diffusional resistances is large and the reactant concentration near the center is very low. Consequently the central core of the pellet does not support any reaction and the precious catalyst in this region is unutilised. This can be avoided by coating the catalyst only in the annular region. For low  $\phi$ , the concentration is high, everywhere in the pellet, and hence the entire pellet is effective.

One can determine the effectiveness of the catalyst pellet. The effectiveness factor,  $\eta$  is defined as,

$$\eta = \frac{\text{Actual reaction rate}}{\text{Reaction rate assuming no differential resistance is present.}}$$

The numerator is evaluated by taking into account the fact that the flow of A into the pellet must be equal to the amount of A that has reacted.

Hence,

$$\text{Numerator} = De \left. \frac{dC_{AS}}{dr} \right|_{r=R} 4\pi R^2$$

$$\begin{aligned}
 &= De \, 4\pi R \, C_{AS} \left. \frac{dC}{dS} \right|_{S=R} \\
 &= De \, 4\pi R \, C_{AS} [\phi \coth \phi - 1]
 \end{aligned}$$

$$\text{Denominator} = k'' C_{AS}^n S \cdot \frac{4}{3} \pi R^3.$$

This yields,

$$\eta = \frac{3}{\phi^2} [\phi \coth \phi - 1]$$

On a log - log plot, the variation of  $\eta$  on  $\phi$  is depicted in Fig 7.11,

For large  $\phi$ ,  $\eta = 3/\phi$  and for low  $\phi$ ,  $\eta = 1$ .

For a first order reaction,  $\phi$  is independent of  $C_{AS}$ , hence  $\eta$  is independent of  $C_{AS}$ . The surface concentration is the same as the bulk concentration, when external mass transfer rates are high.

The actual reaction rate in a pellet is hence  $\eta \left. r_A'' \right|_S$ . The design equation of the reactor is,

$$W = F_{A0} \int_0^{X_1} \frac{dX_A}{-r_A'' \eta}$$

For general kinetics,  $\eta$  depends on  $C_{AS}$  and this varies with conversion  $X$  as we go along a reactor.

This is a pseudo-homogeneous model, since here we don't distinguish between the two phases i.e., gas phase and the solid phase in the reactor. Other models exist which explicitly account for the existence of the two phases. We will see these later. In general  $\eta$  is less than unity. Consequently, the inclusion of internal diffusional effect results in the need for a large amount of catalyst than what is needed when there are no diffusional resistances.

### **Intrinsic Kinetics and Apparent Kinetics:**

Intrinsic kinetics represents the kinetics of the reaction in the absence of external mass transfer resistance and internal diffusional resistance. This is the concentration dependency of reaction rate purely due to the three steps of adsorption of reactant surface reaction and the desorption of the products as determined by the concentration on the catalyst. This is hence the true kinetics or intrinsic kinetics or inherent kinetics. The concentration dependencies of the reaction rate can be obtained by proposing a mechanism and assuming one of the steps is the rate determining one. The other steps can be taken to be at equilibrium. Alternatively we can assume that the intermediate species are at pseudo-steady state as discussed earlier.

When internal diffusional resistances are present the concentration dependency of the reaction rate gets modified. One can again measure the reaction rates at different concentrations and obtain the reaction rate dependency on concentration. This gives the kinetics of the reaction which is masked/modified by the mass transfer resistance. This kinetics is the measured rate of the reaction and its concentration dependency can be different from that measured in the absence of diffusion effects.

The two kinetic parameters are order of the reaction 'n' and the activation energy, 'E'. We will now see how internal diffusion effects modifies these parameters.

The kinetics of the reaction which is measured in the presence of the reaction which is measured in the presence of internal diffusional resistance is called the apparent kinetics.

Consider a reaction which is  $n^{\text{th}}$  order in reactant A, i.e.,

$$-r_A = k C_A^n$$

When internal diffusional resistance is high, the rate of reaction observed is,

$$-r_A = \eta k C_A^{S^n}$$

where,  $\eta$  is the internal effectiveness factor.

For large value of resistances, i.e., high Thiele Modulus,  $\phi$ , we have the asymptotic relationship

$$\eta = \left( \frac{2}{n+1} \right)^{\frac{1}{2}} \frac{3}{\phi_n}$$

For an  $n^{\text{th}}$  order reaction,

$$\phi_n = R \sqrt{\frac{k C_S^{n-1} S_a}{De}}$$

Hence for large  $\phi$  if we measure the reaction rates at different concentrations,  $C_S$  it is given by,

$$\begin{aligned} -r_A &\propto \frac{C^{S^n}}{\sqrt{C_S^{n-1}}} \\ &\propto C_S^{n - \frac{n-1}{2}} \\ &\propto C_S^{\frac{n+1}{2}} \end{aligned}$$

Hence the observed reaction rate exhibits a  $\frac{n+1}{2}$ th order dependency on concentration, when the actual rate of reaction is  $n^{\text{th}}$  order. Thus an  $n^{\text{th}}$  order reaction would appear to be an  $n'^{\text{th}}$  order reaction where,  $n' = \frac{n+1}{2}$ . This is apparent order of the reaction. The kinetics of a first order reaction does not get modified.

The activation energy represents the temperature dependency of the reaction rate. In the presence of strong diffusional resistance, the temperature dependency is given by,

$$\begin{aligned} -r_A &\propto \frac{k}{\sqrt{k}} \\ &\propto k^{\frac{1}{2}} \end{aligned}$$

Hence the temperature dependency is given by an activation energy which is half of the true value when strong internal diffusional resistance is present..

#### 7.4 Internal and external mass transfer resistances:

In the above analysis we have considered the effect of only one resistance at a time either the internal diffusional resistance or the external mass transfer resistance. The steps which determine reaction rate occur sequentially as described earlier. The slowest steps are the ones where the resistance is largest.

Consider a simple electrical circuit with three resistances in series  $R_1, R_2, R_3$  such that  $R_1 \gg R_2, R_3$ . The current flowing through the resistance is given by Voltage divided by the sum of the resistances. Here we can get significant increase in the current by reducing  $R_1$ . The increase in the current when we reduce  $R_2, R_3$  will be only minimal. Hence we have to find which is the rate controlling step to take a proper action.

When a reaction is external mass transfer limited we can increase the rate by increasing the velocity or flow rate through the bed. This increases mass transfer coefficient and hence reaction rate. If the flow rate is very high, we might get poor conversion since the residence time will be lowered.

If internal diffusion is rate controlling we must reduce the size of the particle. This will give a higher  $\eta$ . Very small sized particles will increase the pressure drop across the reactor.

If the reaction is the rate controlling step, we can increase the rate by increasing temperature.

When a reactant A flows past a catalyst pellet a concentration gradient is established near the surface across a thin layer. This is the mass transfer boundary layer. This is analogous to the momentum boundary layer across which the momentum varies from 0 to 99 % of the free stream velocity. Similarly at the outer edge of the mass transfer boundary layer the concentration is 99 % of the bulk value  $C_A^0$  and the surface concentration is  $C_A^S$ . The variation of this concentration can be approximated to be linear. In this case the mass transfer coefficient is given as  $k = \frac{D_{AB}}{\delta}$ , where  $\delta$  is the thickness of the boundary layer. This can vary from point to point and the above relationship is valid locally. This can be averaged over the surface. The correlation for mass transfer,

$$Sh = 2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}$$

yield average mass transfer coefficient.

~~The concentration profile when mass transfer resistance is present is,~~

We next show how the reaction rate is determined in a porous pellet when both the external and internal resistances are present.

The rate of mass transfer to pellet

$$= k_m A_p (C_{A0} - C_{AS})$$

The rate of reaction in the pellet

$$= k_r A_p C_{AS} \eta$$

Here  $A_s$  is the total internal area of the pellet available for reaction. At steady-state one has

$$k_m A_p (C_{A0} - C_{AS}) = k_r A_s C_{AS} \eta$$

or,

$$C_{AS} = \frac{k_m A_p C_{A0}}{k_m A_p + k_r A_s \eta}$$

The reaction rate is hence given by,

$$\begin{aligned} &= \frac{k_r A_s \eta k_m A_p C_{A0}}{k_m A_p + k_r A_s \eta} \\ &= \frac{\eta k_r A_s C_{A0}}{1 + \eta \left( \frac{k_r A_s}{k_m A_p} \right)} \\ &= \Omega k_r A_s C_{A0}. \end{aligned}$$

Here  $\Omega$  is called the overall effectiveness factor and consider both internal and external mass transfer. Here  $\Omega < \eta$ . If  $k_m A_p \gg k_r A_s$ , then external mass transfer resistance can be neglected and the reaction rate is governed by internal effectiveness factor,

$$r_A = \eta k_r A_s C_{A0}.$$

Residence time calculation: The information of the residence time etc has to be used to generate the residence time for a particular reaction to achieve a degree of conversion.

The design equation can hence be written by modifying the rate using the overall effectiveness factor.

Consider a shell – balance as shown in **Fig 7.12**,

We have,

$$F_A \Big|_z + F_A \Big|_{z+dz} + r_A'' S \rho_b A \Delta z \Omega = 0$$

where  $\rho_b = \text{bed density} = \rho_p (1 - \varepsilon_b)$

$$\text{or } \frac{dF_A}{dz} = \Omega r_A'' S \rho_b A$$

$F_A$  is in terms of  $C_{Ab}$  the bulk concentration  $r_A''$  is in terms of concentration in the solid phase. Using the overall effectiveness factor  $\Omega$  one can write the rate  $r_A''$  in terms of the bulk gas phase concentration and we can find how  $C_{Ab}$  varies with  $z$ . This is called a pseudo homogenous model. Here we do not write the equations separately for each of the phases. In a heterogenous model we would consider each phase separately. The solution of the above equation helps us determine the residence time needed for a desired conversion.

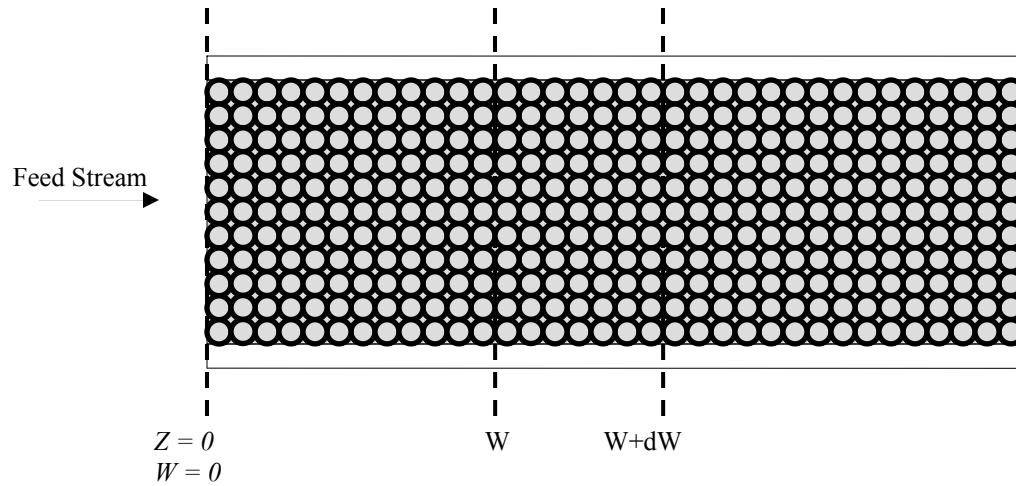


Fig. 7.4 Shell balance for a packed bed reactor indicating the shell chosen  $W$  the weight of the catalyst can also be used as the independent variable.

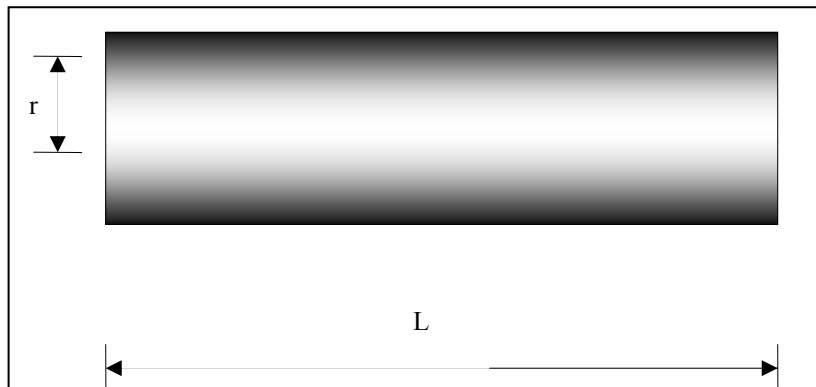


Fig. 7.5. Cylindrical pore inside whose surface catalyst is deposited



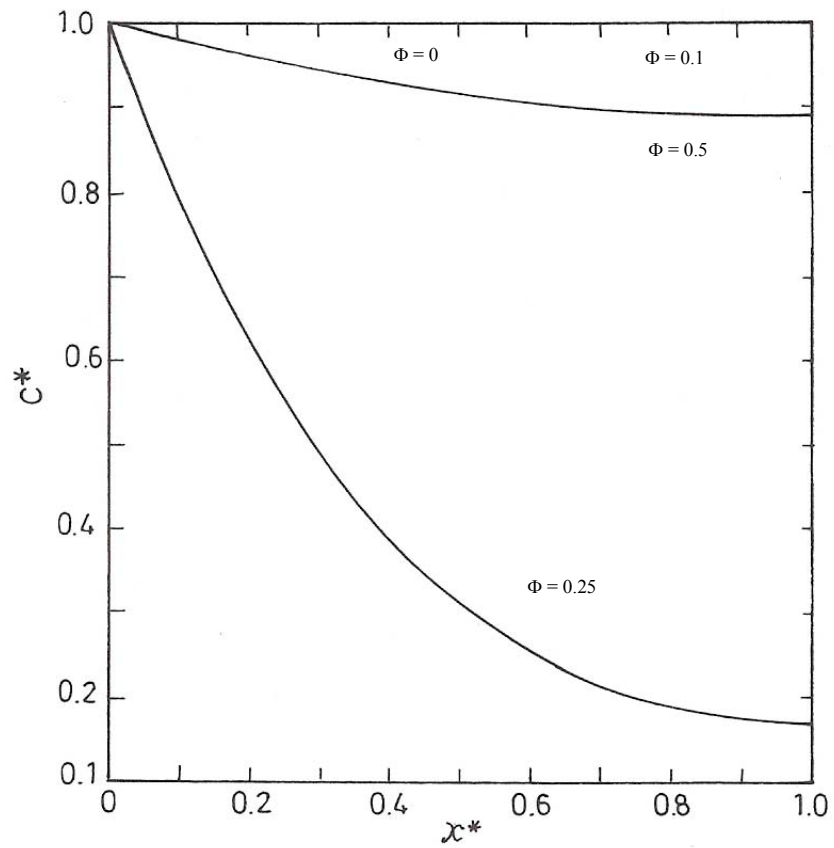


Fig . 7.6. Concentration profiles as a function of spatial position  $x^*$  ( $x/L$ ) for various Thiele Modulus for diffusion along a pore

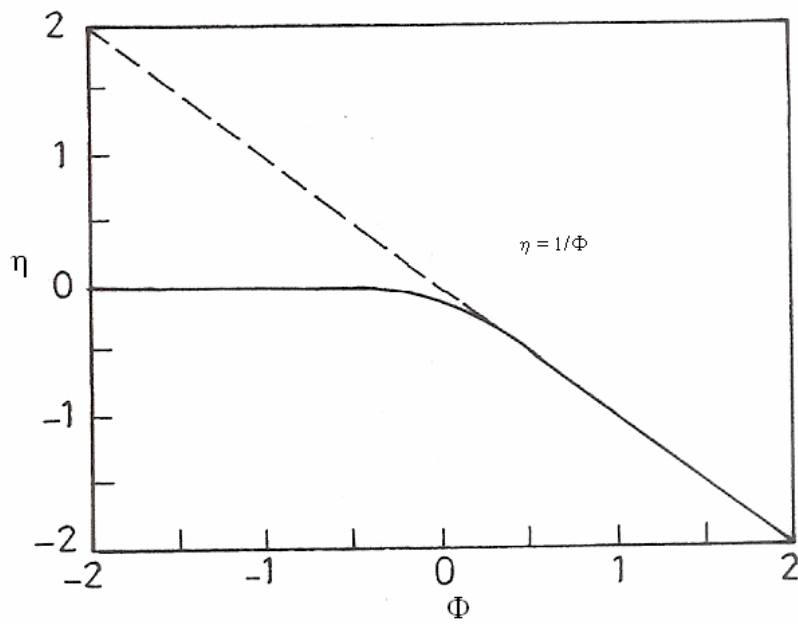


Fig. 7.7. Effectiveness factor as a function of the Thiele modulus (log-log plot of a cylindrical pore)

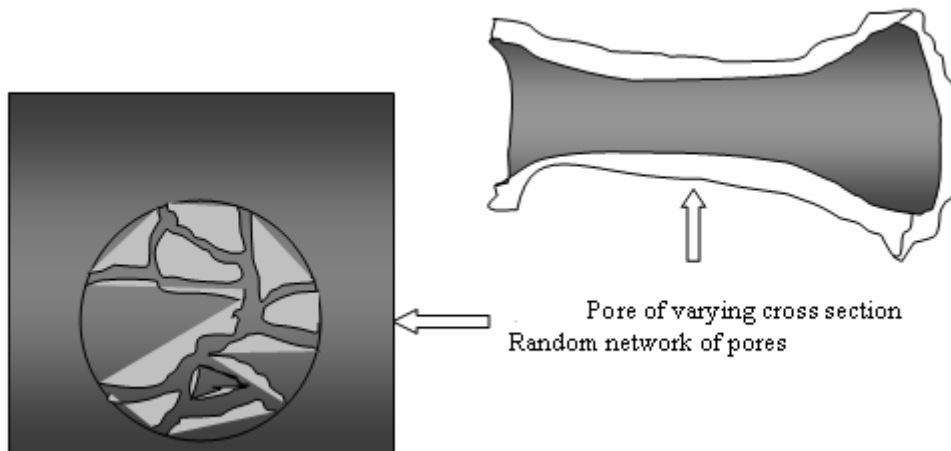


Fig. 7.8 Catalyst particle showing random network of pores and a pore with varying cross-sectional area

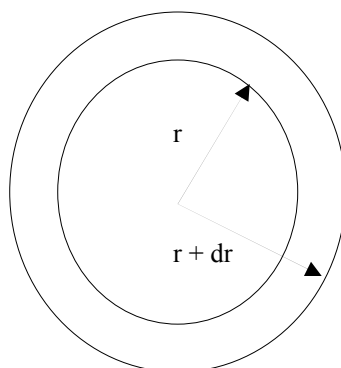


Fig. 7.9 Annular element for spherical shell

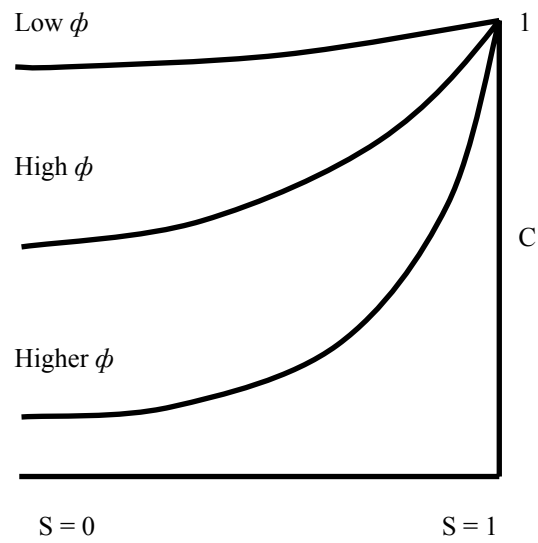


Fig. 7.10 Variation of concentration as a function of S for various Thiele Modulus for a spherical pellet

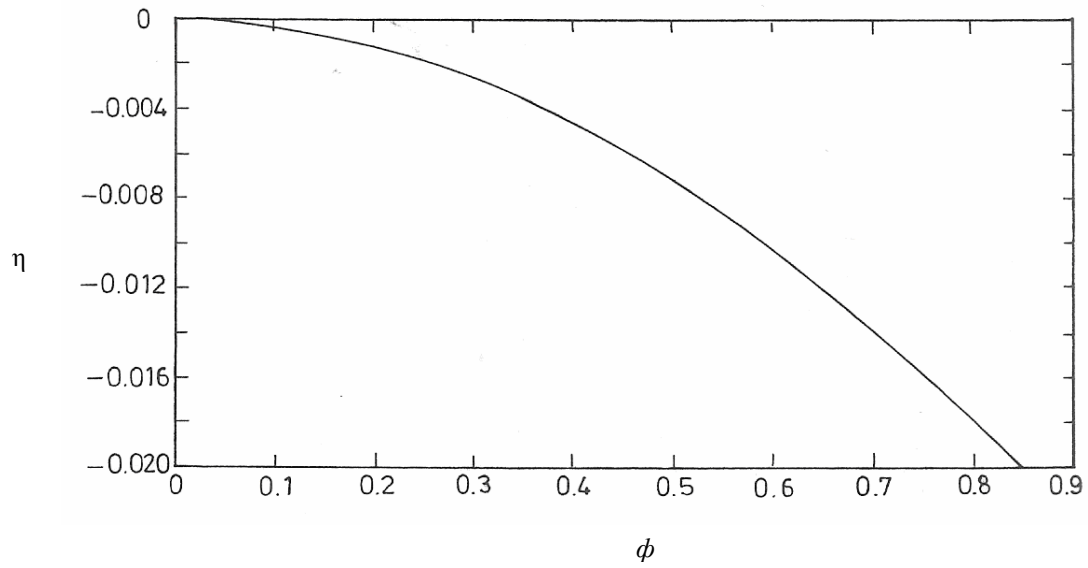


Fig. 7.11 Variation of effectiveness factor as a function of Thiele Modulus (log-log plot for a spherical pellet)

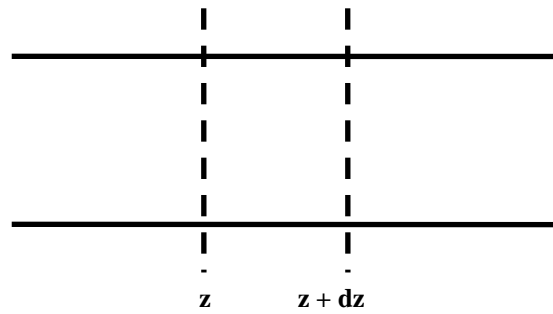


Fig. 7.12 Shell chosen for differential balance of packed bed reactor