



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

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**SCHOOL OF BIO AND CHEMICAL ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING**

UNIT – 1: NON - IDEAL REACTOR -SCHA1504

Unit I – Non-Ideal Reactors

The **real reactors** always deviate from the **ideal reactors** because of the **non-ideal flow conditions** within the reactor during the process. In the first unit you are going to study

1. The **non-ideal (real) reactors** and its **design**
2. The **factors** that make up the **contacting or flow pattern** in the non-ideal reactors.
3. **Basic models** used for **non-ideal reactors**

Ideal Reactors

1. PFR (no-axial mixing)
2. MFR (complete mixing)

Non-ideal reactors (real reactors)

The reactors always deviate some degree from these ideal behaviors called real reactors.

The deviation from ideal flow patterns may be caused by

1. Stagnant regions in the vessel (dead zone)
2. **Bypassing or short-circuiting of the fluid**
3. Channeling
4. **Recycling of fluid**
5. Due to vortices and turbulences at inlet and outlet

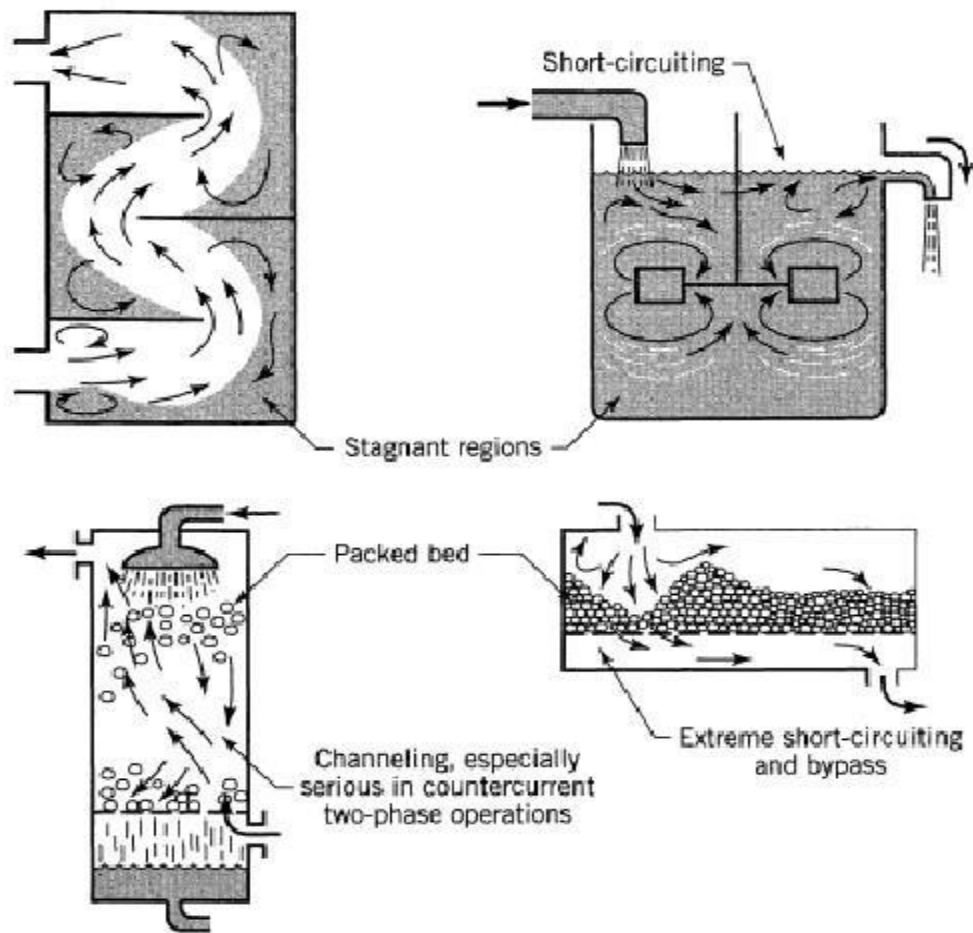


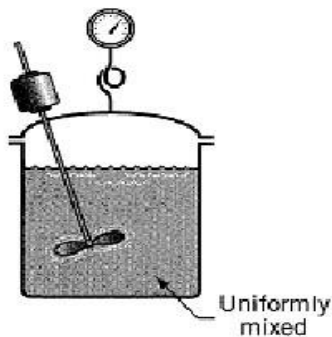
Figure — Nonideal flow patterns which may exist in process equipment.

Factors that make up the contacting or flow pattern are:

1. The RTD – residence time distribution of fluid flowing through the vessel.
2. The state of aggregation of fluid and
3. The earliness and lateness of fluid mixing in the vessel

Residence Time Distribution Function

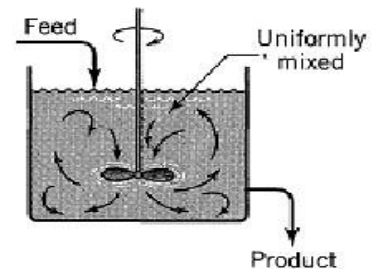
- The **time it takes a molecule to pass through a reactor** is called the residence time of the molecule in the reactor.
- It is clear that **elements of fluid taking different routes** through the reactor may take **different lengths of time** to pass through it.
- So there is a distribution of residence time of the fluid material within the reactor.
- The distribution of these times for the stream of fluid leaving the vessel is called the **exit age distribution, E** , or the **residence time distribution RTD of fluid**.



Batch Reactor



Plug Flow Reactor



Mixed Flow Reactor

- In an **ideal PFR** – all the molecules within the reactor having the same length of time.
 - In an **ideal batch reactor** - all the molecules within the reactor having the same length of time
 - The **ideal PFR and BR** are the only reactors in which all the fluid elements in the reactors have the **same residence time**.
 - In all other reactors, the various molecules spend different times inside the reactor, **Ex: MFR**
 - The feed introduced into the MFR at any given time completely mixed with the material already in the reactor.
-
- Some of the molecules entering the MFR leave it almost immediately, because the material is continuously removed from the reactor, other molecules remain in the reactor almost forever because **all the material is never withdrawn at one time from the reactor**. Many of the molecules leave the reactor after spending a period of time which is somewhere close to the mean residence time.
 - The **distribution of residence time** can significantly **affects the performance of reactor**.
 - The **RTD of a reactor** is a characteristic of the mixing that occurs in the reactor.

RTD Measurement

The RTD is determined experimentally by using an inert chemical called a tracer (dyes and radioactive materials).

Characteristics of chemical tracer:

1. It should be non-reactive
2. It should be completely soluble in the system fluid
3. It should be easily detectable
4. Physical properties of the tracer should be similar to those of the system and
5. It should not adsorb on the walls or others surfaces in the vessel.

Experimental Methods for Finding E

1. Pulse input
2. Step input
3. Periodic input
4. Random input

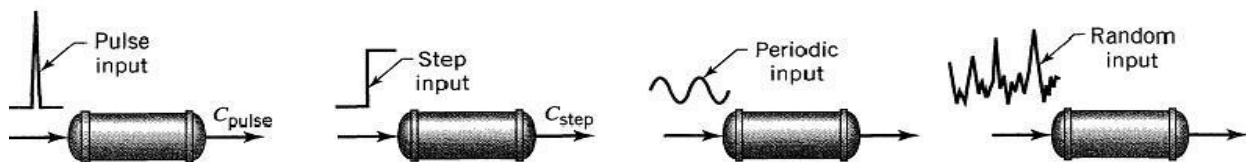


Figure — Various ways of studying the flow pattern in vessels.

1.The Pulse Input Experiment

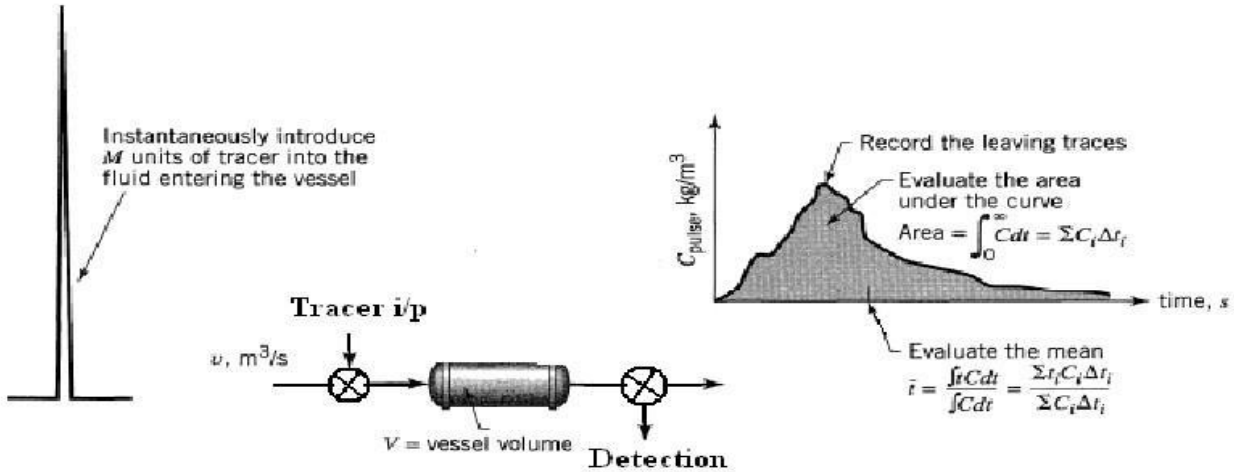


Figure — The useful information obtainable from the pulse trace experiment.

- The known quantity of **tracer** (M kg or moles) is suddenly **injected in one shot into the fluid entering** the vessel in a very short time period
- The **tracer concentration in the exit stream is measured as a function of time.**
- In RTD analysis, the effluent concentration-time curve is referred to as the **C curve** (**C_{pulse} curve**).
- The concentration of effluent stream **increases with time, reaches a maximum value and then falls**, eventually approaching zero.

The amount of tracer material, ΔM , leaving the vessel between t and $t+\Delta t$ is obtained by the material balance of the tracer

$$\Delta M = C v \Delta t \quad (1)$$

v is the volumetric flow rate of the effluent from the vessel

ΔM is the amount of material that has spent an amount of time between t and $t+\Delta t$ in the vessel

Eqn (1) / M

$$\frac{\Delta M}{M} = \frac{C v}{M} \Delta t = \frac{C}{M/v} \Delta t \quad (2)$$

Where M is the total amount of tracer injected into the vessel

$\Delta M / M$ is the fraction of material that has residence time between t and $t+\Delta t$ in the vessel

Let us define E is

$$E = \frac{C v}{M} = \frac{C}{M/v} \quad (3)$$

$$\frac{\Delta M}{M} = E \Delta t \quad (4)$$

whenever M is not known directly, it can be obtained by measuring the tracer concentration in the effluent stream and summing all the amounts of materials, ΔM , between time $t = 0$ and $t = \infty$.

Eqn (1) may be rewritten as

$$\int_0^M dM = \int_0^{\infty} C v dt \quad (5)$$

$$\int_0^M dM = v \int_0^{\infty} C dt \quad (6)$$

$$M / v = \int_0^{\infty} C \, dt \quad (7)$$

Combining equations (3) and (7)

$$E = \frac{C}{\int_0^{\infty} C \, dt} \quad (8)$$

$$\int_0^{\infty} C \, dt = \sum_0^{\infty} C_i \, \Delta t_i = \text{Area under the } C \text{ curve} = M / v$$

$$\left(\begin{array}{c} \text{Area under the} \\ C_{\text{pulse}} \text{ curve} \end{array} \right): \quad A = \int_0^{\infty} C \, dt \equiv \sum_i C_i \Delta t_i = \frac{M}{v} \quad \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right]$$

$$\left(\begin{array}{c} \text{Mean of the} \\ C_{\text{pulse}} \text{ curve} \end{array} \right): \quad \bar{t} = \frac{\int_0^{\infty} t C \, dt}{\int_0^{\infty} C \, dt} \equiv \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v} \quad [\text{s}]$$

E curve from C curve

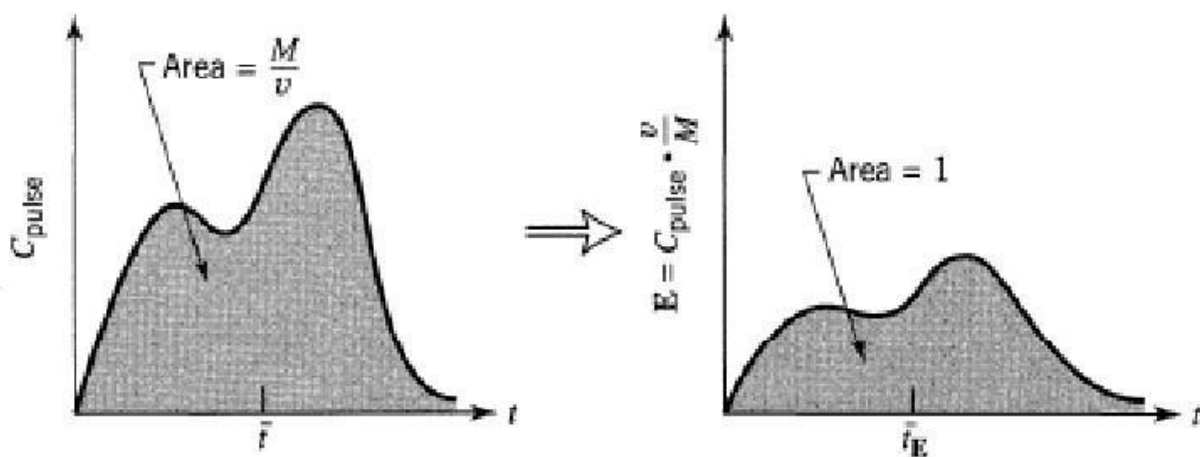


Figure: — Transforming an experimental C_{pulse} curve into an E curve.

Transforming an E curve into E_θ curve

We have another RTD function E_θ . Here time is measured in terms of mean residence time $\theta = t/\bar{t}$. Thus

$$E_\theta = \bar{t}E = \frac{V}{v} \cdot \frac{C_{\text{pulse}}}{M/v} = \frac{V}{M} C_{\text{pulse}}$$

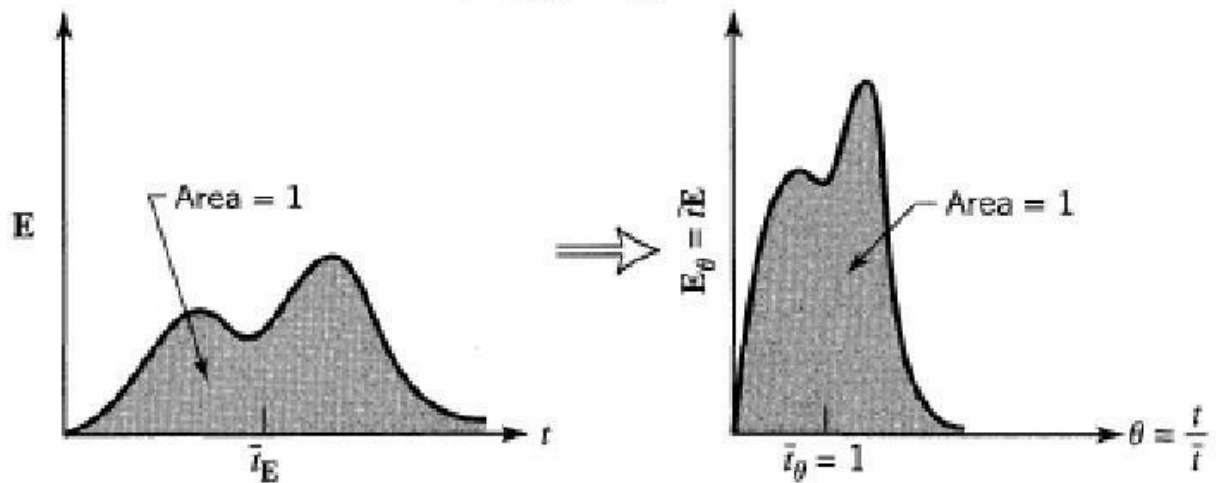


Figure . — Transforming an E curve into an E_θ curve.

2. The Step Experiment

- Consider $v \text{ m}^3/\text{s}$ of fluid flowing through a vessel of volume V .
- Now at time $t = 0$ switch from ordinary fluid to fluid containing tracer with tracer concentration C_{max} and measure the outlet concentration of tracer, C_{step} , in the effluent stream as a function of time

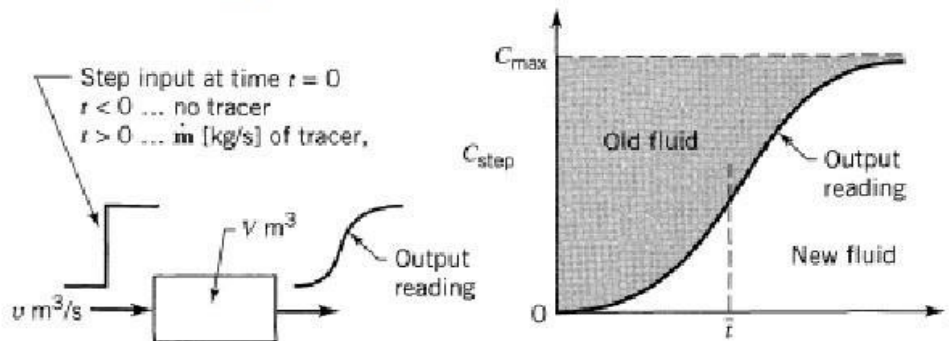


Figure — Information obtainable from a step tracer experiment.

$$C_{\max} = \frac{\dot{m}}{v} \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right]$$

$$\left(\text{shaded area} \right) = C_{\max} \bar{t} = \frac{\dot{m}V}{v^2} \left[\frac{\text{kg} \cdot \text{s}^2}{\text{m}^3} \right]$$

$$\bar{t} = \frac{\int_0^{C_{\max}} t dC_{\text{step}}}{\int_0^{C_{\max}} dC_{\text{step}}} = \frac{1}{C_{\max}} \int_0^{C_{\max}} t dC_{\text{step}}$$

$$F = \frac{C_{\text{step}}}{C_o}$$

$$\therefore C_{\max} = C_o$$

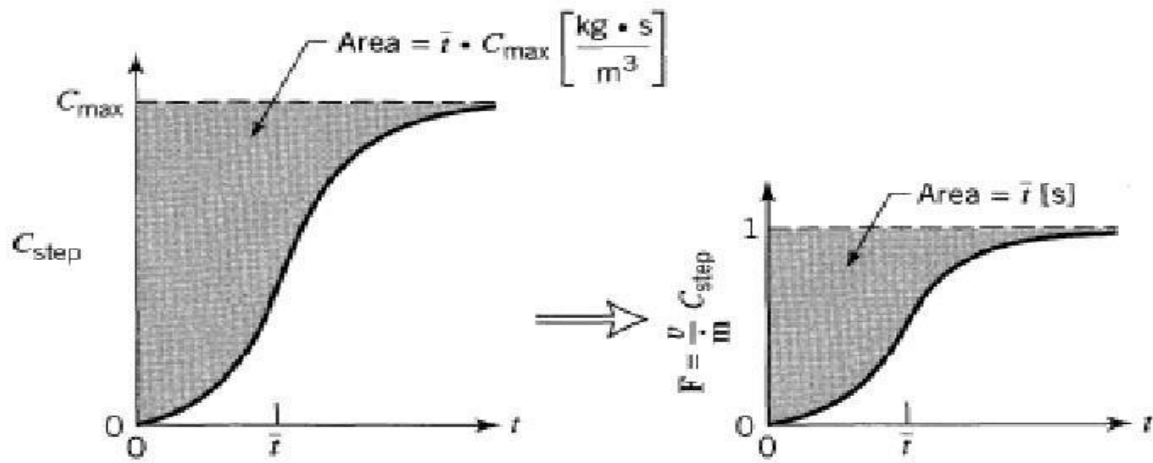


Figure 1 — Transforming an experimental C_{step} curve to an F curve.

Relationship between the F and E curves

- Consider that there is a **steady flow of main fluid** through the vessel and at time $t=0$, we **switch to tracer fluid** and **measure the rising concentration of tracer fluid** in the effluent stream, the F curve.
- At any time $t>0$, the tracer fluid and only tracer fluid in the effluent stream is younger than t . Therefore,

$$\left(\text{fraction of tracer fluid in the effluent stream} \right) = \left(\text{fraction of the effluent stream that has been in the vessel for less than time } t \right)$$

$$F = \int_0^t E \, dt \quad (1) \quad \left(\because \int_0^t E \, dt + \int_t^\infty E \, dt = 1 = \int_0^\infty E \, dt \right)$$

$$1 - F = \int_t^\infty E \, dt = \left(\text{fraction of the effluent stream that has been in the vessel for longer than time } t \right) \quad (2)$$

$$\int_t^\infty E \, dt = 1 - \int_0^t E \, dt \quad (3)$$

$$\int_t^\infty E \, dt = 1 - F \quad (4)$$

F is the cumulative RTD function

On differentiating eqn (1) with respect to t , we get

$$\frac{dF}{dt} = E$$

This is the relationship b / w E and F

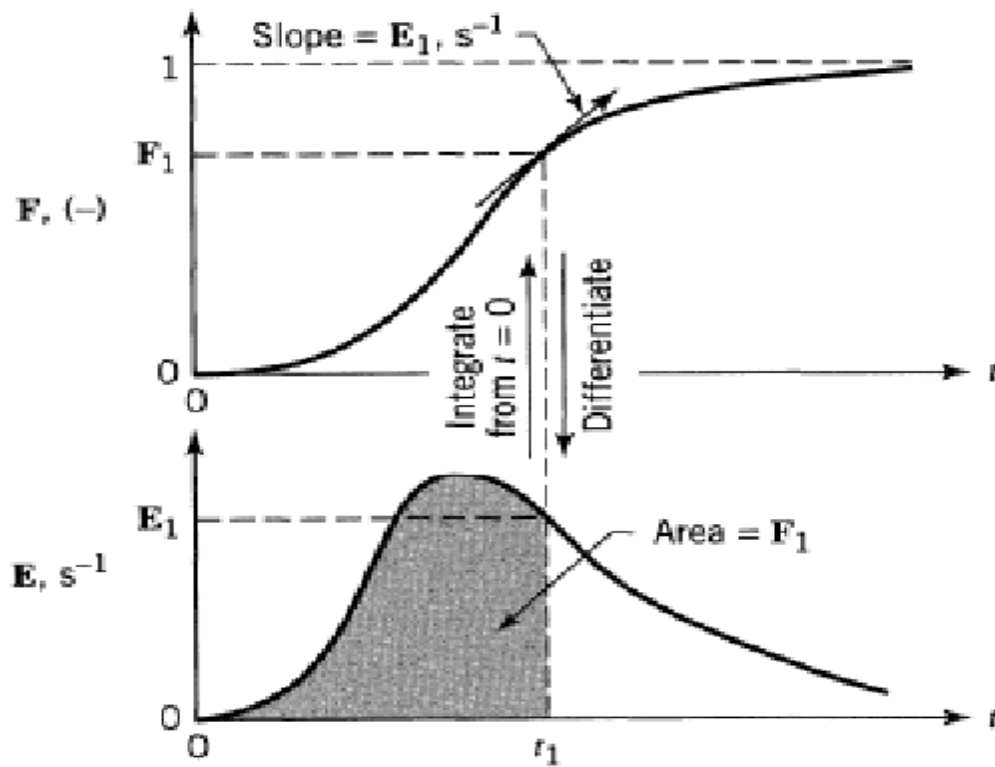


Figure — Relationship between the **E** and **F** curves.

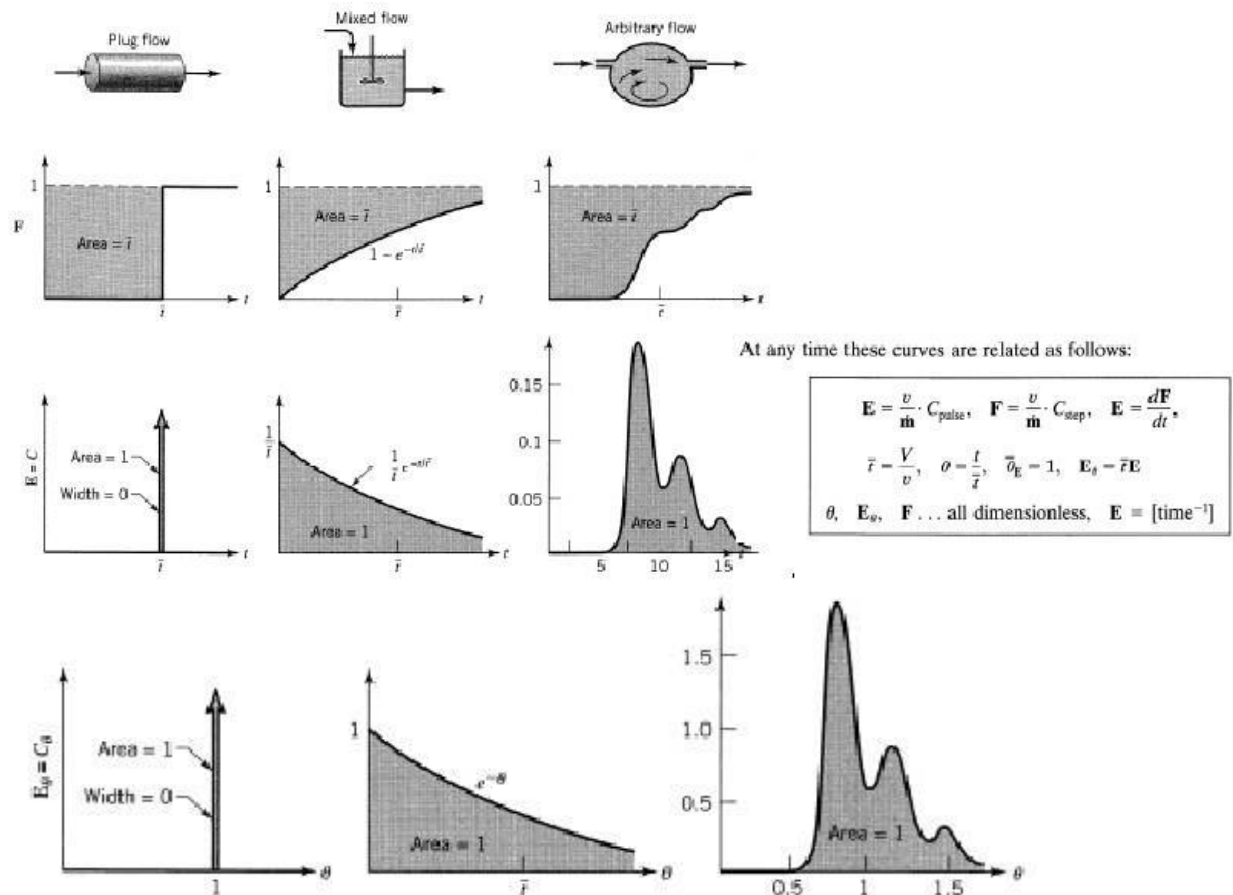


Figure — Properties of the E and F curves for various flows. Curves are drawn in terms of ordinary and dimensionless time units.

Conversion in non-ideal flow reactors

To evaluate the reactor behavior in general we have to know four factors

1. Kinetics of the reaction
2. The RTD of fluid in the reactor
3. The earliness or lateness of fluid mixing in the reactor
4. Whether the fluid is micro or macro fluid

States of aggregation of the flowing stream

Two extreme states of aggregation of the flowing material based upon its nature are:

1. **Microfluid** – A fluid in which molecules are free to move everywhere, collide, and intermix is called as microfluid. It exhibits no segregation. **Example: gases and thin liquids.**
2. **Macrofluid** – A fluid in which globules or aggregates, each containing large number of molecules, of given age do not mix with other globules is called as a macrofluid. It exhibits complete segregation. **Example: very viscous liquids, noncoalescing droplets.**

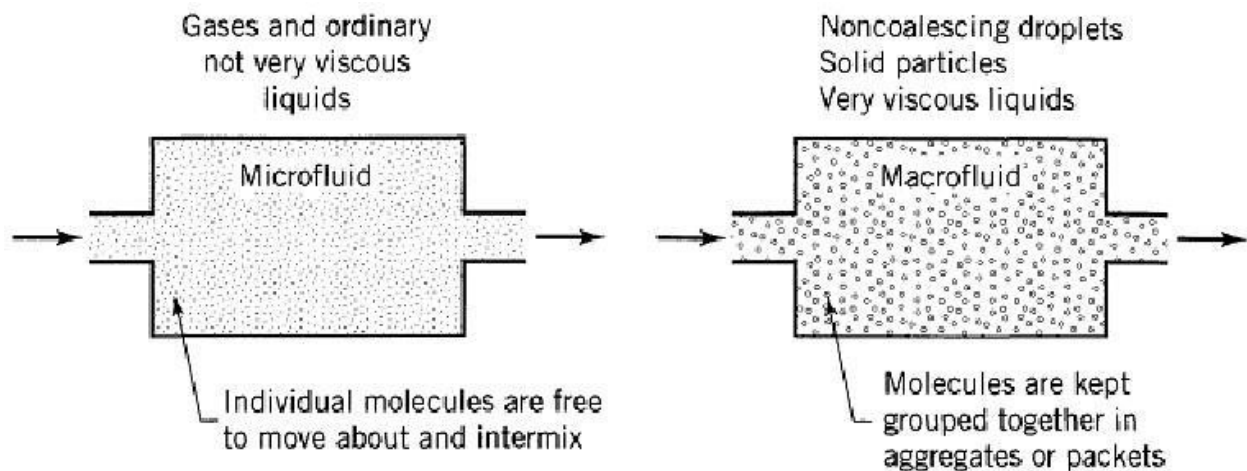


Figure — Two extremes of aggregation of fluid.

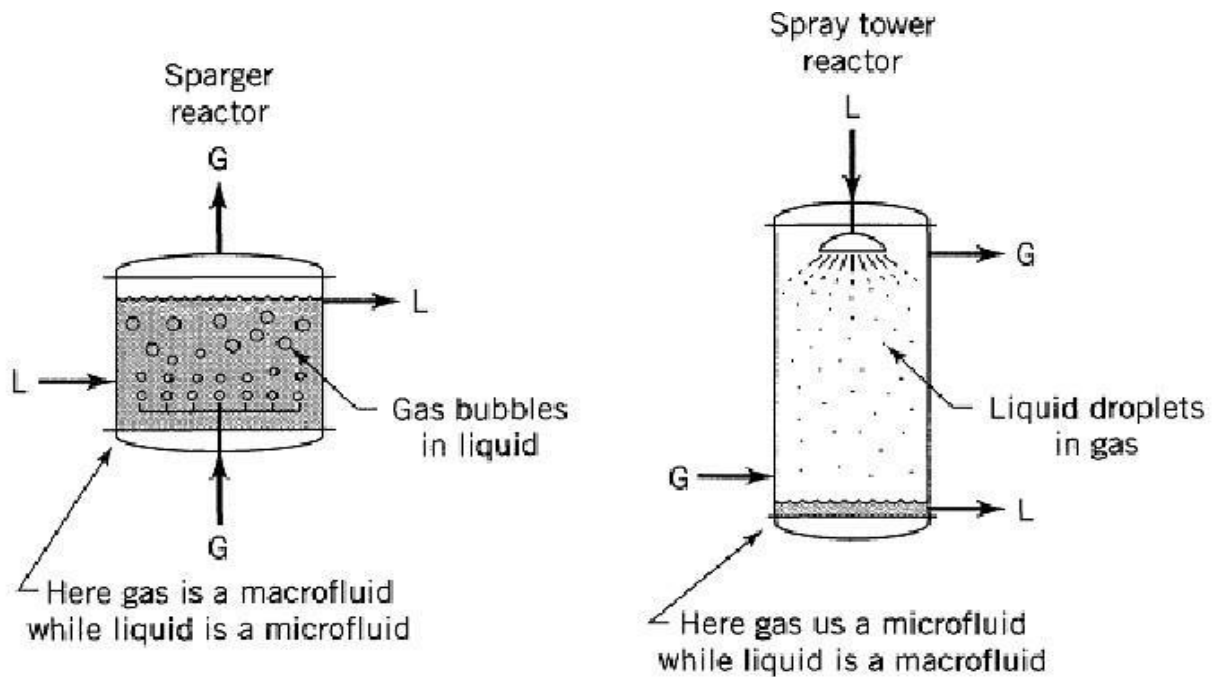


Figure — Examples of macro- and microfluid behavior.

Early and late mixing of fluids

The fluid elements of a single flowing stream can mix with each other early or late in their flow through a vessel.

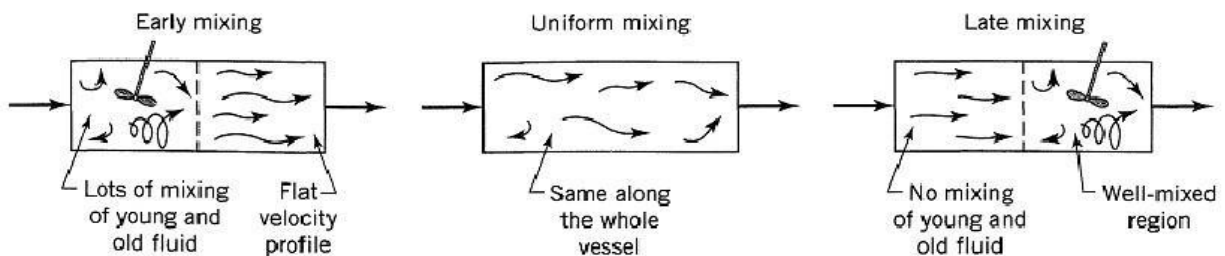


Figure — Examples of early and of late mixing of fluid.

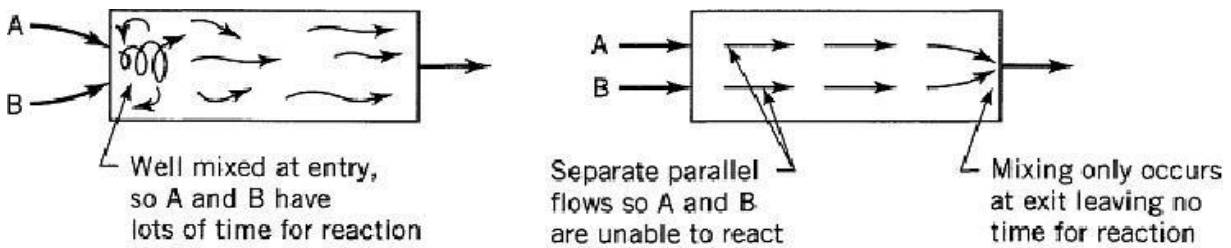


Figure — Early or late mixing affects reactor behavior.

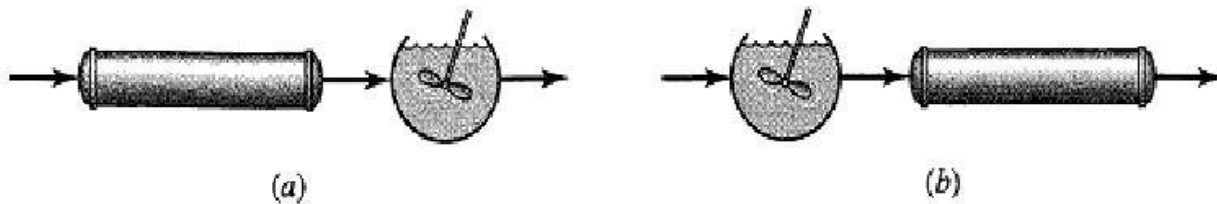


Figure — This shows the latest and the earliest mixing we can have for a given RTD.

- Consider that a second order reaction is carried out in these two setups.
- In (a) the reactants start at high concentration and reacts away rapidly because $n > 1$.
- In (b) the fluid drops immediately to a low concentration. Since the rate of reaction drops more rapidly than does the concentration you will end up with a lower conversion.
- For microfluids

Late mixing favors reactions with $n > 1$

Early mixing favors reactions with $n < 1$

For $n=1$, the conversion is unaffected by mixing as for first order reactions conversion is independent of concentration $dX_A/dt = k(1-X_A)$

- For **macrofluids**, imagine little aggregates of fluid residing for different lengths of time in the reactor.
- Each aggregate of macrofluid acts as its own **little/tiny batch reactor** and reacts accordingly and therefore the **fluid elements have different compositions**.
- The reaction time in any one of these **tiny batch reactors** is equal to the time that aggregate spends in the reaction environment.
- So in order to determine the **mean composition in the exit stream from the reactor** we have to take into account factors such as the **kinetics and the RTD function E**.

$$\left(\begin{array}{c} \text{mean concentration} \\ \text{of reactant} \\ \text{in exit stream} \end{array} \right) = \sum_{\text{all elements of exit stream}} \left(\begin{array}{c} \text{concentration of} \\ \text{reactant remaining} \\ \text{in an element of} \\ \text{age between } t \\ \text{and } t + dt \end{array} \right) \left(\begin{array}{c} \text{fraction of exit} \\ \text{stream which is} \\ \text{of age between } t \\ \text{and } t + dt \end{array} \right)$$

$$\left(\frac{\bar{C}_A}{C_{A0}} \right)_{\text{at exit}} = \int_0^{\infty} \left(\frac{C_A}{C_{A0}} \right)_{\text{for an element or little batch of fluid of age } t} \cdot E \, dt$$

or in terms of conversions

$$\bar{X}_A = \int_0^{\infty} (X_A)_{\text{element}} \cdot E \, dt$$

or in a form suitable for numerical integration

$$\frac{\bar{C}_A}{C_{A0}} = \sum_{\text{all age intervals}} \left(\frac{C_A}{C_{A0}} \right)_{\text{element}} \cdot E \, \Delta t$$

- for first-order reactions $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = e^{-kt}$
- for second-order reactions $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = \frac{1}{1 + kC_{A0}t}$
- for an n th-order reaction $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = [1 + (n - 1)C_{A0}^{n-1}kt]^{1/1-n}$

Book Reference

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2. Smith. J.M., Chemical Engineering Kinetics, 3rd Edition, McGraw Hill, 1981.
3. Gavhane. K. A., Chemical Reaction Engineering – II, 2nd Edition, Nirali Prakashan, 2013.
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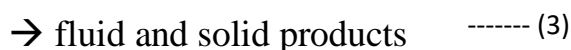
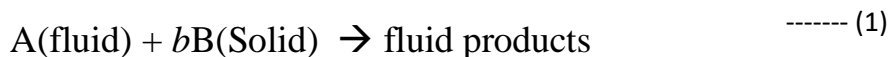
DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 2: NON-CATALYTIC REACTIONS

Catalytic Reaction Kinetic Model

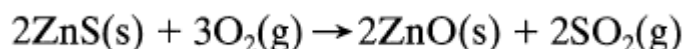
Introduction:

This section deals with the class of heterogeneous reactions in which a gas or liquid contacts with a solid, reacts with it, and transforms it into product. Such reactions may be represented by:

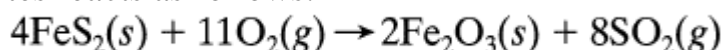


Fluid-solid reactions are numerous and of great industrial importance. Those in which the solid does not appreciably change in size during reaction are as follows:

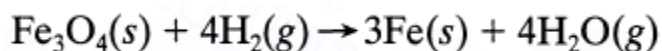
- a) *The roasting (or oxidation) of sulfide ores to yield the metal oxides.* For example, in the preparation of zinc oxide the sulfide ore is mined, crushed, separated from the gangue by flotation, and then roasted in a reactor to form hard white zinc oxide particles according to the reaction.



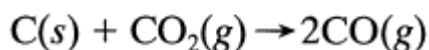
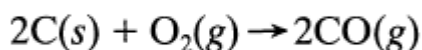
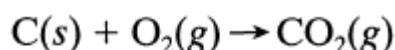
Similarly, iron pyrites reacts as follows:



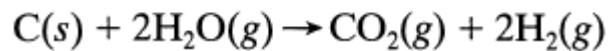
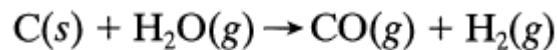
- b) *The preparation of metals from their oxides by reaction in reducing atmospheres.* For example, iron is prepared from crushed and sized magnetite ore in continuous-countercurrent, three stage, fluidized bed reactors according to the reaction:



The most common example of reactions where the solid changes its size are carbonaceous reactions. For example, with an insufficient amount of air, producer gas is formed by the following reactions:



With steam, water gas is obtained by the reactions-



Still other examples are the dissolution reactions, the attack of metal chips by acids, and the rusting of iron.

Selection of a Model

The requirement for a good engineering model is that it be the closest representation of reality which can be treated without too many mathematical complexities. It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with it. Unfortunately, in today's age of computers, this all too often happens.

For the non-catalytic reaction of particles with surrounding fluid, we consider two simple idealized models, the *progressive-conversion model* and the *shrinking unreacted-core model*.

Progressive-Conversion Model (PCM):

In present model, we assume that reactant gas enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle. Thus, solid reactant is converted continuously and progressively throughout the particle as shown in Figure 2.8.

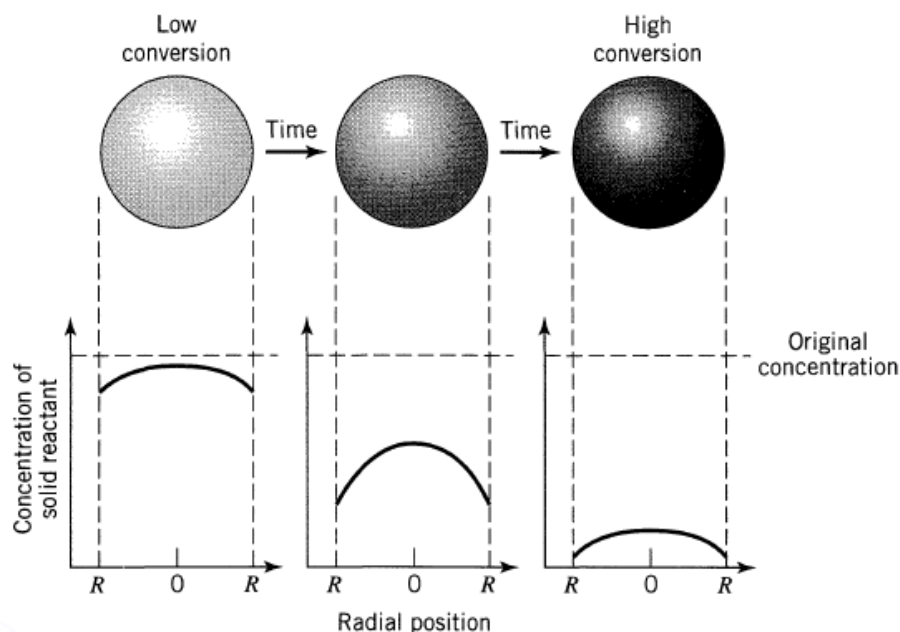


Figure 2.8: According to the PCM, reaction proceeds continuously throughout the solid particle

Shrinking-Core Model:

In this model a different approach of reaction taking place within solid surface has been visualized. In this visualization, we assume that the reaction occurs first at the outer skin of the particle. The reaction zone is then moves into the solid and leaves behind completely converted material and inert solid. This is referred to as “ash”. Thus, at any time there exists an unreacted core of material which shrinks in size during reaction, as shown in Figure 2.9.

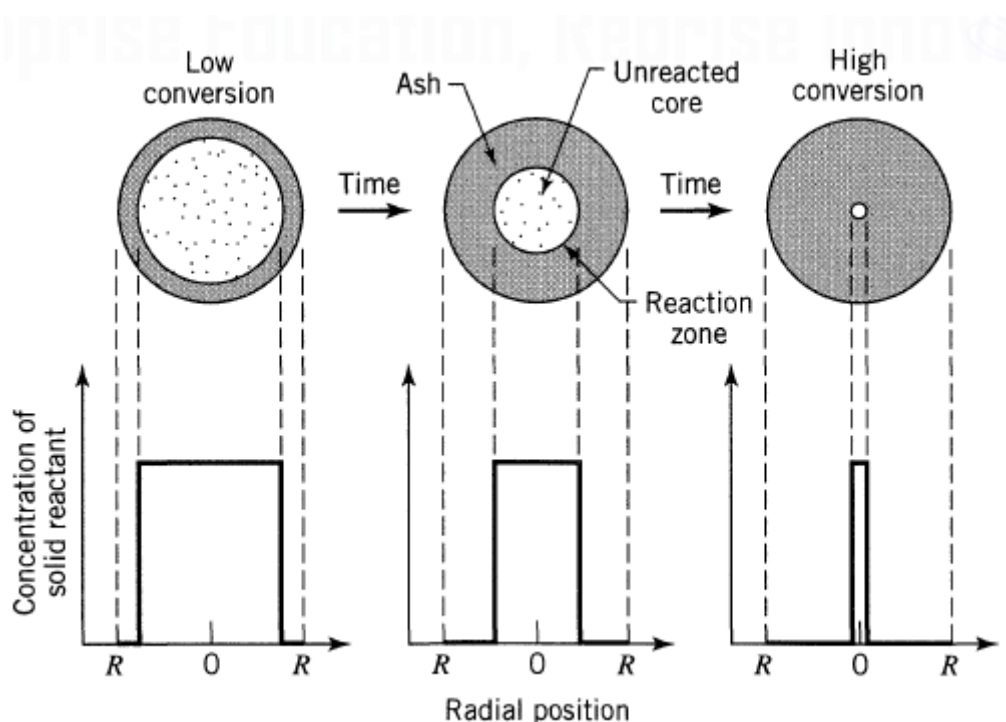


Figure 2.9: According to the shrinking-core model, reaction proceeds at a narrow front which moves into the solid particle. Reactant is completely converted as the front passes by.

In most cases the *shrinking-core model (SCM)* approximates real particles more closely than does the *progressive-conversion model (PCM)*.

SHRINKING-CORE MODEL FOR SPHERICAL PARTICLES OF UNCHANGING SIZE:

Since the SCM seems to reasonably represent reality in a wide variety of situations, we need to develop its kinetic equations in the following section. In doing this we consider the *surrounding fluid to be a gas*. However, this is done only for convenience since the analysis applies equally well to liquids.

The model was first developed by Yagi and Kunii (1955, 1961), who visualized five steps occurring in succession during reaction as described by figure 2.10.

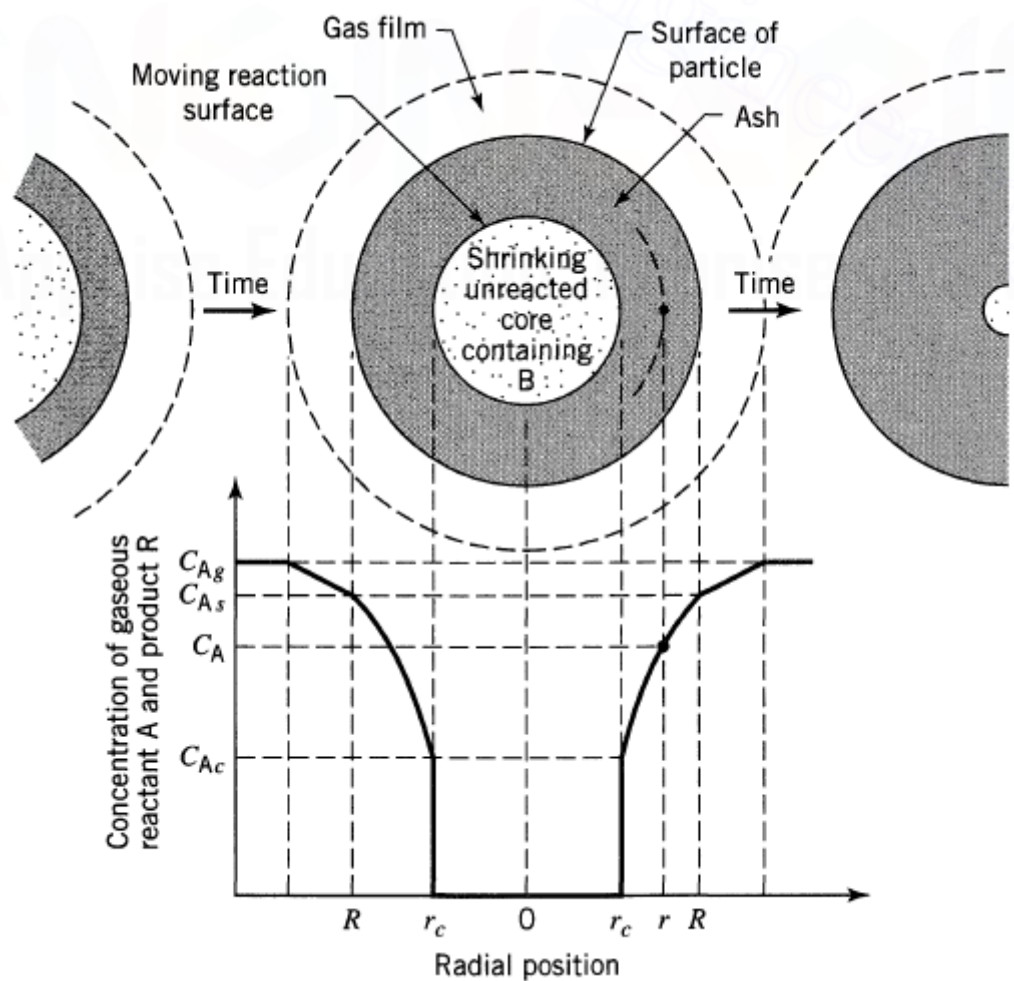


Figure 2.10: Representation of concentrations of reactants and products for the reaction $A(g) + bB(s) \rightarrow \text{solid product}$ for a particle of unchanging size.

- Step 1.* Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.
- Step 2.* Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.
- Step 3.* Reaction of gaseous A with solid at this reaction surface.
- Step 4.* Diffusion of gaseous products through the ash back to the exterior surface of the solid.
- Step 5.* Diffusion of gaseous products through the gas film back into the main body of fluid.

The above mentioned steps can vary according to the reactions. For example, if there is no gaseous products generation then step 4 & 5 is neglected and does not contribute towards resistance to the reaction. In the analysis of determining kinetic model we will only consider the resistances from step 1, 2 & 3.

1. Diffusion through gas film controls:

Whenever the resistance of the gas film controls, the concentration profile for gaseous reactant A will be shown as in figure 2.11.

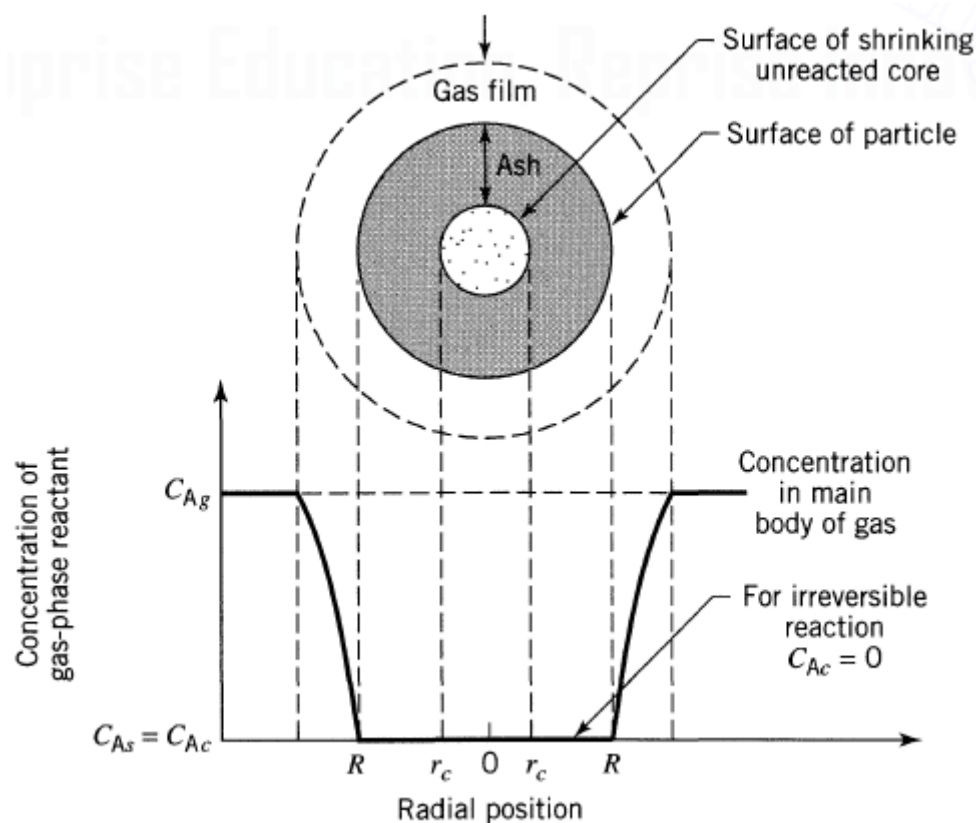


Figure 2.11: Representation of a reacting particle when diffusion through the gas film is the controlling resistance.

From the above figure we can observe that, no gaseous reactant is present at the particle surface; hence, the concentration driving force, $C_{Ag} - C_{As}$ becomes C_{Ag} and is constant at all times during reaction of the particle. Considering the stoichiometry from equations 1, 2 & 3, and taking unchanging exterior surface as S_{ex} we can write

$$dN_B = b dN_A.$$

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{1}{4\pi R^2} \frac{dN_B}{dt} = -\frac{b}{4\pi R^2} \frac{dN_A}{dt} = b k_g (C_{Ag} - C_{As}) = b k_g C_{Ag} = \text{constant} \quad \text{----- (4)}$$

let ρ_B , be the molar density of B in the solid and V be the volume of a particle, the amount of B present in a particle is –

$$N_B = \rho_B V = \left(\frac{\text{moles B}}{\text{m}^3 \text{ solid}} \right) (\text{m}^3 \text{ solid}) \quad \text{----- (5)}$$

The decrease in volume or radius of unreacted core accompanying the disappearance of dN_B moles of solid reactant is then given by –

$$-dN_B = -b dN_A = -\rho_B dV = -\rho_B d\left(\frac{4}{3}\pi r_c^3\right) = -4\pi\rho_B r_c^2 dr_c \quad \text{----- (6)}$$

Replacing eqn 6 in 4 gives the rate of reaction in terms of the shrinking radius of unreacted core, or –

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{\rho_B r_c^2}{R^2} \frac{dr_c}{dt} = bk_g C_{Ag} \quad \text{----- (7)}$$

where k_g is the mass transfer coefficient between fluid and particle. Rearranging and integrating eqn 7 –

$$\begin{aligned} -\frac{\rho_B}{R^2} \int_R^{r_c} r_c^2 dr_c &= bk_g C_{Ag} \int_0^t dt \\ t &= \frac{\rho_B R}{3bk_g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right] \end{aligned} \quad \text{----- (8)}$$

let the time for complete conversion of a particle be τ , then by taking $r_c = 0$ in eqn 8 we get –

$$\boxed{\tau = \frac{\rho_B R}{3bk_g C_{Ag}}} \quad \text{----- (9)}$$

The radius of unreacted core in terms of fractional time for complete conversion is obtained by combining Eqs. 8 and 9, or

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

This can be written in terms of fractional conversion by noting that –

$$1 - X_B = \left(\frac{\text{volume of unreacted core}}{\text{total volume of particle}} \right) = \frac{\frac{4}{3} \pi r_c^3}{\frac{4}{3} \pi R^3} = \left(\frac{r_c}{R} \right)^3 \quad \text{----- (10)}$$

Therefore,

$$\boxed{\frac{t}{\tau} = 1 - \left(\frac{r_c}{R} \right)^3 = X_B} \quad \text{----- (11)}$$

Thus we obtain the relationship of time with radius and with conversion, which is shown graphically in Figs. 2.12 and 2.13.

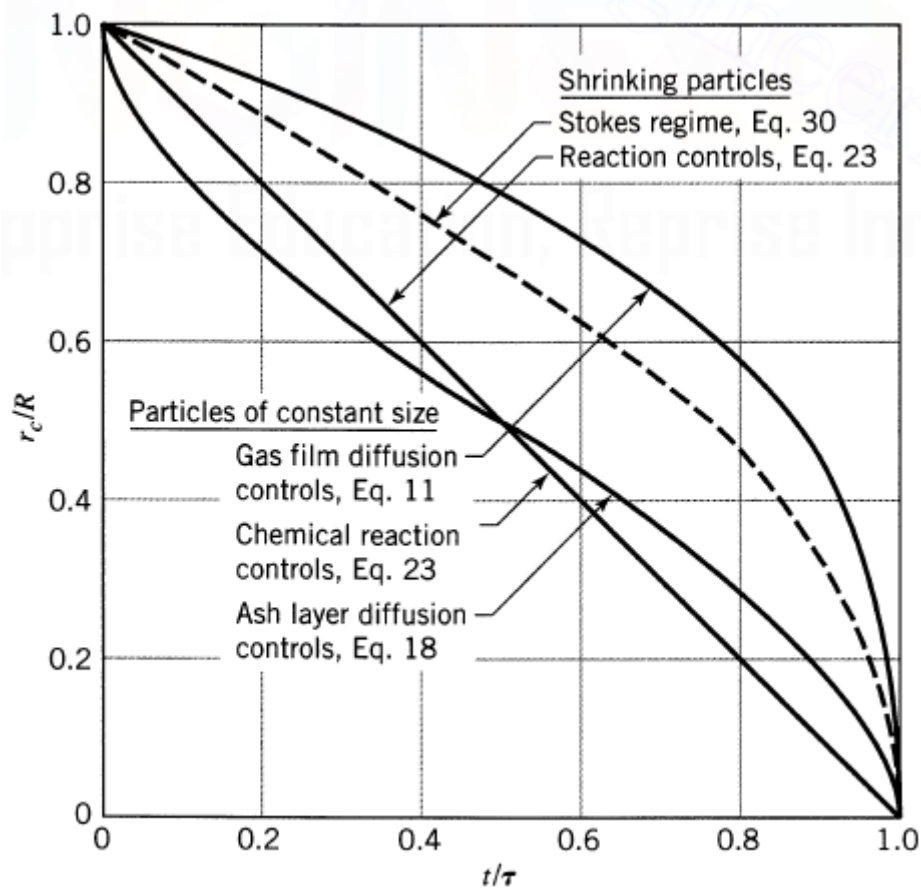


Figure 2.12: Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete reaction.

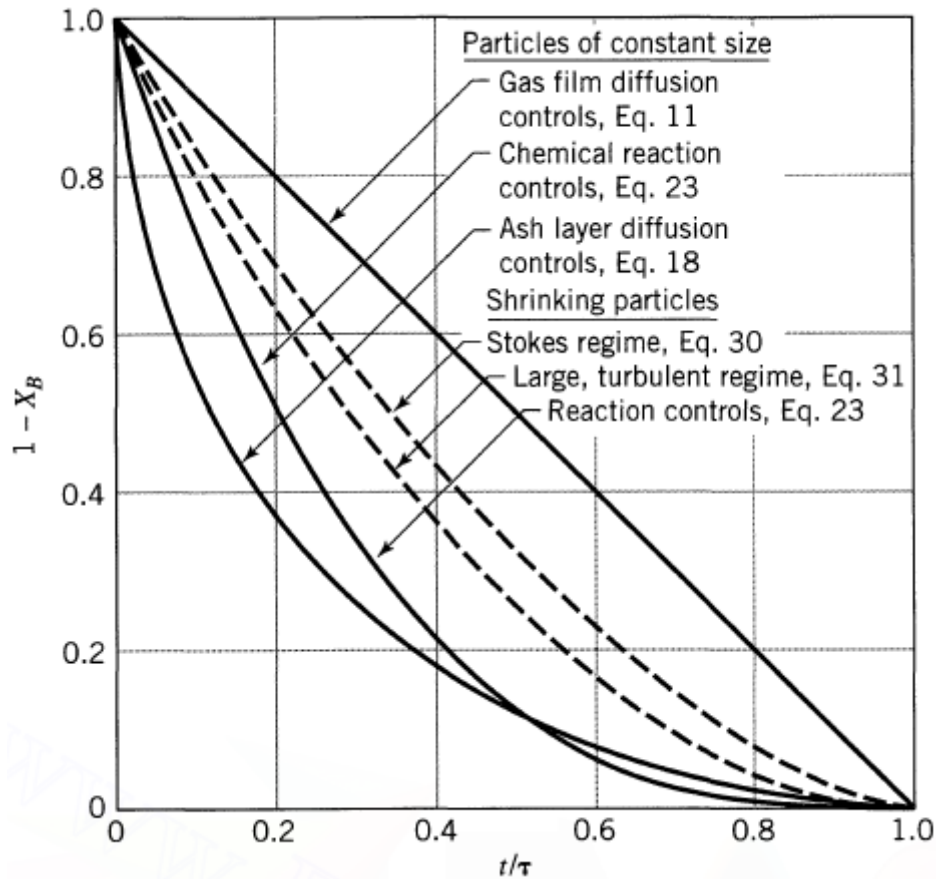


Figure 2.13: Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete reaction.

2. Diffusion through Ash Layer Controls:

Figure 2.14 illustrates the situation in which the resistance to diffusion through the ash controls the rate of reaction. To develop an expression between time and radius, such as Eq. 8 for film resistance, requires a two-step analysis. First examine a typical partially reacted particle, writing the flux relationships for this condition. Then apply this relationship for all values of r_c ; in other words, integrate r , between R and 0.

Consider a partially reacted particle as shown in Fig. 2.14. Both reactant A and the boundary of the unreacted core move inward toward the center of the particle. But for GIS systems the shrinkage of the unreacted core is slower than the flow rate of A toward the unreacted core by a factor of about 1000, which is roughly the ratio of densities of solid to gas. Because of this it is reasonable for us to assume, in considering the concentration gradient of A in the ash layer at any time that the unreacted core is stationary.

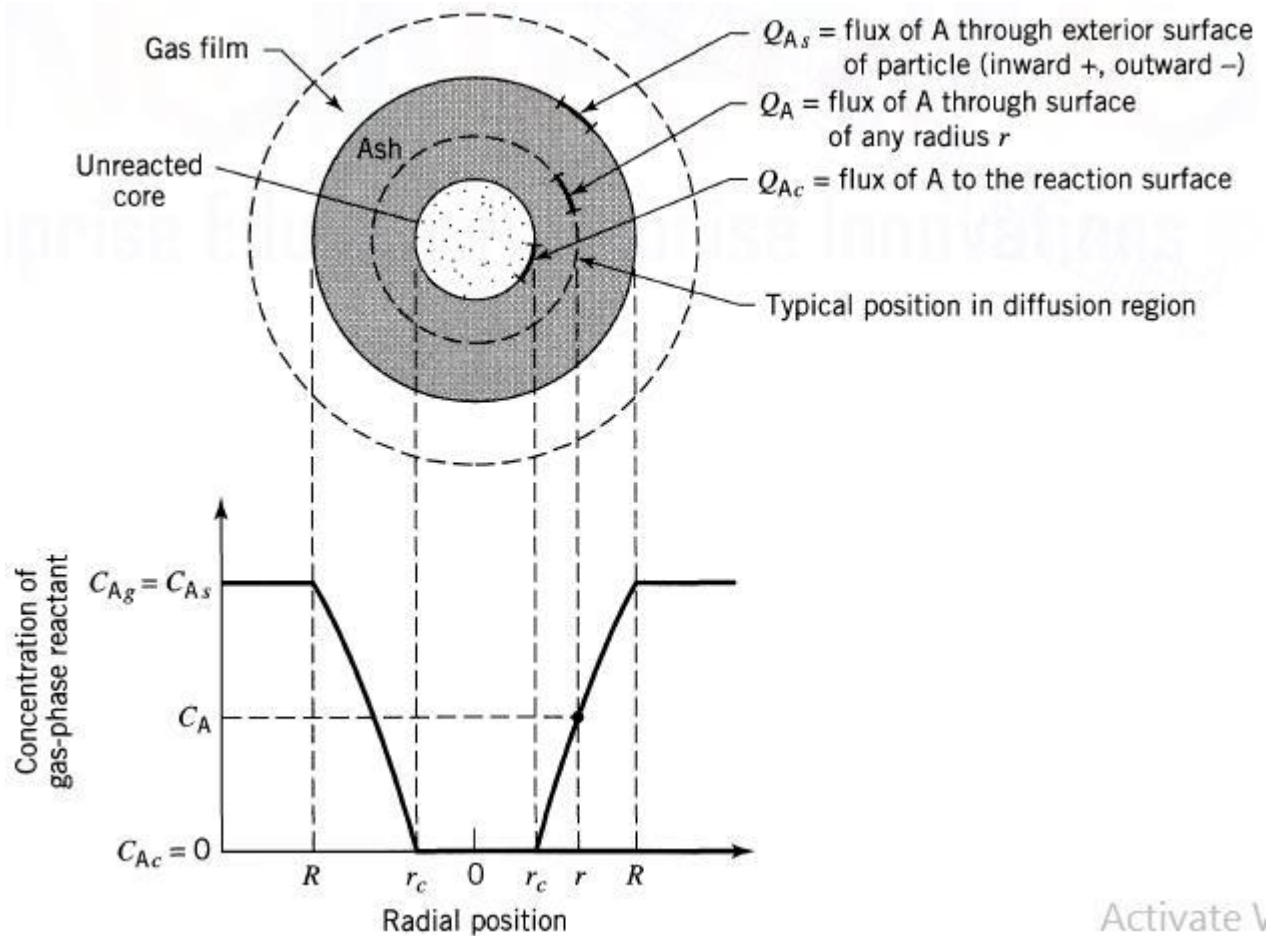


Figure 2.14: Representation of a reacting particle when diffusion through the ash layer is the controlling resistance.

For GIS systems the use of the steady-state assumption allows great simplification in the mathematics which follows. Thus the rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface, or –

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{constant} \quad \text{----- (12)}$$

For convenience, let the flux of A within the ash layer be expressed by Fick's law for equimolar counter diffusion. Then, noting that both Q_A and dC_A/dr are positive, we have –

$$Q_A = \mathcal{D}_e \frac{dC_A}{dr} \quad \text{----- (13)}$$

where \mathcal{D}_e is the effective diffusion coefficient of gaseous reactant in the ash layer.

Combining equations 12 & 13 for any r ,

$$-\frac{dN_A}{dt} = 4\pi r^2 \mathcal{D}_e \frac{dC_A}{dr} = \text{constant} \quad \text{----- (14)}$$

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

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

or,

$$-\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathcal{D}_e C_{Ag} \quad \text{----- (15)}$$

The above expression represents the conditions of a reacting particle at any time.

In the second part of the analysis we let the size of unreacted core change with time. *For a given size of unreacted core, dN_A/dt is constant; however, as the core shrinks the ash layer becomes thicker, lowering the rate of diffusion of A.* Consequently, Eq. 15 contains three variables, t , N_A , and r_c , one of which must be eliminated or written in terms of the other variables before integrating the equation with respect to time and other variables. As with film diffusion, let us eliminate N_A by writing it in terms of r_c . This relationship is given by Eq. 6; hence, replacing in Eq. 15, separating variables, and integrating, we obtain –

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

OR

$$t = \frac{\rho_B R^2}{6b \mathcal{D}_e C_{Ag}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] \quad \text{----- (16)}$$

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

$$\boxed{\tau = \frac{\rho_B R^2}{6b \mathcal{D}_e C_{Ag}}} \quad \text{----- (17)}$$

The progression of reaction in terms of the time required for complete conversion is found by dividing equation 16 by equation 17, or

$$\frac{t}{\tau} = 1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \quad \text{----- (18a)}$$

which in terms of fractional conversion, as given in equation 10, becomes –

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \quad \text{----- (18b)}$$

The above results are presented graphically by figures 2.12 & 2.13.

3. **Chemical Reaction Controls:**

Figure 2.15 illustrates concentration gradients with in a particle when chemical reaction controls.

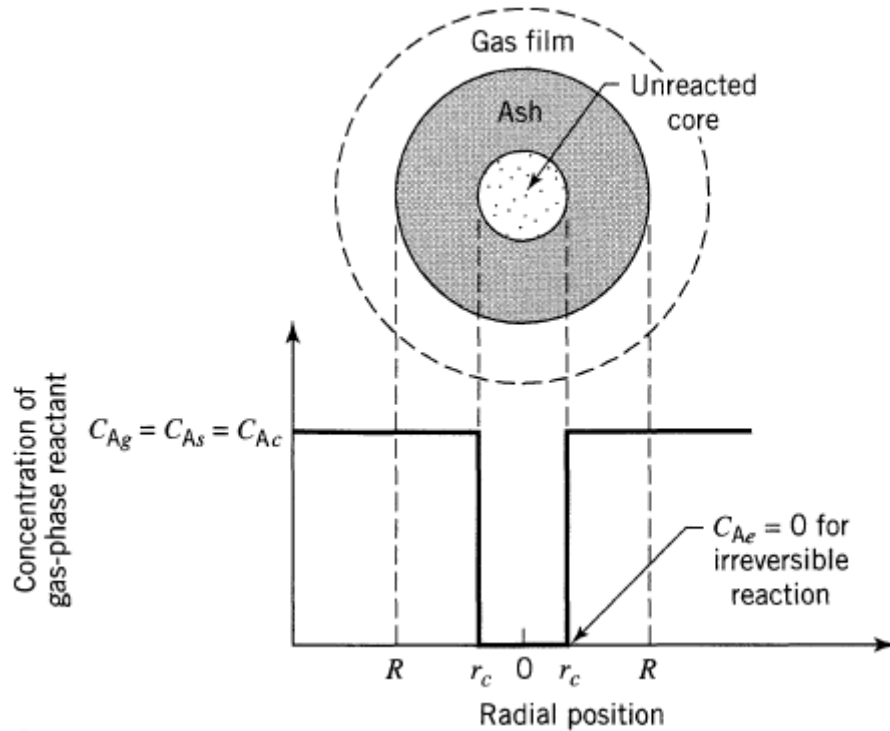


Figure 2.15: Representation of a reacting particle when chemical reaction is the controlling resistance, the reaction being $A(g) + bB(s) \rightarrow \text{products}$.

Since the progress of the reaction is unaffected by the presence of any ash layer, the rate is proportional to the available surface of unreacted core. Thus, based on unit surface of unreacted core, r_c , the rate of reaction for the stoichiometry of equations 1, 2 & 3, is –

$$-\frac{1}{4\pi r_c^2} \frac{dN_A}{dt} = -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = bk''C_{Ag} \quad \text{----- (19)}$$

where k'' is the first-order rate constant for the surface reaction. Writing N_B in terms of the shrinking radius, as given in Eq. 6, we obtain –

$$-\frac{1}{4\pi r_c^2} \rho_B 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_B \frac{dr_c}{dt} = bk''C_{Ag} \quad \text{----- (20)}$$

which on integration becomes:

$$-\rho_B \int_R^{r_c} dr_c = bk''C_{Ag} \int_0^t dt$$

or

$$t = \frac{\rho_B}{bk''C_{Ag}} (R - r_c) \quad \text{----- (21)}$$

The time τ required for complete conversion is given at $r_c = 0$ by –

$$\tau = \frac{\rho_B R}{bk''C_{Ag}} \quad \text{----- (22)}$$

The decrease in radius or increase in fractional conversion of the particle in terms of τ is found by combining equations 21 and 22. Thus,

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \quad \text{----- (23)}$$

This result is plotted in figures. 2.12 & 2.13.

RATE OF REACTION FOR SHRINKING SPHERICAL PARTICLES

When no ash forms, as in the burning of pure carbon in air, the reacting particle shrinks during reaction, finally disappearing. This process is illustrated in figure 2.16. For a reaction of this kind we visualize the following three steps occurring in succession.

Step 1. Diffusion of reactant A from the main body of gas through the gas film to the surface of the solid.

Step 2. Reaction on the surface between reactant A and solid.

Step 3. Diffusion of reaction products from the surface of the solid through the gas film back into the main body of gas. Note that the ash layer is absent and does not contribute any resistance.

As with particles of constant size, let us see what rate expressions result when one or the other of the resistances controls.

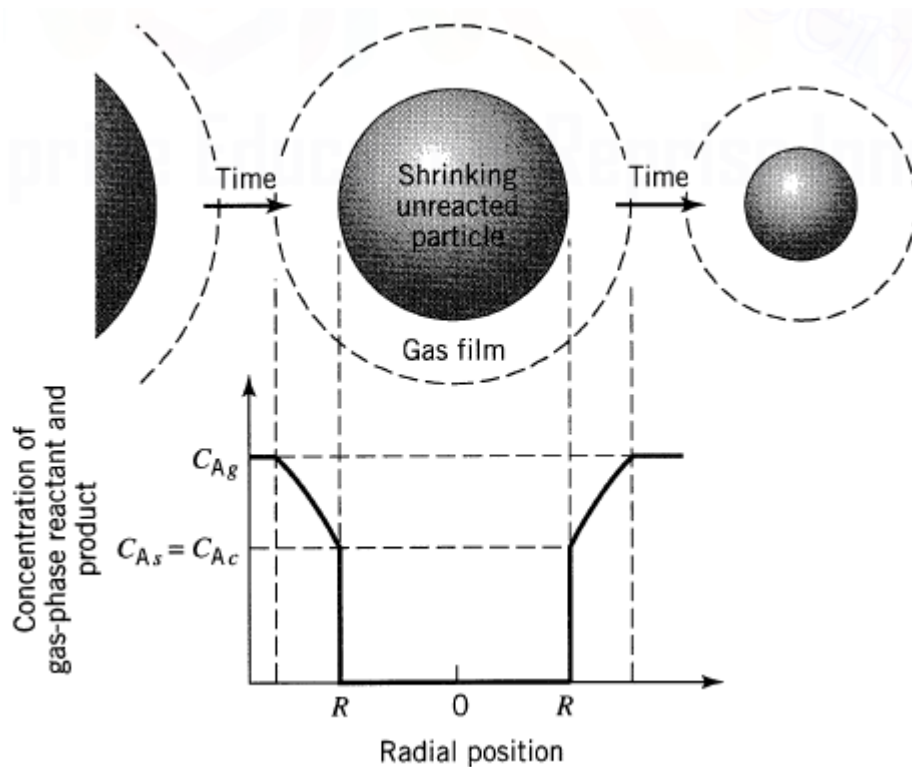


Figure 2.16: Representation of concentration of reactants and products for the reaction $A(g) + bB(s) \rightarrow rR(g)$ between a shrinking solid particle and gas.

1. **Chemical Reaction Control:**

When chemical reaction controls, the behavior is identical to that of particles of unchanging size; therefore, Fig. 25.7 and Eq. 21 or 23 will represent the conversion-time behavior of single particles, both shrinking and of constant size.

2. **Gas Film Diffusion Controls:**

Film resistance at the surface of a particle is dependent on numerous factors, such as the relative velocity between particle and fluid, size of particle, and fluid properties. These have been correlated for various ways of contacting fluid with solid, such as packed beds, fluidized beds, and solids in free fall. As an example, for mass transfer

of a component of mole fraction y in a fluid to free-falling solids Froessling (1938) gives –

$$\frac{k_g d_p y}{\mathcal{D}} = 2 + 0.6(\text{Sc})^{1/3}(\text{Re})^{1/2} = 2 + 0.6 \left(\frac{\mu}{\rho \mathcal{D}} \right)^{1/3} \left(\frac{d_p u \rho}{\mu} \right)^{1/2} \quad \text{----- (24)}$$

During reaction a particle changes in size; hence k_g also varies. In general k_g rises for an increase in gas velocity and for smaller particles. As an example eqn. 24 shows that –

$$k_g \sim \frac{1}{d_p} \quad \text{for small } d_p \text{ and } u \quad \text{----- (25)}$$

$$k_g \sim \frac{u^{1/2}}{d_p^{1/2}} \quad \text{for large } d_p \text{ and } u \quad \text{----- (26)}$$

Equation 25 represents particles in *Stokes law regime*. Now we will develop expression for conversion-time for such particles.

Stokes Regime (Smaller particles): When a particle, originally of size R_0 has shrunk to size R , we may write –

$$dN_B = \rho_B dV = 4\pi\rho_B R^2 dR$$

Thus, similar to equation 7, we have

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = \frac{\rho_B 4\pi R^2}{4\pi R^2} \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = b k_g C_{Ag} \quad \text{----- (27)}$$

Since in the Stokes regime equation 24 reduces to

$$k_g = \frac{2\mathcal{D}}{d_p} = \frac{\mathcal{D}}{R} \quad \text{----- (28)}$$

combining equation 27 & 28 and integrating

$$\int_{R_0}^R R dR = \frac{b C_{Ag} \mathcal{D}}{\rho_B} \int_0^t dt$$

or,

$$t = \frac{\rho_B R_0^2}{2bC_{Ag}\mathcal{D}} \left[1 - \left(\frac{R}{R_0} \right)^2 \right]$$

The time for complete disappearance of a particle is thus

$$\tau = \frac{\rho_B R_0^2}{2bC_{Ag}\mathcal{D}} \quad \text{----- (29)}$$

and on combining we get

$$\frac{t}{\tau} = 1 - \left(\frac{R}{R_0} \right)^2 = 1 - (1 - X_B)^{2/3} \quad \text{----- (30)}$$

This relationship of *size versus time* for *shrinking particles in the Stokes regime* is shown in Figs. 2.12 and 2.13, and it well represents small burning solid particles and small burning liquid droplets.

Particles of Different Shape: Conversion-time equations similar to those developed above can be obtained for various –shaped particles, and table 2.2 summarizes these expressions.

Table 2.2: Conversion Time Expressions for Various Shapes of Particles, Shrinking Core Model

	$X_B = 1 - \frac{1}{L}$ $L = \text{half thickness}$	$\frac{t}{\tau} = X_B$		$\frac{t}{\tau} = X_B + (1 - X_B) \ln(1 - X_B)$		$\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$	
		$\tau = \frac{\rho_B L}{bk_g C_{Ag}}$		$\tau = \frac{\rho_B L^2}{2b\mathcal{D}_t C_{Ag}}$		$\tau = \frac{\rho_B L}{bk'' C_{Ag}}$	
Constant Size Particles	Cylinder $X_B = 1 - \left(\frac{r_c}{R}\right)^2$	$\tau = \frac{\rho_B R}{2bk_g C_{Ag}}$		$\tau = \frac{\rho_B R^2}{4b\mathcal{D}_t C_{Ag}}$		$\tau = \frac{\rho_B R}{bk'' C_{Ag}}$	
	Sphere $X_B = 1 - \left(\frac{r_c}{R}\right)^3$	(11) $\frac{t}{\tau} = X_B$ (10) $\tau = \frac{\rho_B R}{3bk_g C_{Ag}}$		(18) $\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ (17) $\tau = \frac{\rho_B R^2}{6b\mathcal{D}_t C_{Ag}}$		(23) $\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ (22) $\tau = \frac{\rho_B R}{bk'' C_{Ag}}$	
Shrinking Sphere	Small particle Stokes regime	(30) $\frac{t}{\tau} = 1 - (1 - X_B)^{2/3}$ (29) $\tau = \frac{\rho_B R_0^2}{2b\mathcal{D}_t C_{Ag}}$		Not applicable		$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R_0}{bk'' C_{Ag}}$	
	Large particle ($u = \text{constant}$)	(31) $\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ $\tau = (\text{const}) \frac{R_0^{3/2}}{C_{Ag}}$		Not applicable		$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R}{bk'' C_{Ag}}$	

DETERMINATION OF THE RATE-CONTROLLING STEP

The kinetics and rate-controlling steps of a fluid-solid reaction are deduced by noting how the progressive conversion of particles is influenced by particle size and operating temperature. This information can be obtained in various ways, depending on the facilities available and the materials at hand. The following observations are a guide to experimentation and to the interpretation of experimental data.

- a) **Temperature:** The chemical step is usually much more temperature-sensitive than the physical steps; hence, experiments at different temperatures should easily distinguish between ash or film diffusion on the one hand and chemical reaction on the other hand as the controlling step.
- b) **Time:** Figures 2.12 and 2.13 show the progressive conversion of spherical solids when chemical reaction, film diffusion, and ash diffusion in turn control. Results of kinetic runs compared with these predicted curves should indicate the rate controlling step. Unfortunately, the difference between ash diffusion and chemical reaction as controlling steps is not great and may be masked by the scatter in experimental data.
- c) **Particle Size:** Equations 8, 16 and 21, along with equations 24 and 25 shows that the time needed to achieve the same fractional conversion for particle of different but unchanging sizes is given by –

$$\begin{array}{ll} t \propto R^{1.5 \text{ to } 2.0} & \text{for film diffusion controlling (the exponent drops as} \\ & \text{Reynolds number rises)} \\ t \propto R^2 & \text{for ash diffusion controlling} \\ t \propto R & \text{for chemical reaction controlling} \end{array}$$

Thus kinetic runs with different sizes of particles can distinguish between reactions in which the chemical and physical steps control.

- d) **Ash versus Film Resistance:** When a hard solid ash forms during reaction, the resistance of gas-phase reactant through this ash is usually much greater than through the gas film surrounding the particle. Hence in the presence of a non-flaking ash layer, film resistance can safely be ignored. In addition, ash resistance is unaffected by changes in gas velocity.

- e) **Predictability of Film Resistance:** The magnitude of film resistance can be estimated from dimensionless correlations such as eqn. 24. Thus an observed rate approximately equal to the calculated rate suggests that film resistance controls.

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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 3: CATALYST AND CATALYTIC REACTIONS

UNIT-3 CATALYSTS AND CATALYTIC REACTIONS

Because the chemical, petrochemical, and petroleum industries rely heavily on catalytic processing operations and because of the utility of catalysts in remediating environmental problems (e.g., emissions from motor vehicles), chemical engineers must be cognizant of the fundamental and applied aspects of catalysis. In more modern terms the following definition is appropriate: *A catalyst is a substance that affects the rate or the direction of a chemical reaction, but is not appreciably consumed in the process.* There are three important aspects of the definition. First, a catalyst may increase or decrease the reaction rate. Second, a catalyst may influence the direction or selectivity of a reaction. Third, the amount of catalyst consumed by the reaction is negligible compared to the consumption of reactants.

Catalysts work by providing alternative mechanism involving a different transition state of lower energy. Thereby, the activation energy of the catalytic reaction is lowered compared to the uncatalyzed reaction as shown in Fig 3.1.

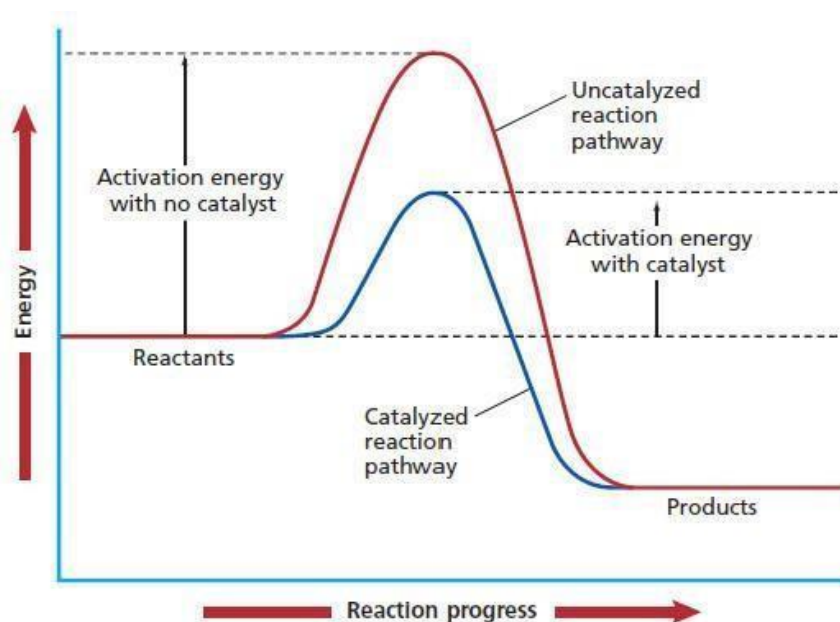
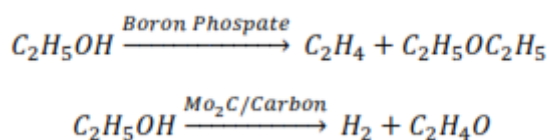


Figure 3.1 Comparison of activation energies of exothermic catalytic and non-catalytic reactions

A catalyst accelerates both the rates of the forward and reverse reaction. Equilibrium of a reversible reaction is not altered by the presence of the catalyst. For example, when oxidation of SO_2 is carried out in the presence of three different catalysts, namely Pt, Fe_2O_3 and V_2O_5 , the equilibrium composition is the same in all three cases. Another important characteristic of catalyst is its effect on selectivity. The presence of different catalysts can result in different product distribution from the same starting material. For example, decomposition of ethanol in the presence of different catalysts results in different products as shown

below.



Types of catalytic reactions

Catalytic reactions can be divided into two main types –

1. Heterogeneous
2. Homogeneous

Heterogeneous catalysis

In heterogeneous catalytic reaction, the catalyst and the reactants are in different phases. Reactions of liquid or gases in the presence of solid catalysts are the typical examples. An example is the Contact Process for manufacturing sulphuric acid, in which the sulphur dioxide and oxygen are passed over a solid vanadium oxide catalyst producing sulphur trioxide. Several hydrocarbon transformation reactions such as cracking, reforming, dehydrogenation, and isomerization also fall in this category.

Homogeneous catalysis

In a homogeneous catalytic reaction, the catalyst is in the same phase as the reactants. Typically, all the reactants and catalysts are either in one single liquid phase or gas phase. Most industrial homogeneous catalytic processes are carried out in liquid phase. Ester hydrolysis involving general acid-base catalysts, polyethylene production with organometallic catalysts and enzyme catalysed processes are some of the important examples of industrial homogeneous catalytic processes.

SURFACE AREA AND ADSORPTION

Since a catalytic reaction occurs at the fluid-solid interface, a large interfacial area can be helpful or even essential in attaining a significant reaction rate. In many catalysts, this area is provided by a porous structure; the solid contains many fine pores, and the surface of these pores supplies the area needed for the high rate of reaction. The area possessed by some porous materials is surprisingly large. A typical silica-alumina cracking catalyst has a pore volume of 0.6 cm³/g and an average pore radius of 4 nm. The corresponding surface area is 300 m²/g.

A catalyst that has a large area resulting from pores is called a *porous catalyst*. Examples of these include the Raney nickel used in the hydrogenation of vegetable and animal oils, the platinum-on-alumina used in the reforming of petroleum naphtha to obtain higher octane ratings, and the promoted iron used in ammonia synthesis. Sometimes pores are so small that they will admit small molecules but prevent large ones from entering. Materials with this type of pore are called

molecular sieves, and they may be derived from natural substances such as certain clays and zeolites, or be totally synthetic.

Not all catalysts need the extended surface provided by a porous structure, however. Some are sufficiently active so that the effort required to create a porous catalyst would be wasted. For such situations one type of catalyst is the monolithic catalyst. Monolithic catalysts are normally encountered in processes where pressure drop and heat removal are major considerations.

For the moment, let us focus our attention on gas-phase reactions catalysed by solid surfaces. The molecules at a surface of a material experience imbalanced forces of intermolecular interaction which contribute to the surface energy. It causes accumulation of molecules of a solute or gas in contact with the substance. This preferential accumulation of substrate molecules at the surface is called adsorption which is purely surface phenomenon.

The surface active material is referred to as the adsorbent and the molecules which are accumulated on the adsorbent called adsorbate molecules. The strength by which adsorbate molecules are attached with the adsorbents determines the nature of adsorption. Physisorption (or physical adsorption) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours. The term van der Waals adsorption is synonymous with physical adsorption. Chemisorption (or chemical adsorption) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds.

Table 3.1 Physical *vs* Chemical Adsorption

Parameter	Physical adsorption	Chemisorption
Adsorbent	All Solids	Some Solids
Adsorbate	All gases below critical temperature	Some chemically reactive gases
Temperature range	Low temperature	Generally high temperature
Heat of adsorption	Low, order of heat of condensation	High, order of heat of reaction
Rate (activation energy)	Very rapid, low E	Nonactivated, low E; activated, high E
Coverage	Multilayer possible	Monolayer adsorption
Reversibility	Highly reversible	Often irreversible
Importance	For determination of surface area and pore size	For determination of active-center area and elucidation of surface-reaction kinetics

When an adsorbed molecule receives energy equal to or greater than the energy of

adsorption, it will leave the surface. This phenomenon is the reverse of adsorption and is called as desorption. When the number of molecules striking the surface and staying there is equal to the number of molecules that are leaving (evaporating) the surface is called to be in equilibrium.

Adsorption Isotherms

A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. They are generally classified in the five main categories. In Figure 3.2, adsorbate partial pressures (P) are normalized by dividing by the saturation pressure at the temperature in question (P_0).

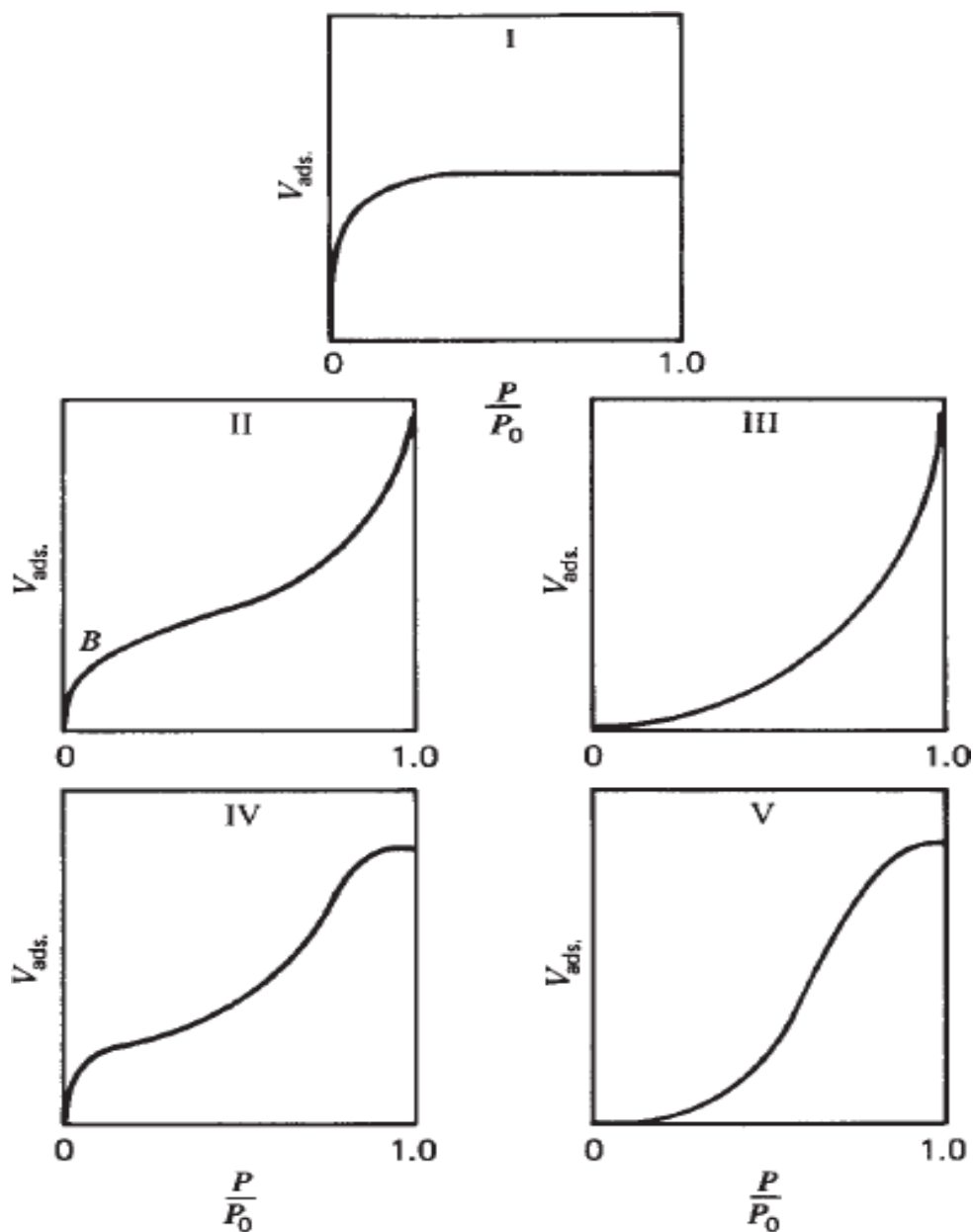


Figure 3.2 Five types of isotherms for adsorption.

Type I, referred to as *Langmuir-type adsorption*, is characterized by a monotonic approach to a limiting amount of adsorption, which presumably corresponds to formation of a monolayer. This type of behaviour is that expected for chemisorption. No other isotherms imply that one can reach a saturation limit corresponding to completion of a monolayer.

Type II is typical of the behaviour normally observed for physical adsorption. At values of P/P_0 approaching unity, capillary and pore condensation phenomena occur. The knee of the curve corresponds roughly to completion of a monolayer. A statistical monolayer is built up at relatively low values of P/P_0 (0.1 to 0.3).

Type IV behaviour is similar to type II behaviour except that a limited pore volume is indicated by the horizontal approach to the right-hand ordinate axis. This type of curve is relatively common for porous structures of many kinds. Hysteresis effects associated with pore condensation are often, but not always, encountered in this type of system. They arise from the effects of surface curvature on vapour pressure.

Types III and V are relatively rare. They are typical of cases in which the forces giving rise to monolayer adsorption are relatively weak. Type V differs from type III in the same manner that type IV differs from type II.

Freundlich Adsorption Isotherm

It is an empirical relation between the amount of an adsorbate adsorbed per unit weight (x/m , mg/g) of adsorbent and the adsorbate equilibrium concentration (C_e , $moles/l$) in the fluid as follows:

$$x/m = K C_e^n \quad (3.1)$$

Where, K and n are Freundlich coefficients
 x = weight of adsorbate adsorbed on m unit weight of adsorbent
 C_e = equilibrium concentration of adsorbate

From equation (3.1), we get

$$\log(x/m) = \log K + n \log C_e \quad (3.2)$$

The coefficients K and n can be determined from the intercept and slope of a plot of $\log(x/m)$ versus $\log C_e$.

Langmuir Adsorption Isotherm

In the Langmuir model the adsorbent surface is considered to possess a number of active interaction sites for adsorption. Langmuir derived a relation between adsorbed material and its equilibrium concentration. His assumptions are:

1. There are fixed adsorption sites on the surface of the adsorbent. At a given temperature and pressure some fraction of these sites are occupied by adsorbate molecules. Let this fraction be θ

2. Each site on the surface of the adsorbent can hold one adsorbate molecule.
3. The heat of adsorption is the same for each site and is independent of θ .
4. There is no interaction between molecules on different sites.

Since the adsorption is limited to complete coverage by a monomolecular layer, the surface may be divided into two parts: the fraction θ covered by the adsorbed molecules and the fraction $1 - \theta$, which is bare. Since only those molecules striking the uncovered part of the surface can be adsorbed, the rate of adsorption per unit of total surface will be proportional to $1 - \theta$; that is,

$$r_a = k_a p(1 - \theta) \quad (3.3)$$

The rate of desorption will be proportional to the fraction of covered surface

$$r_d = k_d \theta \quad (3.4)$$

At equilibrium,

Rate of adsorption = Rate of desorption

$$\begin{aligned} k_a p(1 - \theta) &= k_d \theta \\ \theta &= \frac{k_a p}{k_d + k_a p} = \frac{Kp}{1 + Kp} = \frac{v}{v_m} \end{aligned} \quad (3.5)$$

Where,

$K = k/k'$ is adsorption equilibrium constant, expressed in units of (pressure)⁻¹.

The concentration form of Eq. (3.5) can be obtained by introducing the concept of an adsorbed concentration \bar{C} , expressed in moles per gram of catalyst. If \bar{C}_m represents the concentration corresponding to a complete monomolecular layer on the catalyst, then the rate of adsorption, (moles/s. g catalyst) is, by analogy with Eq.(3.3),

$$r_a = k_c C_g (\bar{C}_m - \bar{C}) \quad (3.6)$$

Where k_c is the rate constant for the catalyst and \bar{C} is the concentration of absorbable component in the gas. Similarly, Eq.3.4 becomes

$$r_d = k'_c \bar{C} \quad (3.7)$$

At equilibrium the rates given by Eqs. (3.6) and (3.7) are equal, so that

$$\theta = \frac{\bar{C}}{\bar{C}_m} = \frac{K_c C_g}{1 + K_c C_g} \quad (3.8)$$

Where $K_c = k_c/k_c'$

Rearranging equation (3.8), we get

$$\frac{C_g}{\bar{C}} = \frac{1}{K_c \bar{C}_m} + \frac{C_g}{\bar{C}_m} \quad (3.9)$$

If we plot $\frac{c_g}{c}$ vs C_g , we will get a straight line.

Slope of which will be $\frac{1}{\bar{c}_m}$ and

Intercept as $\frac{1}{K_c \bar{c}_m}$.

For chemisorptions Langmuir's equation works very well but fails for the cases where multilayer formation takes place.

Multilayer Adsorption – BET Isotherm

Important assumption of Langmuir theory is the formation of monolayer. Because of monolayer formation saturation in adsorption would reach at higher equilibrium concentration of the adsorbate. This type of adsorption occurs due to short range chemical forces which do not allow penetration through the primary adsorbed molecules. Multilayer formation has been observed when molecules are adsorbed through weak forces (long range forces normally under physical adsorption) due to cohesive forces exerted by the molecules of the adsorbate.

At high pressure multilayer adsorption takes place. The theory of multimolecular (multilayer) adsorption was developed by Stephen Brunauer, Paul Emmet and Edward Teller and is called BET isotherm. This isotherm derived by them successfully accounts for all types of adsorption.

It assumes that the surface possesses uniform, localized sites and that adsorption on one site does not affect adsorption on neighboring sites just as in Langmuir theory. Also, molecules can be adsorbed in second, third and n^{th} layers with the surface available for layer equal to the coverage of the next lower layer. The development is briefly summarized as follows: Equation 3.5 can be rearranged to the form

$$\frac{p}{v} = \frac{1}{K v_m} + \frac{p}{v_m} \quad (3.10)$$

Brunauer, Emmet and Teller adapted this equation of multilayer adsorption and arrived at the result

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{c v_m p_0} \quad (3.11)$$

Where p_0 is the saturation or vapor pressure and c is a constant for the particular temperature and gas-solid system.

According to Eq.(3.11), a plot of $\frac{p}{v(p_0 - p)}$ vs $\frac{p}{p_0}$

should give a straight line. The intercept and slope the straight line can be given as,

$$I = \frac{1}{v_m c} \quad (3.12)$$

$$S = \frac{(c - 1)}{c v_m} \quad (3.13)$$

Solving these equations for the volume of adsorbed gas corresponding to a monomolecular layer gives

$$v_m = \frac{1}{I + S} \quad (3.14)$$

The volume can be readily converted to the number of molecules adsorbed.

$$N = \frac{v_m N_0}{V} \quad (3.15)$$

Where N_0 is Avogadro's number, 6.02×10^{23} molecules/mole, and V is the volume per mole of gas at conditions of v_m . Since v_m is recorded at standard temperature and pressure, $V = 22,400 \text{ cm}^3/\text{g mole}$.

However, to determine the absolute surface area it is necessary to select a value for the area covered by one adsorbed molecule. If this is α , the total surface area is given by

$$S_g = N\alpha \quad (3.16)$$

If v_m is based on a 1 g sample, then S_g is the total surface per gram of solid adsorbent. Emmett and Brunauer proposed that α is the projected area of a molecule on the surface when the molecules are arranged in close two-dimensional packing. This value is slightly larger than that obtained by assuming that the adsorbed molecules are spherical and their projected area on the surface is circular. The proposed equation is

$$\left(\frac{3}{17} \right)$$

$$\alpha = 1.09 \left[\frac{M}{N_0 \rho} \right]^{2/3} \quad (3.17)$$

Where M is molecular weight and ρ is the density of the adsorbed molecules. For N_2 at -195.8°C , $\rho = 0.808 \text{ g/cm}^3$, the area per molecule from is $16.2 \times 10^{-16} \text{ cm}^2$, or 16.2 \AA^2 .

VOID VOLUME AND SOLID DENSITY

The simplest method of determining the void volume or the pore volume of a given catalyst sample is to measure the increase in weight that occurs when the pores are filled with a liquid of known density. Water, carbon tetrachloride, and various hydrocarbons have been used successfully. The procedure involves boiling a known weight of dry catalyst pellets in the liquid for 20 to 30 min to displace the air in the pores. After the boiling fluid is replaced with cool liquid, the pellets are placed on an absorbent cloth and rolled to remove the excess liquid. They are then weighed. The void volume per gram of catalyst (V_g) can then be determined from

$$V_g = \frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_L W_{\text{dry}}} \quad (3.18)$$

One can employ this technique to determine the total volume of the pores with radii between approximately 10 and 1500 . This approach is limited in accuracy by the fact that it is difficult to dry the external surface of the particles without removing liquid from the large pores. Some liquid also tends to be retained around the points of contact between particles. These two sources of error offset one another. Any air retained within the pores after boiling will lead to erroneous results.

A more accurate procedure is the *helium-mercury method*. One places a known weight of catalyst (m_p) in a chamber of known volume. After the chamber has been evacuated, a known quantity of helium is admitted. The volume of helium displaced by a sample of catalyst is measured (V_{He}). The volume of helium displaced is a measure of the volume occupied by the solid material. Then the helium is removed, and the volume of mercury displaced is measured (V_{Hg}). Since mercury will not fill the pores of most catalysts at atmospheric pressure, the difference in volumes gives the pore volume of the catalyst sample.

$$V_{\text{void}} = V_{\text{Hg}} - V_{\text{He}} \quad (3.19)$$

and the void volume per gram (V_g) is

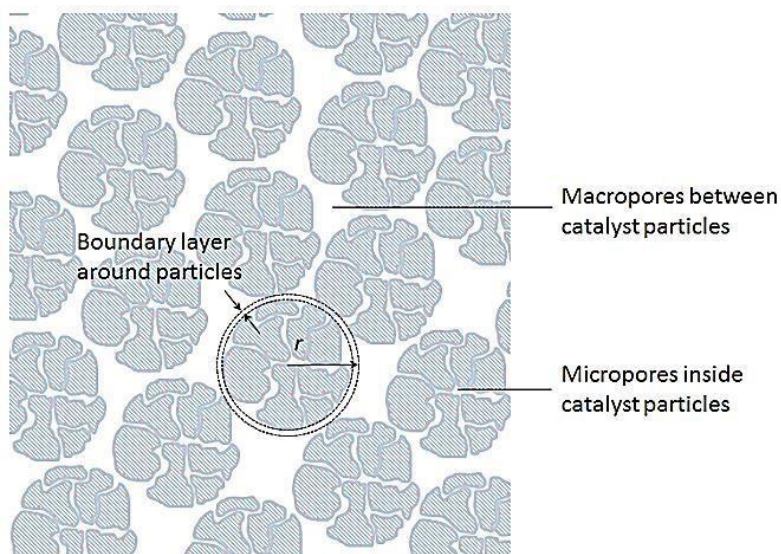
$$V_g = \frac{V_{Hg} - V_{He}}{W} \quad (3.20)$$

This method permits one to determine the pore volume corresponding to pore radii less than 75,000 Å. From the volume of helium displaced (solid volume) and the weight of the sample, the density of the solid phase, ρ_s , can be obtained. Then the void fraction, or porosity, of the particle, ε_p , may be calculated from the equation

$$\varepsilon_p = \frac{\text{void (pore) volume of the particle}}{\text{total volume of particle}} = \frac{m_p V_g}{m_p V_g + m_p / \rho_s} = \frac{V_g \rho_s}{V_g \rho_s + 1} \quad (3.21)$$

To avoid excessive pressure drops and improve mechanical strength, porous particles often must be pelleted to sizes of 1/16 to 1 in. Usually the pellets are

cylindrical, although spherical and granular assemblies are sometimes used. Agglomeration of porous particles gives a pellet containing two void regions: The



void spaces within the particles are commonly termed *micropores*, and the void regions between particles are called *macropores*. Hence such materials are said to contain bidisperse pore systems (Figure 3.3).

Figure 3.3 Porous Catalyst

PORE-VOLUME DISTRIBUTION

The effectiveness of the internal surface for catalytic reactions can depend not only on the extent of the void spaces (V_g), but also on the size of the openings. Therefore it is desirable to know the distribution of void volume in a catalyst according to size of the opening. This is a difficult problem because the void spaces in a given particle are non-uniform in size, shape, and length, and normally are interconnected.

There are two established methods for measuring the distribution of pore volumes.

Mercury Penetration Technique

Since mercury does not wet most substances and will not spontaneously penetrate pores by capillary action, it must be forced into the pores by the application of external pressure. The required equilibrated pressure is inversely proportional to the size of the pores, only slight pressure being required to intrude mercury into large macropores, whereas much greater pressures are required to force mercury into small pores. Mercury porosimetry analysis is the progressive intrusion of mercury into a porous structure under stringently controlled pressures.

If mercury is placed in contact with a pore opening, the surface tension of the mercury acts along the line of contact with the opening equal in length to the perimeter of the opening and creating a force-resisting entry. By equating the force due to surface tension (which tends to keep mercury out of a pore) to the applied force, Ritter and Drake Obtained (The Washburn equation)

$$\pi a^2 p = -2\pi a \sigma \cos \theta$$

$$a = \frac{-2\sigma \cos \theta}{p} \quad (3.22)$$

Where 'a' is the pore radius, p is applied pressure, θ is the contact angle between the mercury and pore wall and surface tension of mercury is 0.48 N/m². While θ probably varies somewhat with the nature of the solid surface, 140° appears to be a good average value. Then the working equation for evaluating the radius corresponding to a given pressure is

$$a (\text{\AA}) = \frac{87.5 \times 10^5}{p (\text{psi})} \quad (3.23)$$

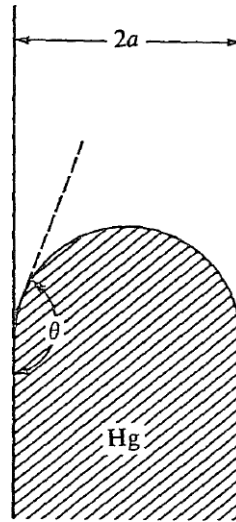


Figure 3.4 Mercury penetration in a pore of radius 'a'

By measuring the volume of mercury that intrudes into the sample material with each pressure change, the volume of pores in the corresponding size class is known. The volume of mercury that enters pores is measured by a mercury penetrometer.

The penetrometer is constructed of glass (an insulator) and filled with mercury (a conductor). The stem of the penetrometer is a capillary that acts as a reservoir for the analytical volume of mercury. The stem is plated with metal (a conductor). The two conductors, mercury, and the metal plating, are separated by glass, thus forming a coaxial capacitor. As pressure forces mercury out of the capillary and into the sample, the mercury inside the capillary decreases and so is the capacitance. The decrease in capacitance, therefore, is proportional to the volume of mercury leaving the capillary with each change in pressure

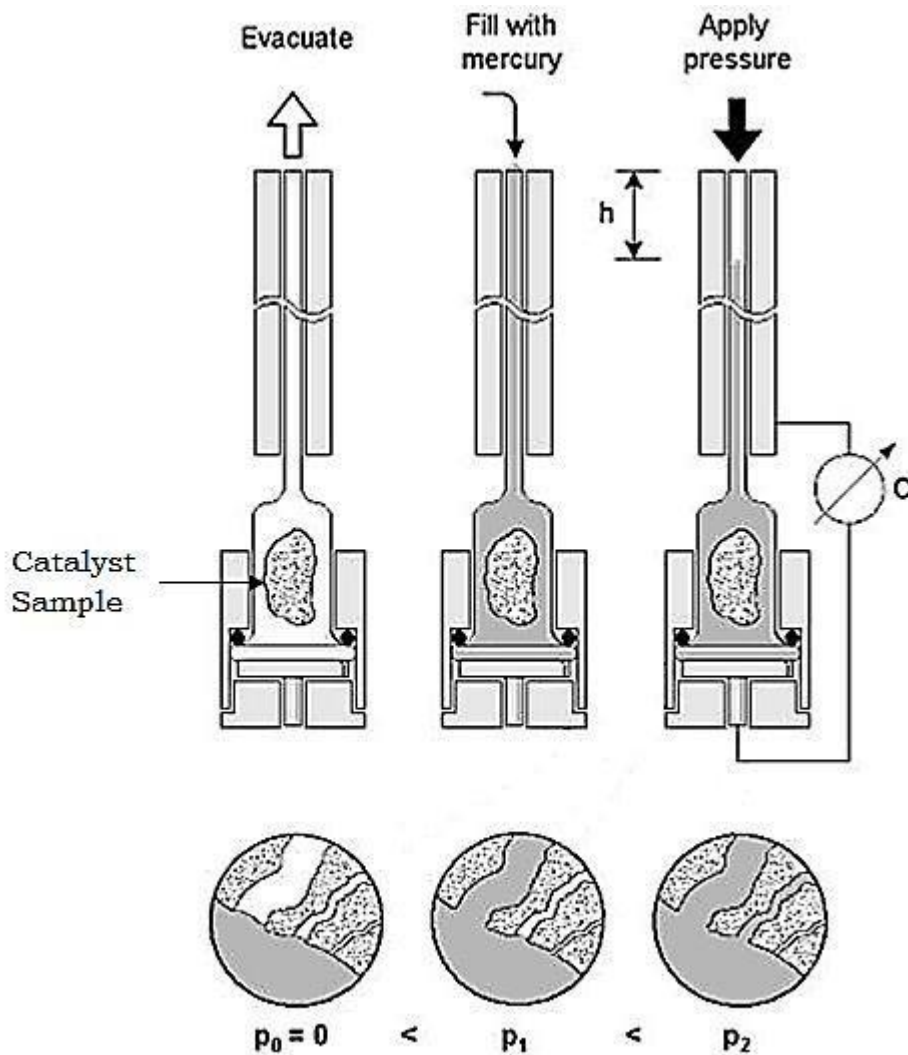


Figure 3.5 Mercury Intrusion Porosimetry

Nitrogen-desorption Method

As the low-temperature nitrogen adsorption experiment is continued to higher pressures multilayer adsorption occurs, and ultimately the adsorbed films are thick enough to bridge the pore. Then further uptake of nitrogen will result in capillary condensation. Since the vapour pressure decreases as the capillary size decreases, such condensation will occur first in the smaller pores. Condensation will be complete, as $p/p_0 \rightarrow 1.0$, when the entire void region is filled with condensed nitrogen. Now, if the pressure is reduced by a small increment, a small amount of nitrogen will evaporate from the meniscus formed at the ends of the largest pores. Pores which are emptied of condensate in this way will be those in which the vapour pressure of nitrogen is greater than the chosen pressure. The Kelvin equation gives the relationship between vapour pressure and radius of the concave surface of the meniscus of the liquid. Since some of the nitrogen is adsorbed on the surface, and therefore not present because of capillary condensation, the Kelvin relationship must be-corrected for the thickness δ of the adsorbed layers. With this

correction, the pore radius is related to the saturation-pressure ratio (vapour pressure in the pore p divided by the normal vapour pressure p_0) by

$$a - \delta = \frac{-2\sigma V_l \cos \theta}{R_g T \ln(p/p_0)} \quad (3.24)$$

Where V_l = molal volume of the condensed liquid

σ = surface tension

θ = contact angle between surface and condensate

Since nitrogen completely wets the surface covered with adsorbed nitrogen, $\theta = 0^\circ$ and $\cos \theta = 1$. The thickness δ depends on p/p_0 . The exact relationship has been the subject of considerable study, but Halsey's form

$$\delta = A \left(\ln \frac{p_0}{p} \right)^{-1/n} \quad (3.25)$$

Where A and n depend on the nature of the catalyst surface, is generally used.

For nitrogen at -195.8°C (normal boiling point) Eq. (3.24), for $a - \delta$ in Angstroms, becomes

$$a - \delta = 9.52 \left(\ln \frac{p_0}{p} \right)^{-1} \quad (3.26)$$

Wheeler proposes for Eq.(3.25)

$$\delta (\text{\AA}) = 7.34 \left(\ln \frac{p_0}{p} \right)^{-1/3} \quad (3.27)$$

For a chosen value of p/p_0 , Eqs. (3.26) and (3.27) give the pore radius above which all pores will be empty of capillary condensate. Hence, if the amount of desorption is measured for various p/p_0 , the pore volume corresponding to various radii can be evaluated. By combining mercury-penetration and nitrogen-desorption measurements, pore-volume information can be obtained over the complete range of radii in a pelleted catalyst containing both macro- and micropores.

Some models for quantitative treatment of the effectiveness of the internal catalyst surface require only the average pore radius, rather than the distribution of pore volumes. Wheeler has developed a simple equation for which requires only surface-area and pore-volume measurements. Suppose all the pores in a hypothetical particle are straight, cylindrical, not interconnected, and have the same radius and length L . The average pore radius may be found by writing equations for the total surface and volume in the hypothetical particle and equating these quantities to the surface $m_p S_g$ and volume $m_p V_g$ in the actual particle; i.e.

$$m_p S_g = (2\pi \bar{a} L) n \quad (3.28)$$

$$m_p V_g = (\pi \bar{a}^2 L) n \quad (3.29)$$

Where m_p and n are the mass and number of pores per particle. Dividing the two equations gives the Wheeler average pore radius,

$$(3.30)$$

$$\bar{a} = \frac{2V_g}{S_g}$$

CATALYST PREPARATION

Experimental methods and techniques for catalyst manufacture are particularly important because chemical composition is not enough by itself to determine activity. The physical properties of surface area, pore size, particle size, and particle structure also have an influence. These properties are determined to a large extent by the preparation procedure. The two most commonly used techniques for catalyst preparation are the only ones we shall consider:

1. Precipitation or gel formation of the active component or components through the interaction of aqueous solutions of two or more chemical compounds.
2. Impregnation of a carrier using a solution containing a compound of the catalyst component desired.

Precipitation or gel formation

Precipitation provides a method of obtaining the solid material in a porous form. It consists of adding a precipitating agent to aqueous solutions of the desired components. Washing, drying, and sometimes calcination and activation are

subsequent steps in the process. For example, a magnesium oxide catalyst can be prepared by precipitating the magnesium from nitrate solution by adding sodium carbonate. The precipitate of MgCO_3 is washed, dried, and calcined to obtain the oxide. Such variables as concentration of the aqueous solutions, temperature, and time of the drying and calcining steps may influence the surface area and pore structure of the final product. This illustrates the difficulty in reproducing catalysts and indicates the necessity of carefully following tested recipes. Of particular importance is the washing step to remove all traces of impurities, which may act as poisons.

A special case of the precipitation method is the formation of a colloidal precipitate which gels. The steps in the process are essentially the same as for the usual precipitation procedure. Catalysts containing silica and alumina are especially suitable for preparation by gel formation, since their precipitates are of a colloidal nature.

In some instances a porous material can be obtained by mixing the components with water, milling to the desired grain size, drying, and calcining. Such materials must be ground and sieved to obtain the proper particle size. A mixed magnesium and calcium oxide catalyst can be prepared in this fashion. The carbonates are milled wet in a ball machine, extruded, dried, and reduced by heating in an oven.

Impregnation

One of the simplest, most commonly used techniques for preparing a catalyst involves dispersing an active component (or components) on a support material. Catalyst *carriers* (support) provide a means of obtaining a large surface area with a small amount of active material. This is important when expensive agents such as platinum, nickel, and silver are used.

The steps in the preparation of a catalyst impregnated on a carrier may include

1. Evacuating the carrier,
2. Contacting the carrier with the impregnating solution,
3. Removing the excess solution,
4. Drying,
5. Calcination and activation.

For example, a nickel hydrogenation catalyst can be prepared on alumina by soaking the evacuated alumina particles with nickel nitrate solution, draining to remove the excess solution, and heating in an oven to decompose the nitrate to nickel oxide. The final step, reduction of the oxide to metallic nickel, is best carried out with the particles in place in the reactor by passing hydrogen through the equipment. Activation *in situ* prevents contamination with air and other gases which might poison the reactive nickel.

The nature of the support can affect catalyst activity and selectivity. This effect presumably arises because the support can influence the surface structure of the atoms of dispersed catalytic agent. For example, changing from silica to alumina carrier may change the electronic structure of deposited platinum atoms.

This question is related to the optimum amount of catalyst that should be

deposited on a carrier. When only a small fraction of a monomolecular layer is added, increases in amount of catalyst should increase the rate. However, it may not be helpful to add large amounts to the carrier. For example, the conversion rate of the ortho to para hydrogen with a NiO catalyst deposited on alumina was found to be less for 5.0 wt % NiO than for 0.5 wt % NiO. The dispersion of the catalyst on the carrier may also be an important factor in such cases. The nickel particles were deposited from a much more concentrated NiNO₃ solution to make the catalyst containing 5.0 wt % NiO. This may have led to larger nickel particles. That is, many more nickel atoms were deposited on top of each other, so that the dispersion of nickel on the surface was less uniform than with the 0.5 wt % catalyst.

PROMOTERS AND INHIBITORS

As normally used, the term "catalyst" designates the composite product used in a reactor. Components of the catalyst must include the catalytically active substance itself and may also include a carrier, promoters, and inhibitors.

A *promoter* is a substance added during the preparation of a catalyst which improves activity or selectivity or stabilizes the catalytic agent so as to prolong its life. The promoter is present in a small amount and by itself has little activity. There are various types, depending on how they act to improve the catalyst. Perhaps the most extensive studies of promoters have been in connection with iron catalysts for the ammonia synthesis reaction. It was found that adding Al₂O₃ (other promoters are CaO, K₂O) prevented reduction (by sintering) in surface area during catalyst use and gave an increased activity over a longer period of time. Some promoters are also believed to increase the number of active centres and so make the existing catalyst surface more active.

An *inhibitor* is the opposite of a promoter. When added in small amounts during catalyst manufacture, it lessens activity, stability, or selectivity. Inhibitors are useful for reducing the activity of a catalyst for an undesirable side reaction. For example, silver supported on alumina is an excellent oxidation catalyst. In particular, it is used widely in the production of ethylene oxide from ethylene. However, at the same conditions complete oxidation to carbon dioxide and water also occurs, so that selectivity to C₂H₄O is poor. It has been found that adding halogen compounds to the catalyst inhibits the complete oxidation and results in satisfactory selectivity.

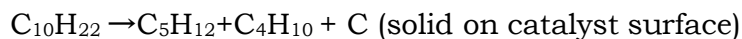
POISONING AND DEACTIVATION OF CATALYSTS

Since the earliest days of heterogeneous catalysis, decreases in activity during use have been observed. The rates at which catalyst deactivation processes take place may be fast or slow. In some cases the decline in activity is so rapid that the catalyst ceases to function effectively after a few minutes or hours of exposure to a reactant feed stream. On the other hand, there are cases where the deactivation processes occur so slowly that the catalyst may function effectively for months or years. In the design of commercial catalytic processes, one obviously must take these factors into account so as to allow for periodic replacement or regeneration of the heterogeneous catalyst.

If the deactivation is rapid and caused by the decomposition or degradation of reactants or products on the catalyst surface, the process is termed *fouling*. In this

case a deposit is formed on the surface or in the pores that physically blocks a portion of the catalyst and prevents it from catalyzing the reaction. Such fouling is particularly rapid with silica–alumina cracking catalysts, and in this application, the design of a unit for catalyst regeneration is as important as the design of the reactor proper.

An example of a cracking reaction leading to fouling might be



The carbon deposit may be burned off with oxygen and/or steam to regenerate the catalyst so that the active surface is no longer covered.

If the activity of the catalyst is slowly modified by chemisorption of materials that are not easily removed, the deactivation process is termed *poisoning*. It is usually caused by preferential adsorption of small quantities of impurities (poisons) present in the feed stream. Adsorption of extremely small amounts of the poison (a small fraction of a monolayer) is often sufficient to cause very large losses in catalytic activity. The bonds linking the catalyst and poison are often abnormally strong and highly specific. Consequently, the process is often irreversible.

If the process is reversible, a change in the temperature or the composition of the gas to which it is exposed may be sufficient to restore catalyst activity. This process is referred to as *reactivation*. If the preferential adsorption of the poison cannot readily be reversed, a more severe chemical treatment or complete replacement of the catalyst may be necessary.

In addition to fouling and poisoning, there is a third catalyst deactivation process that is commonly encountered in industrial practice. This is the phenomenon known as *aging*. Aging involves a loss in specific activity because of a loss in catalyst surface area arising from crystal growth or sintering processes. The rate of the aging process becomes more rapid as the temperature increases. It may also be increased by the presence of certain components of the feed stream or product stream or of trace constituents of the catalyst. In some cases a flux or glaze capable of blocking catalyst pores may be produced.

Various schemes have been proposed for classifying poisons, but the one that is perhaps the most convenient for chemical engineers interested in reactor design is the classification in terms of the manner by which the poison affects chemical activity. In these terms one can distinguish between four general but not sharply differentiated classes.

Deposited poisons or Diffusion poisons

This phenomenon is closely akin to catalyst fouling. Blockage of pore mouths prevents full use of the interior surface area of the pellet. Entrained dust particles or materials that can react on the catalyst to yield a solid residue give rise to this type of poisoning. Carbon deposition on catalysts used in the petroleum industry falls into this category. The carbon covers the active sites of the catalyst and may also partially plug the pore entrances. This type of poisoning is at least partially reversible, and regeneration can be accomplished by burning to CO and CO₂ with air and/or steam. The regeneration process itself is a heterogeneous reaction, a gas-solid noncatalytic one. In the design, of the reactor, attention must be given to

the regeneration as well as to the reaction parts of the cycle.

Intrinsic activity poisons or Chemisorbed Poisons

These poisons decrease the activity of the catalyst for the primary chemical reaction by virtue of their direct electronic or chemical influence on the catalyst surface or active sites. The mechanism appears to be one that involves coverage of the active sites by poison molecules, removing the possibility that these sites can subsequently adsorb reactant species. Common examples of this type of poisoning are the actions of compounds of elements of the groups Vb and VIb (N, P, As, Sb, O, S, Se, Te) on metallic catalysts.

Selectivity poisons

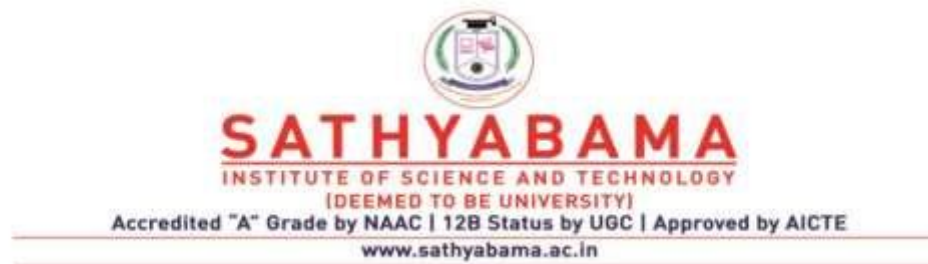
These poisons decrease the selectivity of the catalyst for the main reaction. In many cases impurities in the feed stream will adsorb on the catalyst surface and then act as catalysts for undesirable side reactions. The classic examples of poisons of this class are heavy metals such as Ni, Cu, V, and Fe, which are present in petroleum stocks in the form of organometallic compounds such as porphyrins. When these feed stocks are subjected to catalytic cracking, these organometallic compounds decompose and deposit on and within the catalyst. The metals then act as dehydrogenation catalysts. The product distribution is markedly affected, resulting in lower yields of gasoline and higher yields of light gas, coke, and hydrogen. Very small poison concentrations suffice to produce large changes in selectivity. In cases where a large number of parallel and series reactions are involved, the poison adsorbed is thought to change the activation energy barrier for some of the competitive intermediate steps, resulting in increased rates of undesirable side reactions relative to that of the primary reaction.

Stability poisons

These poisons decrease the structural stability of the catalytic agent or of the carrier by facilitating recrystallizations and other structural rearrangements. Steam acts as this type of a poison for silica-alumina gel catalysts. The steam acts not so much by reducing the intrinsic activity per unit surface area, but by reducing the active area, thus decreasing the activity per unit weight of catalyst. The temperature at which the reactor operates has a marked effect on stability poisoning. Sintering, localized melting, and recrystallization occur much more rapidly at high temperatures than at low temperatures.

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SCHOOL OF BIO AND CHEMICAL ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

UNIT 4: CATALYTIC REACTORS

Heterogeneous Reactions

- For heterogeneous systems, there are two complicating factors that should be accounted for rather than in homogeneous systems.
- The complication of the rate expression and secondly the complication of the contacting patterns for two phase systems.
- Since more than one phase is present, the movement of material from phase to phase must be considered in the rate equation.

- Thus the rate expression in general will incorporate mass transfer terms in addition to the usual chemical kinetics term. These mass transfer terms are different in type and numbers in the different kinds of heterogeneous systems; therefore no single rate expression has general application. For example; the burning of carbon particle in air, how many rate steps are involved?
- $\text{C} + \text{O}_2 \xrightarrow{\hspace{1cm}} \text{CO}_2$

- The figure shows us that there are two steps in series; mass transfer of O_2 to the surface followed by reaction at the surface of particle

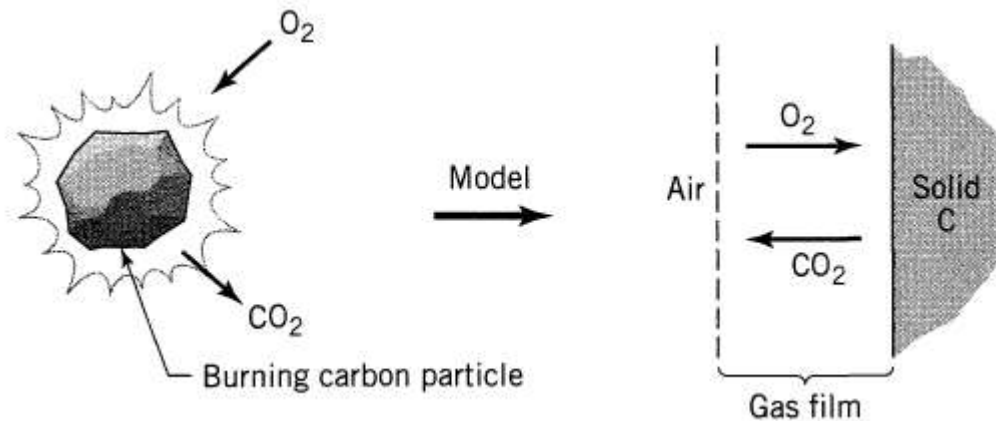


Figure 1: Burning of carbon particle

- In aerobic fermentation, how many rate steps are involved when air bubbles through a tank of liquid which contains dispersed microbes and is taken up by the microbes to produce product.

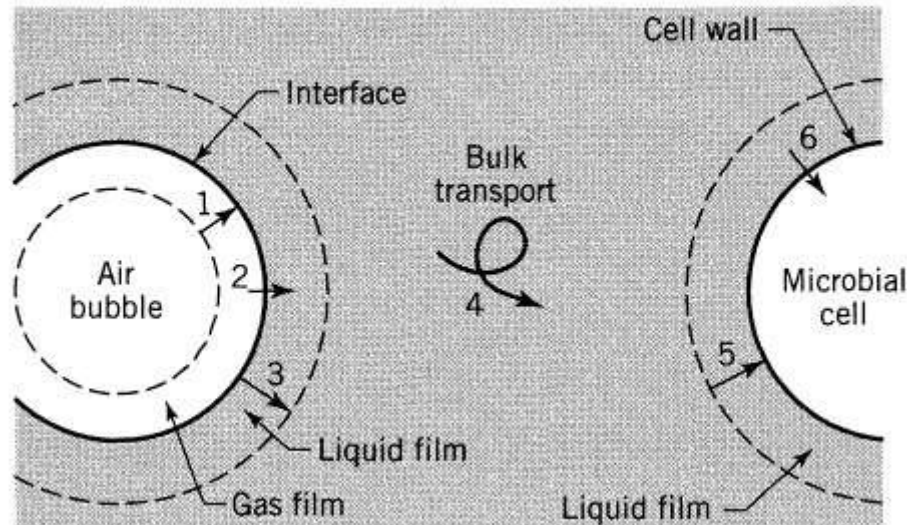


Figure 2: Fermentation reaction

- There are about 7 possible resistance steps, but only one involving the reaction. how many you choose to consider depends on you and the situation.
- To get an overall expression, write the individual rate steps on the same basis (unit surface of burning particle, unit volume of fermenter, unit volume of cell, etc)

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{volume of reactor fluid} \cdot \text{time}}$$

- Or

$$-r'_A = -\frac{1}{W} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{mass of solid} \cdot \text{time}}$$

- Or

$$-r''_A = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{interfacial surface} \cdot \text{time}}$$

- Now put all the mass transfer and reaction steps into the same rate form and combine;

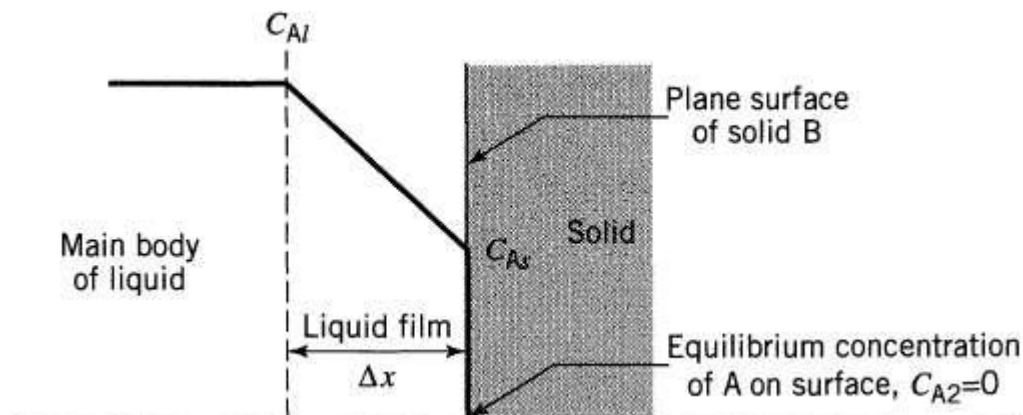
- Or
$$\frac{\text{mol A reacted}}{\text{time}} = (-r_A)V = (-r'_A)W = (-r''_A)S$$

$$r_A = \frac{W}{V} r'_A, \quad r''_A = \frac{V}{S} r_A, \quad r'_A = \frac{S}{W} r''_A$$

- And if the steps are in series as in the previous examples; $r_{\text{overall}} = r_1 = r_2 = r_3$
- if they are parallel; $r_{\text{overall}} = r_1 + r_2$
- Consider steps in series, in general if all steps are linear in concentration, then it is easy to combine them. But if any of the steps are nonlinear, then you will get a messy overall expression. You may try to bypass this nonlinear step in one of the various ways.

- Approximating the r_A versus CA curve by a first-order expression is probably the most useful procedure. Another point: in combining rates the concentration of materials at intermediate conditions are not known, these are the concentrations which are eliminated in combining rates.
- Overall rate for a linear process. Dilute A diffuses thru a stagnant liquid film onto a plane surface consisting of B, reacts there to produce R which diffuses back into the main stream.

- Develop the overall expression for the liquid/solid reaction. $A(l) + B(s) \Rightarrow R(l)$ which takes place on the flat surface.



- By diffusion the flux of A to the surface is
- Reaction is first-order with respect to A, based on unit surface:

$$r''_{A1} = \frac{1}{S} \frac{dN_A}{dt} = -\frac{\mathcal{D}}{\Delta x} (C_{Al} - C_{As}) = k_l (C_{Al} - C_{As}) \quad (1)$$
- At steady-state the flow rate to the surface is equal to the reaction rate at the surface (step in series) so $r''_{A1} = r''_{A2}$ and from (1) and (2)

$$r''_{A2} = \frac{1}{S} \frac{dN_A}{dt} = k'' C_{As} \quad (2)$$

$$k_l (C_{Al} - C_{As}) = k'' C_{As} \quad (3)$$

- Replacing (3) into (i) or (ii) and eliminating C_A which cannot be measured, we get;

$$r''_{A1} = r''_{A2} = r''_A = - \frac{1}{\frac{1}{k_l} + \frac{1}{k''}} C_{Al} = -k_{\text{overall}} C_{Al}, \quad \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

- This shows that $1/k_l$ and $1/k''$ are additive resistances. The addition of resistances to obtain an overall resistance is only possible when the rate is a linear function of the driving force and when the process occurs in series.

Overall rate for a nonlinear process

- When we make just one change; the reaction is second order;

$$r''_{A2} = -k'' C_A^2$$

- Combining the reaction steps to eliminate CA as was done previously is not so simple now, it gives;

$$-r''_A = -r''_{A1} = -r''_{A2} = \frac{k_l}{2 k''} (2 k'' C_{Al} + k_l - \sqrt{k_l^2 + 4 k'' k_l C_{Al}}), \quad \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

- Contacting patterns for two phases**

- There are many ways that two phases can be contacted, and for each the design equation will be unique. When real flow deviates considerably from these, we can do one of two things: (i) we may develop models to mirror actual flow closely, or
- (ii) we may calculate performance with ideal patterns which "bracket" actual flow. Fortunately, most real reactors for heterogeneous systems can be satisfactorily approximated by one of the five ideal flow patterns of the Fig. below. Notable exceptions are the reactions which take place in fluidized beds. There special models must be developed.

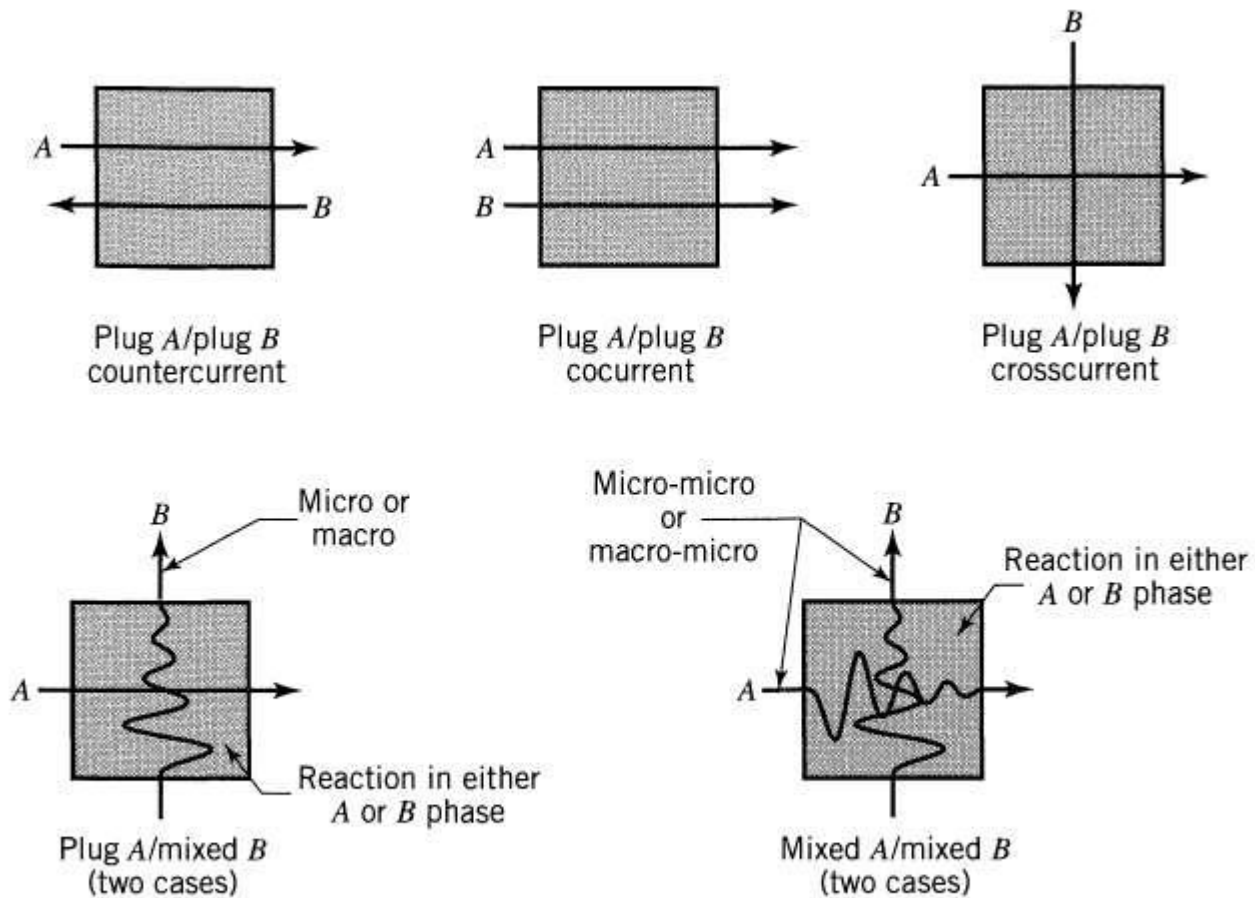


Figure 17.1. Ideal contacting patterns for two flowing fluids.

- In reactor design and scale-up, it is essential to select a flow model which reasonably represents our setup. When you pick a non-representative model and then do computer calculations to the nth degree of accuracy, you will be surprised when design and scale-up do not agree with the predictions. A simple reasonable model is much better than a precise and detailed model which does not represent the contacting. Often the choice of a good flow model and the knowledge of how the flow pattern changes with scale-up spells the difference between success and failure.

- There are two broad classes of catalysts: those that operate at close to ambient temperature with biochemical systems, and the man-made catalysts that operate at high temperature.
- The biochemical catalysts, called enzymes, are found everywhere in the biochemical world and in living creatures, and without their action no life could exist at all. In addition, in our bodies hundreds of different enzymes and other catalysts are busy at work all the time, keeping us alive.

- The man-made catalysts, mostly solids, usually aim to cause the high-temperature rupture or synthesis of materials. These reactions play an important role in many industrial processes, such as the production of methanol, sulphuric acid, ammonia, and various petrochemicals, polymers, paints, and plastics.
- It is estimated that well over 50% of all the chemical products produced today are made with the use of catalysts.

- Consider petroleum. For example, since this consists of a mixture of many compounds, primarily hydrocarbons, its treatment under extreme conditions will cause a variety of changes to occur simultaneously, producing a spectrum of compounds, some desirable, others undesirable.
 - Although a catalyst can easily speed the rate of reactions still when a variety of reactions are encountered, the most important characteristic of a catalyst is its **selectivity**.
 - By this we mean that it only changes the rates of certain reactions, often a single reaction, leaving the rest unaffected. Thus, in the presence of an appropriate catalyst, products containing predominantly the materials desired can be obtained from a given feed.

Rate equations for surface kinetics

- Various theories have been proposed to explain the details of the way catalysts operate (read them). We simply assume that we have a catalyst available to promote a specific reaction and we wish to evaluate the kinetic behaviour of reactants in the presence of the catalyst and then use this information for design.

Levenspiel puts about 5 theories while Richardson's give 3

- Levenspiel: (i) Surface kinetics – happens at the interior or exterior surfaces of the particle
- (ii) Pore diffusion resistance – what may cause the interior of pore to be starved of reactant
- (iii) Particle ΔT – temperature gradient within the particle
- (iv) Film ΔT - between the outer surface of the particle and the main gas stream
- (v) Film Diffusion - resistance/conc. gradient across gas film
- Richardson's give 3 mechanisms: (i) Knudsen Diffusion – when gas molecule diameter larger than pore diameter, collisions b'tn. gas molecules become more preferred
- (ii) Molecular diffusion – When gas molecules are smaller than pore diam. Collisions between molecules become more important.
- (iii) Surface Diffusion – when a gas is adsorbed on inner surfaces of pore

- Because of the great industrial importance of catalytic reactions, considerable effort has been spent in developing theories from which kinetic equations can rationally be developed. The most useful for our purposes supposes that the reaction takes place on an active site on the surface of the catalyst.
- Thus three steps are viewed to occur successively at the surface.
- ***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 (dualsite mechanism)***
- ***Step 3. Products are desorbed from the surface, which then frees the site.***
- In addition, all species of molecules, free reactants, and free products as well as site-attached reactants, intermediates, and products taking part in these three processes are assumed to be in equilibrium. Rate expressions derived from various postulated mechanisms are all of the form

$$\text{rate of reaction} = \frac{(\text{kinetic term})(\text{driving force or displacement from equilibrium})}{(\text{resistance term})}$$



- For example, for a reaction;
- Occurring in inert carrier U, the rate expression when adsorption of A control is;

$$-r_A'' = \frac{k(p_A - p_R p_S / K p_B)}{(1 + K_A p_R p_S / K p_B + K_B p_B + K_R p_R + K_S p_S + K_U p_U)^2}$$

- When chemical reaction between adjacent site

$$-r_A'' = \frac{k(p_A p_B - p_R p_S / K)}{(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_U p_U)^2}$$

attached molecules of A and B control it is

- Each detailed mechanism of reaction with its controlling factor has its corresponding rate equation involving anywhere from three to seven arbitrary constants, the K values. These complicated equations shall not be used but we shall use the contact time or space time instead.
- **Pore diffusion resistance combined with surface kinetics**
- First consider a single cylindrical pore of length L, with reactant A diffusing into the pore, and reacting on the surface by a first-order reaction taking place
$$A \rightarrow \text{product}$$

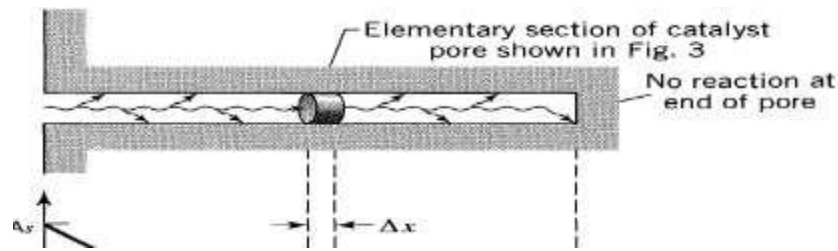
- At the walls of the pore and the product diffusing out of the pore

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

- The rate is given by;

The flow of materials into and out of any section of pore is shown in detail in Fig. 3. At steady state a material balance for reactant A for this elementary

- section gives;
- output - input + disappearance by reaction = 0



- Or in eqn form;

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

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

- Rearranging it gives;
- Taking the limit as Δx approaches zero,

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

- In general, the interrelation between rate constants on different bases is

$$kV = k'W = k''S$$

- Thus for the cylindrical catalyst pore;

$$k = k'' \left(\frac{\text{surface}}{\text{volume}} \right) = k'' \left(\frac{2\pi r L}{\pi r^2 L} \right) = \frac{2k''}{r}$$

- In terms of volumetric units, we have

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

- Which is the frequently met linear differential equation whose general solution is;

$$C_A = M_1 e^{mx} + M_2 e^{-mx}$$

- Where $m = \sqrt{\frac{k}{\mathcal{D}}} = \sqrt{\frac{2k''}{\mathcal{D}r}}$ and M_1 and M_2 are constants

- Here the boundary conditions have to be specified. For this system they are two; at the entrance of the pore, $C_A = C_{As}, \quad \text{at} \quad x = 0$
- And at the end of pore; $\frac{dC_A}{dx} = 0, \quad \text{at} \quad x = L$
- With the appropriate mathematical manipulation, Figure (18.4) is obtained;
- Where $M_1 = \frac{C_{As}e^{-mL}}{e^{mL} + e^{-mL}}, \quad M_2 = \frac{C_{As}e^{mL}}{e^{mL} + e^{-mL}}$
- Hence the concentration of reactants within the pore is $\frac{C_A}{C_{As}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL}$

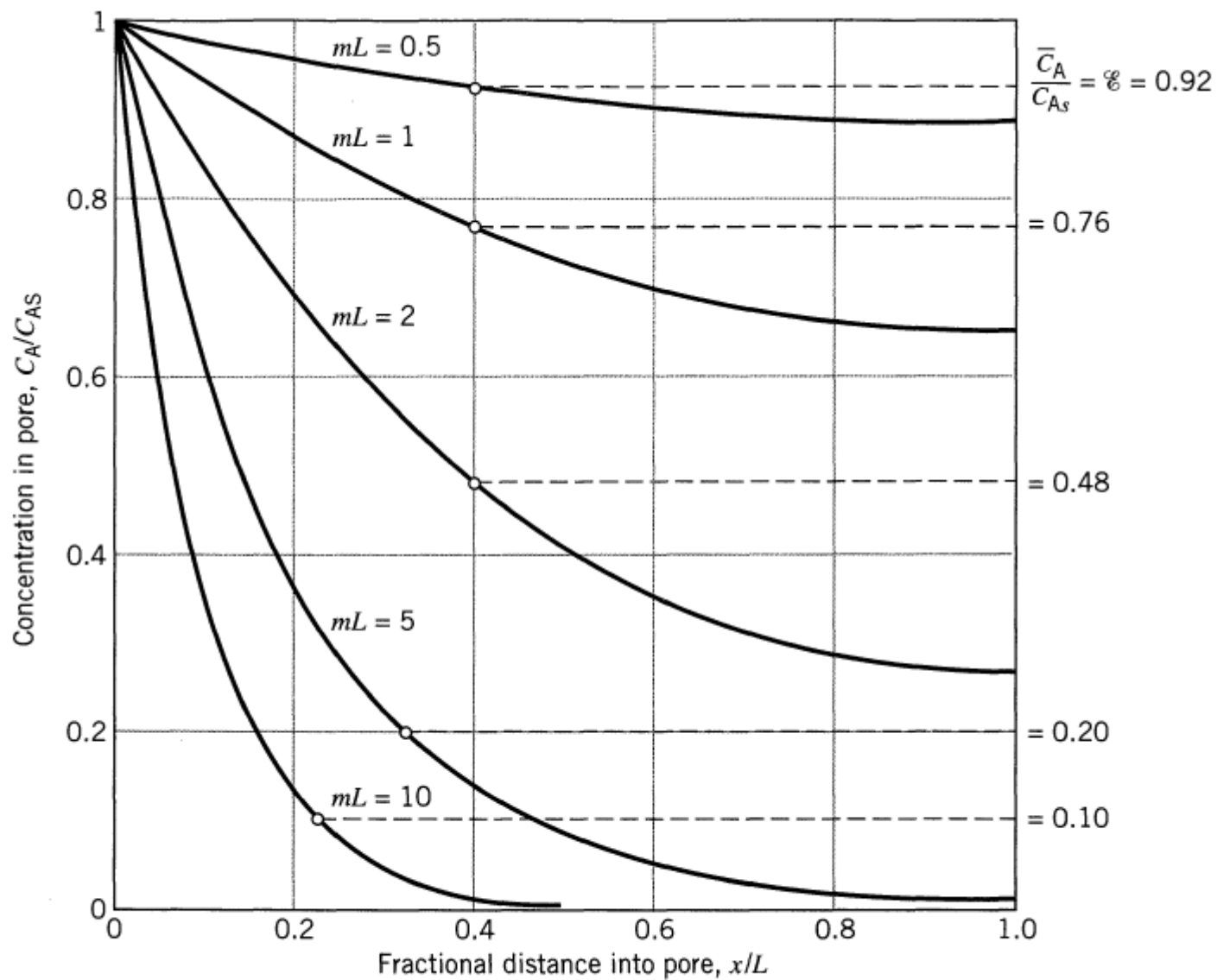


Figure 18.4 Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter $mL = L\sqrt{k/\mathcal{D}}$

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SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT 5: INDUSTRIAL REACTORS & CATALYST DEACTIVATION

THE RATE AND PERFORMANCE EQUATIONS

The activity of a catalyst pellet at any time is defined as

$$\mathbf{a} = \frac{\text{rate at which the pellet converts reactant A}}{\text{rate of reaction of A with a fresh pellet}} = \frac{-r'_A}{-r'_{A0}}$$

In terms of the fluid bathing the pellet the rate of reaction of A should be of the following form:

$$\left(\begin{array}{c} \text{reaction} \\ \text{rate} \end{array} \right) = f_1 \left(\begin{array}{c} \text{main stream} \\ \text{temperature} \end{array} \right) \cdot f_3 \left(\begin{array}{c} \text{main stream} \\ \text{concentration} \end{array} \right) \cdot f_5 \left(\begin{array}{c} \text{present activity of} \\ \text{the catalyst pellet} \end{array} \right)$$

$$-r'_A = k' \cdot C_A^n \cdot \mathbf{a} = k'_0 e^{-E/RT} \cdot C_A^n \cdot \mathbf{a}$$

THE RATE AND PERFORMANCE EQUATIONS

- Similarly, the rate at which the catalyst pellet deactivates may be written as

$$\left(\begin{array}{c} \text{deactivation} \\ \text{rate} \end{array} \right) = f_2 \left(\begin{array}{c} \text{main stream} \\ \text{temperature} \end{array} \right) \cdot f_4 \left(\begin{array}{c} \text{main stream} \\ \text{concentration} \end{array} \right) \cdot f_6 \left(\begin{array}{c} \text{present state of} \\ \text{the catalyst pellet} \end{array} \right)$$

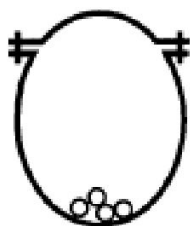
$$-\frac{da}{dt} = k_d \cdot C_i^m \cdot a^d = k_{d0} e^{-E_d/RT} \cdot C_i^m \cdot a^d$$

- where d – Order of deactivation,
 m – Measures the concentration dependency
 E_d – Activation energy or temperature dependency of the deactivation.

The Rate Equation from Experiment

- Experimental devices for studying deactivating catalysts fall into two classes:

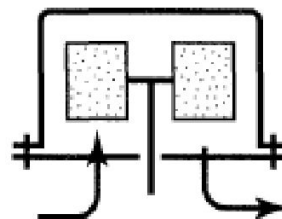
Batch solids—for slow deactivation



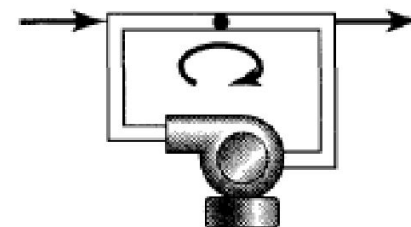
Batch for both
solid and fluid



Plug flow
for fluid



Mixed flow
for fluid



Recycle flow
for fluid

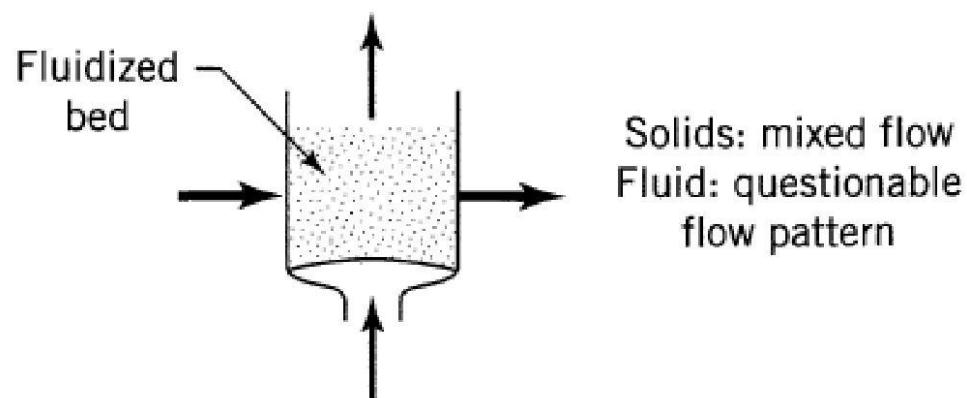
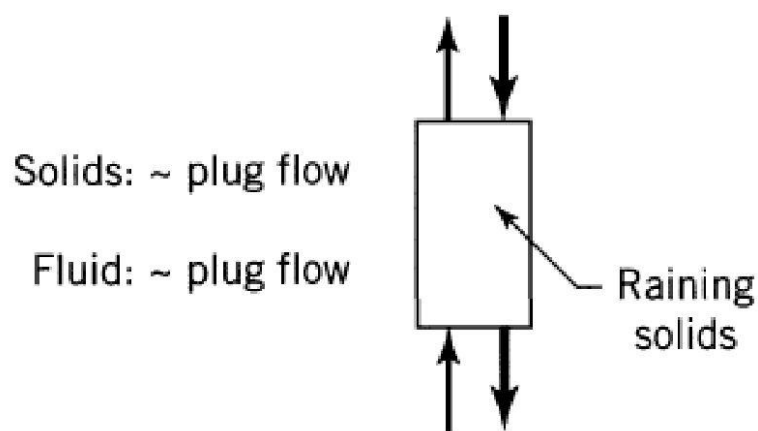
The Rate Equation from Experiment

- Batch-solids devices are much preferred - ease of experimentation.
- Deactivation is slow enough (in the order of minutes or longer)
- Sufficient data on the changing fluid composition can be obtained before exhaustion of the catalyst

The Rate Equation from Experiment

- Experimental devices for studying deactivating catalysts fall into two classes:

Flow of solids—for fast deactivation



The Rate Equation from Experiment

- When deactivation is very rapid (in the order of seconds or less) then a flowing-solids system must be used.
- Cracking catalysts whose activity half-lives can be as short as 0.1 second fall into this class.

The Rate Equation from Experiment

- The method of searching for a rate equation:
 - Start with the simplest kinetic form and see if it fits the data.
 - If it doesn't, try another kinetic form and so on.

The Rate Equation from Experiment

- Type of batch-solids/flowing-fluid reactor to use depends on whether the deactivation expression da/dt is concentration independent or not.
- Concentration independent
 - Any type of batch solids
- Concentration dependent
 - Reactor in which C_A is forced to stay unchanged with time

Batch-Solids: Determining the Rate for Independent Deactivation

$$\left. \begin{aligned} -r'_A &= k' C_A \mathbf{a} \quad \text{with} \quad \varepsilon_A = 0 \\ -\frac{d\mathbf{a}}{dt} &= k_d \mathbf{a} \end{aligned} \right\} \quad \begin{aligned} (14a) \\ (14b) \end{aligned}$$

This represents first-order reaction and first-order deactivation which, in addition, is concentration independent.

Batch-Solids: Determining the Rate for Independent Deactivation

- ***Batch-Solids, Batch-Fluid.***

- Need to develop an expression relating the changing gas concentration with time.

$$-\frac{dC_A}{dt} = \frac{W}{V} \left(-\frac{1}{W} \frac{dN_A}{dt} \right) = \frac{W}{V} (-r'_A) = \frac{W}{V} k' C_A \mathbf{a} \quad (15)$$

$$-\frac{d\mathbf{a}}{dt} = k_d \mathbf{a} \quad (16)$$

Batch-Solids: Determining the Rate for Independent Deactivation

- ***Batch-Solids, Batch-Fluid.***

Integrating Eq. 16 yields

$$\mathbf{a} = \mathbf{a}_0 e^{-k_d t} \quad (17)$$

and for unit initial activity, or $\mathbf{a}_0 = 1$, this becomes

$$\mathbf{a} = e^{-k_d t} \quad (18)$$

Replacing Eq. 18 in Eq. 15 we then find

$$-\frac{dC_A}{dt} = \frac{Wk'}{V} e^{-k_d t} C_A \quad (19)$$

and on separation and integration

$$\ln \frac{C_{A0}}{C_A} = \frac{Wk'}{Vk_d} (1 - e^{-k_d t}) \quad (20)$$

Batch-Solids: Determining the Rate for Independent Deactivation

- ***Batch-Solids, Batch-Fluid.***

This expression shows that even at infinite time the concentration of reactant in an irreversible reaction does not drop to zero but is governed by the rate of reaction and of deactivation, or

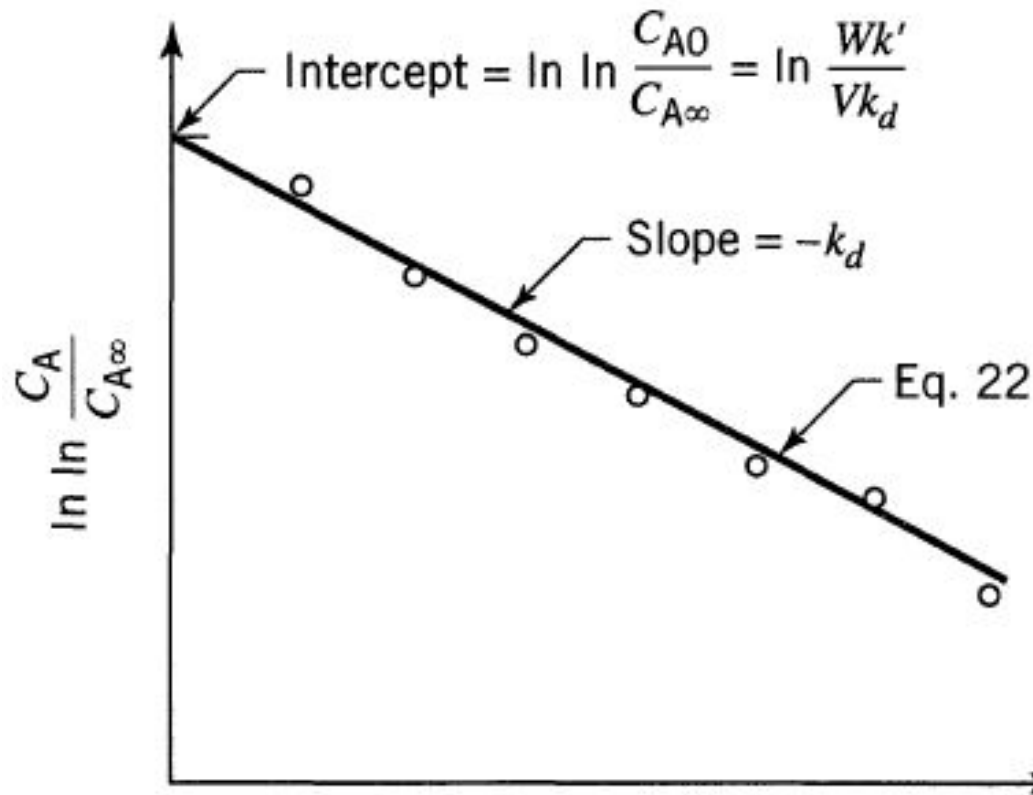
$$\ln \frac{C_{A0}}{C_{A\infty}} = \frac{Wk'}{Vk_d} \quad (21)$$

Combining the above two expression and rearranging then yields

$$\boxed{\ln \ln \frac{C_A}{C_{A\infty}} = \ln \frac{Wk'}{Vk_d} - k_d t} \quad (22)$$

Batch-Solids: Determining the Rate for Independent Deactivation

- ***Batch-Solids, Batch-Fluid.***



Batch-Solids: Determining the Rate for Independent Deactivation

Batch-Solids, Mixed Constant Flow of Fluid. Inserting the rate of Eq. 14a into the performance expression for mixed flow gives

$$\tau' = \frac{WC_{A0}}{F_{A0}} = \frac{W}{v} = \frac{C_{A0} - C_A}{k' a C_A} \quad (23)$$

and on rearrangement

$$\frac{C_{A0}}{C_A} = 1 + k' a \tau' \quad (24)$$

In Eq. 24 the activity varies with the chronological time. To eliminate this quantity integrate Eq. 14b (see Eq. 18) and insert in Eq. 24. Thus

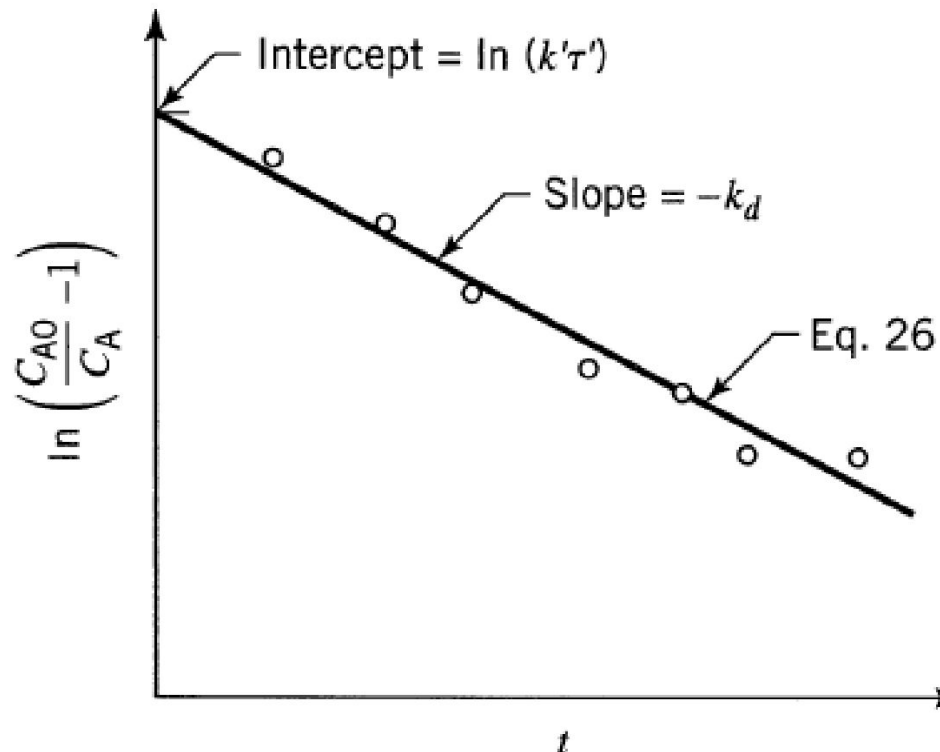
$$\frac{C_{A0}}{C_A} = 1 + k' e^{-k_d \tau'} \tau' \quad (25)$$

Batch-Solids: Determining the Rate for Independent Deactivation

Rearranging gives, in more useful form,

$$\ln \left(\frac{C_{A0}}{C_A} - 1 \right) = \ln(k' \tau') - k_d t$$

(26)



Batch-Solids: Determining the Rate for Independent Deactivation

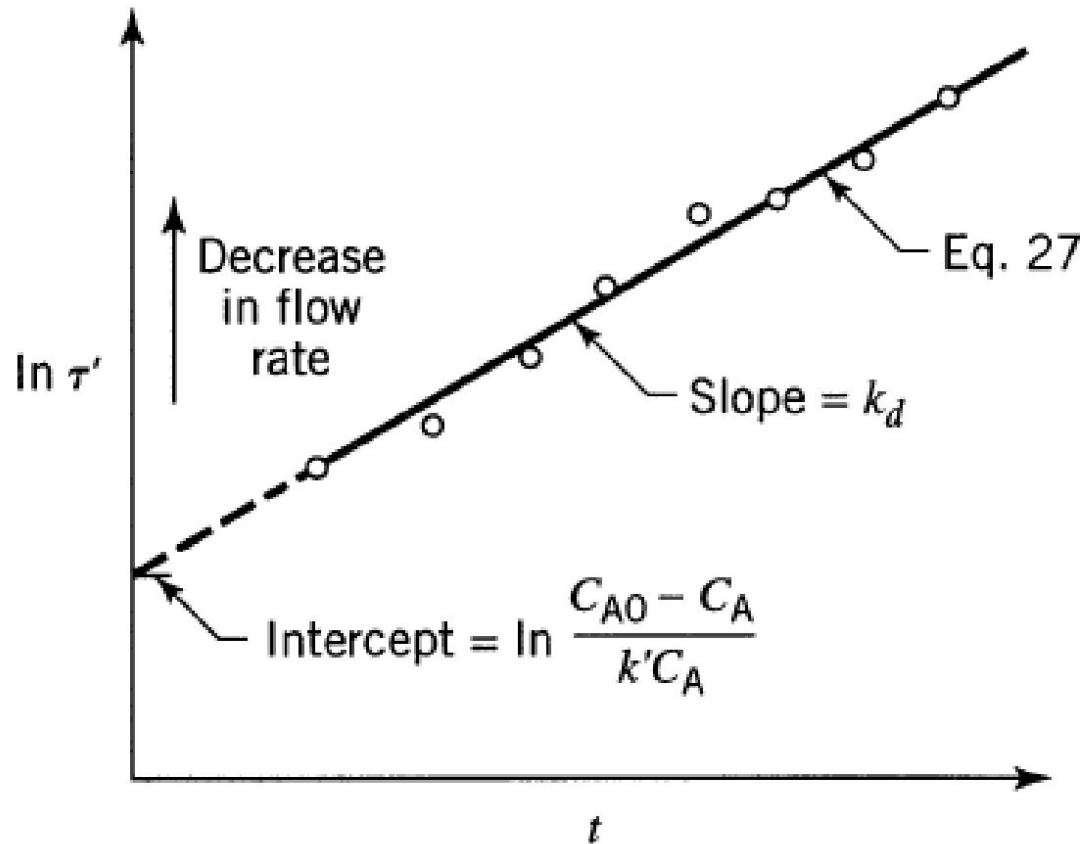
Batch-Solids, Mixed Changing Flow of Fluid (to keep C_A fixed). For steady flow in a mixed reactor we have found

$$\frac{C_{A0}}{C_A} = 1 + k' e^{-k_d t} \tau' \quad (25)$$

To keep C_A constant the flow rate must be slowly changed with time. In fact, it must be lowered because the catalyst is deactivating. Hence the variables in this situation are τ' and t . So, on rearranging we have

$$\ln \tau' = k_d t + \ln \left(\frac{C_{A0} - C_A}{k' C_A} \right) \quad (27)$$

Batch-Solids: Determining the Rate for Independent Deactivation



Batch-Solids: Determining the Rate for Independent Deactivation

Batch-Solids, Plug Constant Flow of Fluid. For plug flow the performance equation combined with the rate of Eq. 14a becomes

$$\frac{W}{F_{A0}} = \int \frac{dX_A}{-r'_A} = \int \frac{dX_A}{k' \mathbf{a} C_A} = \frac{1}{k' \mathbf{a}} \int \frac{dX_A}{C_A} \quad (28)$$

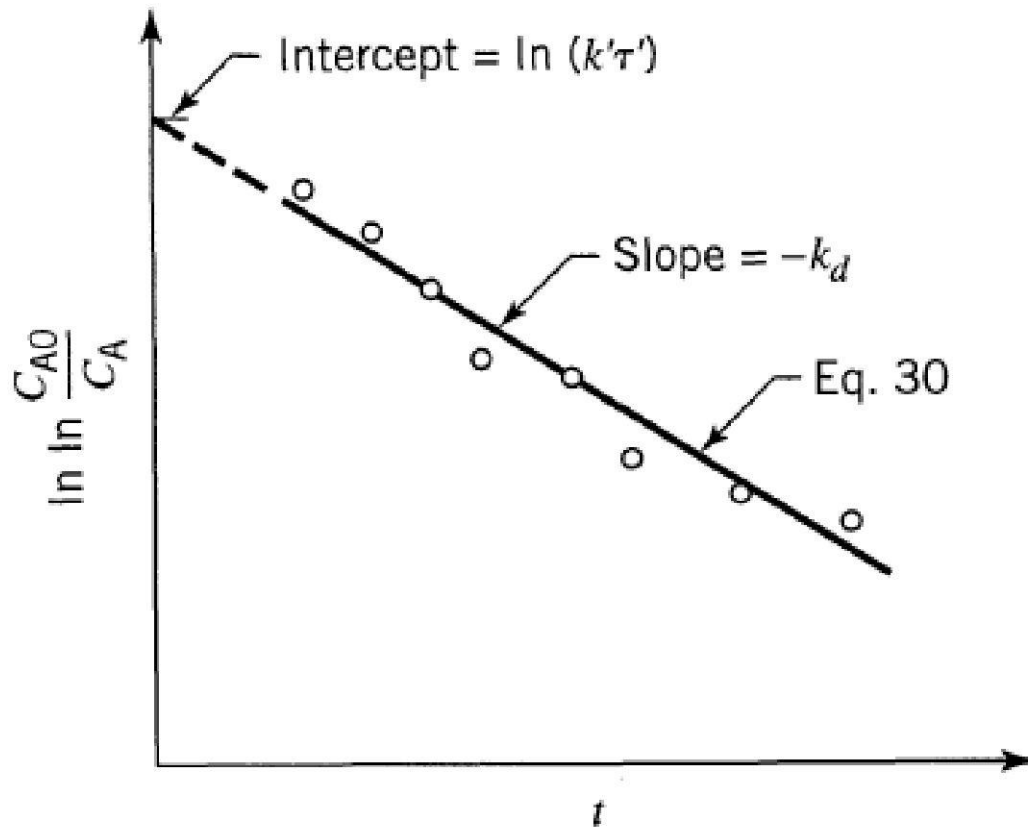
Integrating and replacing \mathbf{a} by the expression of Eq. 18 gives

$$\frac{WC_{A0}}{F_{A0}} = \tau' = \frac{1}{k' \mathbf{a}} \ln \frac{C_{A0}}{C_A} = \frac{1}{k' e^{-k_d t}} \ln \frac{C_{A0}}{C_A} \quad (29)$$

which becomes, on rearrangement,

$$\boxed{\ln \ln \frac{C_{A0}}{C_A} = \ln(k' \tau') - k_d t} \quad (30)$$

Batch-Solids: Determining the Rate for Independent Deactivation



Batch-Solids: Determining the Rate for Independent Deactivation

Batch-Solids, Plug Changing Flow of Fluid (to keep $C_{A, \text{out}}$ fixed). At any instant in the plug flow reactor Eq. 29 applies. Thus noting that τ' and t are the two variables we obtain, on suitable rearrangement,

$$\ln \tau' = k_d t + \ln \left(\frac{1}{k'} \ln \frac{C_{A0}}{C_A} \right) \quad (31)$$

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