UNIT I CATALYSTS
Nature of catalysts, surface area and pore-volume distribution, catalyst preparation.

PART A

1. Define the following and give an example: Catalyst support and Promoter. (Nov/Dec 2017)

   Catalyst support is the material, usually a solid with a high surface area, to which a catalyst is affixed. The activity of heterogeneous catalysts and nanomaterial-based catalysts occurs at the surface atoms. Consequently, great effort is made to maximize the surface area of a catalyst by distributing it over the support. The support may be inert or participate in the catalytic reactions. Typical supports include various kinds of carbon, alumina, and silica.

   Catalyst promoters (or) activator are substances which do not act as catalyst but enhance the efficiency or activity or selectivity or stability of catalyst and prolong catalyst life. For example, the catalytic activity of V2O5 in oxidation of SO2 is enhanced appreciably when sulphates of alkali metals are added in small amounts.

2. List the general characteristics of catalysts. (Nov/Dec 2017)

   The important characteristics of a catalyst are:
   
   (i) Activity
   (ii) Kindling point
   (iii) Specificity
   (iv) Porous and crystalline structure of a catalyst.

   Activity of a catalyst indicates its usefulness and is a measure of the accelerating effect it can have on the rate of reaction. The choice of a catalyst is done on the basis of its activity.

   Kindling point indicates the minimum temperature at which a catalytic process proceeds on a rate sufficient for commercial operation. The catalyst needs to have low kindling point so that less energy is required to preheat the reaction mixture.

   Specificity also means selectivity of the catalyst. Specificity is a property of a catalyst and its indicates its property to speed up the main reaction by suppressing other side reactions.

   Porous structure is an important quality of the catalyst. A commercial catalyst needs to have an extended external surface for maximum rate of reaction. Crystalline structure of the same catalyst strongly reduces the catalyst activity. For example conversion of γ - Al2O3 to α - Al2O3 reduces its activity by several orders of magnitude as a dehydrogenation catalyst.
3. What are the importance of pores in a catalyst particle? (Apr/May 2017) (or) Write about an importance of surface area in catalyst. (Nov/Dec 2016)

(a) Porous structure is an important quality of the catalyst. A commercial catalyst needs to have an extended external surface for maximum rate of reaction. Crystalline structure of the same catalyst strongly reduces the catalyst activity. For example conversion of $\gamma$ - Al$_2$O$_3$ to $\alpha$ - Al$_2$O$_3$ reduces its activity by several orders of magnitude as a dehydrogenation catalyst.

(b) The pores in a catalyst particle have a large surface area available for solid-fluid interaction is highly useful in attaining a significant reaction rate.

(c) When the pores are considerably large and the gas is relatively dense or if the pores are filled with liquid. If free cross section of the porous mass is $\theta$, then diffusion flux per unit total cross section of the porous catalyst is $\theta$ times the diffusion flux under similar conditions with no solid present.

For Example,

(i) Alumina-silica cracking catalyst. It has a pore volume 0.6 cm$^3$/gm. The average pore radius is 4nm. The corresponding surface area is around 300m$^2$/gm.

(ii) Raney Nickel catalyst in the hydrogenation of vegetable and animal oils and platinum-on-alumina catalyst in reforming of petroleum naptha to produce high octane rating are other good example of porous and high surface area catalysts.

4. Differentiate micro and macro pore. (Nov/Dec 2016)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>MICROPORE</th>
<th>MACROPORE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pores with diameter less than 2nm (20 Å$^0$) are called micropores</td>
<td>Pores in the range of greater than 50 nm are called macropores</td>
</tr>
</tbody>
</table>

5. What is bidispersed catalyst? (May/June 2016)

In some porous catalysts having macro-micro pore size distribution is seen.

It is called as bimodal pore size distribution.

Pelletized catalysts or extruded or porous carbon shows such bidisperse structure. In such cases, mean pore radius $r_c$ calculated by equation has very less significance. The micropore on have radius as small as 23 – 25 Å. The mean macropore radius can vary from 15000 Å to 375 Å as the catalyst pellet density increases. Pellets with greater density show micropore diffusion characteristics. While least density pellets show macropore diffusion characteristics.

6. Explain the crude way to find out pore volume of a porous catalyst. (Nov/Dec 2015)

(a) differential (b) cumulative
Pore size distribution can be represented both in differential and cumulative ways. The Fig. 4(a) shows the differential BJH pore distribution of titania sample calcined at 400°C. The figure shows that for the given sample pores were in the range of 2-10 nm. The corresponding cumulative pore distribution is shown in Fig. 4(b).

(b) By mercury intrusion

For macropores materials with pore diameter greater than 50 nm, the mercury intrusion method is preferred. Due to non-wetting nature of mercury on oxide supports, intrusion is met with resistance and mercury is forced to enter the pores of material under pressure. The pore radius ‘r’ is related to the applied pressure P as

\[
P = \frac{(-2\gamma \cos \theta)}{r}
\]

The wetting or contact $\theta$ angle between mercury and solid is on average lies in the range 130-140\(^\circ\) and surface tension of mercury is 0.48 N/m\(^2\). \(p\) is in atm and \(r\) in nanometers.


<table>
<thead>
<tr>
<th>S.No.</th>
<th>CATALYST PROMOTER</th>
<th>CATALYST DEACTIVATOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Catalyst which increases the rate of a reaction is a catalyst promoter</td>
<td>Catalyst which decreases the rate of a reaction is a catalyst deactivator.</td>
</tr>
<tr>
<td>2</td>
<td>It is also called catalyst activator.</td>
<td>It is also called catalyst inhibitor.</td>
</tr>
<tr>
<td>3</td>
<td>They can speed up slow reactions in a sufficient manner to make them commercially feasible.</td>
<td>They can slow down the fast reactions in a sufficient manner to make them commercially feasible.</td>
</tr>
<tr>
<td>4</td>
<td>For example, In the catalytic activity of V(_2)O(_5) in oxidation of SO(_2) is enhanced appreciably when sulphates of alkali metals are added in small amounts.</td>
<td>For example, In the oxidation of ethylene, ethylene oxide is the desirable product. At the same conditions CO(_2) and H(_2)O are also formed by complete oxidation, but this reaction is undesirable and needs to be suppressed. In this process silver supported alumina is a good catalyst but if halogen compound is added, CO(_2) and H(_2)O formation is reduced.</td>
</tr>
</tbody>
</table>

8. What are promoters and inhibitors? (Nov/Dec 2014) (Apr/May 2016)

**Catalyst promoters (or) activator** are substances which do not act as catalyst but enhance the efficiency or activity or selectivity or stability of catalyst and prolong catalyst life. For example, the catalytic
activity of V\textsubscript{2}O\textsubscript{5} in oxidation of SO\textsubscript{2} is enhanced appreciably when sulphates of alkali metals are added in small amounts.

Catalyst inhibitors (or) deactivators are substances which decrease the rate of reaction, or activity or selectivity or stability of the catalyst. For example in the oxidation of ethylene, ethylene oxide is the desirable product. At the same conditions CO\textsubscript{2} and H\textsubscript{2}O are also formed by complete oxidation, but this reaction is undesirable and needs to be suppressed. In this process silver supported alumina is a good catalyst but if halogen compound is added, CO\textsubscript{2} and H\textsubscript{2}O formation is reduced.

9. **What is meant by catalyst?**

A Catalyst is a substance that alters the rate of reaction, but remains unchanged after the reaction. Many chemical reactions which are not feasible under normal conditions can be carried out in the presence of catalyst.

10. **What are the characteristics of catalyst in catalytic reactions?**

   (i) Catalyst remains unchanged at the end of reaction.

   (ii) Very small quantity of catalyst is sufficient to enhance the rate of reaction.

   (iii) Catalyst activates the molecules and reduces the activation energy necessary for a chemical reaction to occur.

   (iv) Catalyst develops new mechanism for a reaction.

   (v) Catalyst does not alter the chemical equilibrium.

   (vi) The activation energy of a catalyzed reaction is comparatively less as compared to non catalyzed reaction.

   (vii) Catalysts plays a specific role in chemical reaction. Therefore a good catalyst for one reaction may be totally ineffective in other reaction.

   (viii) Catalyst can reduce the cost of production.

   (ix) Catalyst can affect yield and selectivity of a chemical reaction because of its ability to change the reaction mechanism.

11. **Define Effectiveness Factor of a catalyst.** (May 2015).

Effectiveness Factor of a catalyst can be defined as:

\[
\text{Effectiveness factor} = \frac{\text{Actual mean reaction rate within pore}}{\text{Rate if not slowed by pore diffusion}}.
\]

12. **What is meant by catalyst Deactivation?**

Activity of catalysts normally decreases with time.

During the course of operation, the activity of catalyst gets reduced and it is not able to provide expected performance. The catalyst needs to be reactivated. Catalyst deactivation may be caused by ageing phenomena. Catalyst deactivation may be very fast. The life of any catalyst generally depends
on type of reactions as well as reaction conditions.

*For example,* catalysts for catalytic cracking lose much of their activity within seconds *due to carbon deposition on the surface and carbon has blocked catalyst pores* while promoted iron catalysts used in ammonia synthesis have a lifetime of years.

13. **What are types of catalyst Deactivation? (May 2012).**

Catalyst Deactivation can be divided into following three categories:

(i) Deactivation by sintering (also called as ageing),
(ii) Deactivation by fouling or coking
(iii) Deactivation by poisoning.

14. **Name the methods of preparing solid catalyst.**

2. Impregnation method
3. Physical mixing of components

15. **Name the three categories of Industrial catalysts.**

1. Bulk catalysts.
2. Supported catalyst.

16. **How will represent pore-volume distribution?**

Pore size distribution can be represented both in differential and cumulative ways.

17. **Define Catalysis.**

“Catalysis” is a term refers to a process in which the rate of reaction is influenced by a substance (catalyst) that remains chemically unaffected.

18. **What is homogeneous catalysis? Give one example.**

Homogeneous catalysis is one in which the reactants, the catalyst and the products are in same or single.

The basis for the any catalytic theory is that first the catalyst and one or more of the reactants form an intermediate complex, a loosely bound compound – which is unstable. This complex then takes part in subsequent reactions which results in the final products and the regenerated catalyst.

The kinetics of the hydrolysis of ethyl acetate catalyzed by hydrochloric acid can be explained by the following mechanism.

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}^+ \rightarrow \text{CH}_3\text{C}00\text{C}_2\text{H}_5 [\text{H}^+] \\
\text{CH}_3\text{C}00\text{C}_2\text{H}_5 [\text{H}^+] + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{C}00\text{H} + \text{H}^+
\]

19. **Does a catalyst alter equilibrium conversion of a chemical reaction? Explain.**

No. With a reversible reaction, a catalyst which increases the rate will increase the rate of both the forward and the backward reaction. This is useful because the catalyst will, cause the reaction...
mixture to reach its equilibrium composition more quickly. So, the catalyst will not change the equilibrium composition of the substance and hence the conversion.

20. **Is the selectivity of multiple reactions affected by catalysts? Explain.**

Yes, the selectivity of multiple reactions is affected by catalysts. It means that the selectivity changes only the rate of desired and undesired materials in the multiple reactions. Thus, in the presence of appropriate catalyst, products containing predominantly the materials desired can be obtained from a given feed.

21. **Give the classification of catalyst.**

There are two broad classes of catalyst;

- Biochemical catalysts, called Enzymes, are found everywhere in the biochemical world and in living creatures and operate at close to ambient temperature.
- Man-made catalysts, mostly solids, usually aim to cause the high-temperature rupture or synthesis of materials.

22. **State the types of catalyst poisoning.**

The decrease in the activity of catalyst due to poisons, which will be defined as substances (either in the reactants stream or produced by reaction) which lower the activity of catalyst.

The types of catalyst poisoning are;

(i) Deposited poisons
(ii) Chemisorbed poisons
(iii) Selectivity poisons
(iv) Stability poisons
(v) Diffusion poisons

23. **Define Effectiveness Factor of a catalyst. (May 2015).**

Effectiveness Factor of a catalyst can be defined as:

Effectiveness factor = actual mean reaction rate within pore /rate if not slowed by pore diffusion.

24. **What are types of catalyst deactivation? (May 2012).**

Activity of catalysts normally decreases with time. The life of any catalyst generally depends on type of reactions as well as reaction conditions. For example, catalysts for catalytic cracking lose much of their activity within seconds due to carbon deposition on the surface while promoted iron catalysts used in ammonia synthesis have a lifetime of years.

25. **Name the components present in catalyst.**

1. Catalytic agent
2. Support /carrier
3. Promoters and Inhibitors
   Catalytic agents may be broadly divided in the following categories:
   Metallic conductors (E.g. Fe, Pt, Ag, etc.)
   Semiconductors (E.g. NiO, ZnO, etc.)
   Insulators (E.g. Al₂O₃, SiO₂, etc.)

27. How will represent pore-volume distribution?
   Pore size distribution can be represented both in differential and cumulative ways.

28. What are the carriers or support used and why they are used with catalyst?
   A catalyst support is the material, usually a solid with a high surface area, to which a catalyst is affixed. The reactivity of heterogeneous catalysts and nanomaterial-based catalysts occurs at the surface atoms. Catalyst support results in highly porous nature - increase of available surface area improve stability improves the heat transfer characteristics. Some of Alumina, Asbestos, Carborundum, Iron oxide, Manganese, Activated carbon, Zinc oxide.

29. What is sol gel method of preparation of catalyst?
   The sol-gel process is a wet-chemical technique (Chemical Solution Deposition) for the fabrication of materials starting from a chemical solution that reacts to produce colloidal particles (sol).
   Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of solid particles (size ranging from 1 nm to 1 μm) dispersed in a solvent. The sol evolves then towards the formation of an inorganic network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. The drying process serves to remove the liquid phase from the gel thus forming a porous material, then a thermal treatment (firing) may be performed in order to favor further polycondensation and enhance mechanical properties.

30. Which catalyst properties can be influenced by promoters?
   Activity, selectivity and stability.

31. What is co-precipitation method of preparation of catalyst?
   Catalyst based on more than one component can be prepared by co precipitation. According to IUPAC nomenclature this term is used for the simultaneous precipitation of normal soluble component with macro component from the same solution by the formation of mixed crystal by adsorption, occlusion or by mechanical entrapment. Co-precipitation is very suitable for the generation of homogeneous distribution of catalyst or for the creation of precursor of definite stoichiometry which can be easily converted into active catalyst.

32. What is incipient wetness method of preparation of catalyst?
Incipient wetness impregnation is a commonly used technique for the synthesis of heterogeneous catalysts. Typically, the active metal precursor is dissolved in an aqueous or organic solution.

Then the metal-containing solution is added to a catalyst support containing the same pore volume as the volume of solution that was added.

Capillary action draws the solution into the pores. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface.

33. What are the main interactions that can occur between metals and support materials?

Electronic interactions; reduced support species on the metal surface; phase formation at interfacial surfaces.

**PART B**

1) Discuss in detail the nature of catalyst and how it increases the rate of reaction. (Nov/Dec 2015, Apr/May 2017) (16 marks)

**General characteristics of catalysts.**

The important characteristics of a catalyst are:

(v) Activity

(vi) Kindling point

(vii) Specificity

(viii) Porous and crystalline structure of a catalyst.

Activity of a catalyst indicates its usefulness and is a measure of the accelerating effect it can have on the rate of reaction. The choice of a catalyst is done on the basis of its activity.

Kindling point indicates the minimum temperature at which a catalytic process proceeds on a rate sufficient for commercial operation. The catalyst needs to have low kindling point so that less energy is required to preheat the reaction mixture.

Specificity also means selectivity of the catalyst. Specificity is a property of a catalyst and its indicates its property to speed up the main reaction by suppressing other side reactions.

Porous structure is an important quality of the catalyst. A commercial catalyst needs to have an extended external surface for maximum rate of reaction. Crystalline structure of the same catalyst strongly reduces the catalyst activity. For example, conversion of $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ reduces its activity by several orders of magnitude as a dehydrogenation catalyst.
2) Derive an expression for the critical pore radius of a catalyst. Also derive an equation to estimate the average pore radius of a cylindrical pore of length ‘L’ and Radius ‘R’. (Nov/Dec 2017) (16 marks) 

(or)

Describe the method of finding (Nov/Dec 2015)

(i) Surface area of catalyst. (8 marks)

(ii) Pore volume and pore volume distribution. (8 marks)

(i) Surface area of catalyst.

Surface area, pore size, pore volume determination

Determination of surface area and pore distribution of catalysts is important to understand the extent of dispersion possible for the active metals. Higher surface area of support results in higher dispersion of the active metals. Hence supports of higher surface area are desirable. Pores are usually formed during drying or calcination of hydroxides precipitates or gel. The size and number of pores determines the internal surface area. Pore size also determines the accessibility of reactants to the active sites and the ability of diffusion of products back to the bulk fluid. Hence pore structure and surface area must be optimized to provide maximum utilization of active sites for a given feed stock.

Working principle and instrumentation

The basic components of volumetric physical adsorption analyzer as shown in Fig. 1 are:

1) Analysis manifold of accurately known volume and temperature

2) Vacuum system with valve to manifold

3) Source of adsorptive gas (typically, N$_2$) with valve to manifold

4) Pressure transducer and temperature sensor

5) Sample tube connected to analysis manifold

6) Liquid nitrogen bath

Determination of internal surface area is based on adsorption and condensation of N$_2$ at liquid N$_2$ temperature, 77K. Initially, the sample is evacuated at 293-523 K (120-250°C) followed by cooling to 77 K by liquid N$_2$. Then gradually the partial pressure of nitrogen above the sample is increased. Some quantity of gas will be adsorbed by the sample and removed from the gas phase. After stabilization the equilibrated pressure is recorded and a mount of nitrogen adsorbed at each equilibrated pressure is noted. The isotherm, volume adsorbed as function of relative pressure $p/p_0$, is plotted from the data. The pressure over the sample is gradually increased until pressure reaches near saturation pressure, by when the complete adsorption isotherm is developed. The desorption isotherm is measured by a step-wise reduction in pressure until a low pressure over the sample is achieved. Although the volumes are adsorbed at different conditions, the values
are reported at STP conditions. Fig. 2 shows a typical N\textsubscript{2} adsorption and desorption isotherm at 77 K for alumina.

![Fig. 1. Basic components of volumetric physical adsorption analyzer](image1)

**Fig. 1. Basic components of volumetric physical adsorption analyzer**

![Isotherm](image2)

**Fig. 2. A typical N\textsubscript{2} adsorption and desorption isotherm at 77 K for alumina**

**Adsorption using Argon and Krypton**

Krypton is used as adsorbate at 77 K for low surface area analysis while, Argon adsorption at 77 K and liquid argon temperature (87K) is often used for micro and mesopores analysis.

To measure very low surface area the number of molecules trapped in the void volume of sample cell needs to be reduced. The number of molecules left in void volume can be reduced by using adsorbate such as Krypton with low vapor pressure at liquid nitrogen temperature. The saturation pressure of Krypton at liquid
nitrogen temperature is 0.35 kPa which is much lower compared to that of N\textsubscript{2} (101.3 kPa). Consequently the number of Krypton molecules in free space of sample cell, at any given relative pressure, is significantly reduced compared to that of nitrogen at liquid nitrogen temperature, though amount of adsorption will be only slightly less. Hence, Krypton adsorption at 77 K is much more sensitive and can be applied to measure surface areas down to 0.05 m\textsuperscript{2}. The cross sectional area used for Krypton is 0.202 nm\textsuperscript{2}.

For analysis of ultramicropores less 0.7 nm, the nitrogen adsorption at 77 K is not satisfactory. The pore width of 0.7 nm corresponds to bilayer thickness of nitrogen molecule. For ultramicropores, pore filling occurs at relative pressure of 10\textsuperscript{-7} to 10\textsuperscript{-5}, where the rate of diffusion and attainment of adsorption equilibration is very slow. Consequently measurement becomes time consuming and may also cause non-equilibrated adsorption isotherms with erroneous results. On the other hand argon fills the micropores of dimension 0.4-0.8 nm in most cases at much higher relative pressure as compared to nitrogen. This leads to accelerated diffusion and equilibration process and result in reduction of analysis time as well as increase in accuracy. Argon adsorption is advantageous for pore size analysis of zeolites and other microporous materials.

The typical surface area values of different supports and catalysts are summarized in Table 1.

**Table 1. Typical surface area values of different support and catalyst.**

<table>
<thead>
<tr>
<th>Support/catalyst</th>
<th>BET surface area m\textsuperscript{2}/g</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>500-2000</td>
<td>Used as support for various process</td>
</tr>
<tr>
<td>Zeolites</td>
<td>500-1200</td>
<td>Used as catalyst and support</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Zeolites</td>
<td>100-600</td>
<td>Fluid catalytic cracking catalysts</td>
</tr>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>100-150</td>
<td>Methanation catalyst</td>
</tr>
<tr>
<td>Cu/Zn/Al\textsubscript{2}O\textsubscript{3}</td>
<td></td>
<td>Methanol synthesis catalyst</td>
</tr>
<tr>
<td>Mn\textsubscript{2}O\textsubscript{2}/Al\textsubscript{2}O\textsubscript{2}</td>
<td>140-180</td>
<td>Catalyst for total oxidation of volatile organic carbon</td>
</tr>
<tr>
<td>Fe\textsubscript{2}/K/Al\textsubscript{2}O\textsubscript{3}</td>
<td>20</td>
<td>Ammonia synthesis catalyst</td>
</tr>
</tbody>
</table>

**Determination of surface area using BET Equation**

As discussed earlier (lecture 4), the BET equation describes the relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage. BET equation can be written in the form:

\[
\frac{p}{v(p_0-p)} = \frac{1}{v_mc} + \frac{c-1}{v_mcp_0} p
\]  \hspace{1cm} (1)

\(p = \) partial pressure of N\textsubscript{2}; \(p_0 = \) saturation pressure at the experimental temperature;
\(v = \) volume adsorbed at \(p\); \(v_m = \) volume adsorbed at monolayer coverage; \(c = \) constant
Monolayer coverage is determined using BET equation. The \( \frac{p}{p_0 - p} \) is plotted as a function of \( \frac{p}{p_0} \).

The plot is linear in the range of relative pressures \( \frac{p}{p_0} = 0.05 - 0.3 \). At higher relative pressure \( p/p_0 \), the BET plot deviates from linearity as non-ideality or pore condensation was not accounted for the derivation of BET equation.

Slope and intercept of this linear plot is used for determination of monolayer capacity \( v_m \).

The intercept and slope from the plot is given as:

\[
\text{Intercept} = \frac{1}{cv_m} \quad \text{Slope} = \frac{(c-1)}{cv_m}
\]

Then the monolayer volume \( v_m \) is given as,

\[
v_m = \frac{1}{\text{slope + intercept}} \text{(STP)}
\]

The total number of \( N_2 \) molecules adsorbed corresponding to monolayer volume \( v_m \) can be calculated as

\[
\text{No. of } N_2 \text{ molecules} = \frac{v_m (m^3) \times 6.02 \times 10^{23} \text{(molecules/mol)}}{0.0224 (m^3/mol)}
\]

Now each adsorbed \( N_2 \) molecule occupies an area of surface comparable to its cross section area 0.162 nm\(^2\).

\[
SA (m^2) = \left[ \frac{v_m (m^3) \times 6.02 \times 10^{23} \text{(molecules/mol)}}{0.0224 (m^3/mol)} \right] \times 16.2 \times 10^{-20} \text{ (m}^2 \text{ / N}_2\text{molecule)}
\]

or

\[
SA (m^2) = v_m (m^3) \times 4.36 \times 10^6 \text{ (m}^{-1}) = 4.36 \times 10^6 v_m
\]

**Pore size**

(a) **By gas adsorption**

Pore size and pore size distribution can be determined using Kelvin equation. Kelvin equation relates equilibrium vapor pressure \( (P) \) of a liquid contained in a capillary to equilibrium pressure of the same liquid over a free surface \( (P_o) \):

\[
\ln \frac{P}{P_o} = -\frac{2\gamma V_{\text{mole}} \cos \theta}{rRT} \quad \text{------------------------ (1)}
\]

\( \gamma = \) surface tension of liquid nitrogen

\( \theta = \) contact angle (usually zero for liquid \( N_2 \))

\( V_{\text{mole}} = \) the molar volume of liquid nitrogen

\( r = \) radius of pore

\( R = \) gas constant
At any equilibrium pressure, $P$, pore of radius less than $r'$ will be filled with the condensed vapor. Application of Kelvin equation to all points of an isotherm at relative pressure greater than that corresponding to monolayer volume where capillary condensation begins to occur, will yield information concerning the volume of gas adsorbed in pores of different radii. For nitrogen as adsorbate and substituting values of various constants the Kelvin equation can be written as

$$
\ln \frac{P}{P_o} = \frac{-2\gamma V_{aq} \cos \theta}{rRT}
$$

or

$$
r_k (nm) = 0.41 \log \frac{P}{P_0} \quad \text{------------------------(2)}
$$

$\gamma = 8.72$ mN/m
$\theta = 0$
$V_{aq} = 34.68 \times 10^{-6}$ m$^3$ / mol
$T = 77$ K
$R = 8.314$ J / K mol

The $r_k$ is the radius into which condensation occurs at the required relative pressure. This radius is called Kelvin radius. However, Kelvin radius is not the actual pore radius since some adsorption has already occurred on the pore wall prior to condensation leaving a central core of radius $r_k$. Conversely an adsorbed film remains on the wall when evaporation of the centre core takes place.

![Condensed liquid](image)

Fig. 3. Schematic showing Kelvin radius and actual pore radius during pore condensation

Then if $r'$ is the actual pore radius and the thickness of the adsorbed film is $t$ (Fig 4) then

$$
r (nm) = r_k + t = \frac{2\gamma V_{aq}}{RT \ln \frac{P}{P_0}} + t = 0.41 \log \frac{P}{P_0} + t \quad \text{------------------------(3)}
$$

Pore size distribution can be obtained by the analysis of either adsorption or desorption isotherm branches. Kelvin equations as described is applied to the desorption branch of hysteresis loop as it is more appropriate to assign wetting angle to a pore filled with liquid that possess a well defined meniscus. If $h$ is the effective height of a monolayer then thickness of adsorbed layer $t$ is given as

$$
t = \left(\frac{V}{V_m}\right)h
$$

Here $V$ is the volume of
gas adsorbed and ‘\(V_m\)' is the volume of adsorbed monolayer. When the packing of adsorbate is in hexagonal mode then for nitrogen \(h = 3.6A^0\) and for cubic packing \(h = 4.3 A^0 = 0.43\) nm. The ‘\(t\)' at a given relative pressure can also be calculated using Halsey equation

\[
t = 3.54 \times \left[ \frac{5}{2.303 \times \log \frac{P_0}{P}} \right]^{\frac{1}{3}} \quad (\text{nm})
\]

---

**Pore size distribution**

Most common method for determination of pore size distribution is BJH (Barrett-Joyner-Halenda) method. Assumptions are:

(i) Condensation occurs in pores when a critical relative pressure is reached corresponding to the Kelvin radius ‘\(r_k\)'

(ii) When evaporation or condensation occurs, a multilayer of adsorbed film exist on the pore wall and this film has same depth/thickness as the adsorbed film on a non porous surface

(iii) Actual pore volume evaporation is composed of the volume evaporated out of the central core plus the volume desorbed from the film left on the pore walls

Steps in for determination of pore size distribution are as follows:

1. \(P/P_0\) and \(V_{gas}\) (STP, \(cm^3/g\)) data obtained directly from isotherm

2. Then Kelvin radius ‘\(r_k\)' is calculated from Kelvin equation using zero wetting angle for \(N_2\) from equation(2)

3. Then the film thickness \(t\) calculated from Halsey equation(4) at each \(P/P_0\)

4. Then the pore radius \(r_p\) calculated from equation (3)

5. Mean values of \(r_k\) and \(r_p\) in each decrement are calculated from successive entries

6. Change in film thickness \(\Delta t\) is calculated from difference of successive values of \(t\)

7. Then \(\Delta V_{gas}\), that is the change in adsorbed volume between successive \(P/P_0\) values, is determined by subtracting successive values

8. Thereafter \(\Delta V_{liq}\) that is the volume of liquid corresponding to \(\Delta V_{gas}\) is calculated as follows

\[
\Delta V_{liq} = \frac{\Delta V_{gas}}{22.4 \times 10^3} \times 34.6 = \Delta V_{gas} \times 1.54 \times 10^{-3} \text{ cm}^3/\text{g}
\]
9. Then $\Delta t \Sigma S$ is determined. This represents the volume change of the adsorbed film remaining on the walls of the pores from which the central core has previously evaporated. This volume is the product of the film area $\Sigma S$ and the decrease in film depth $\Delta t$.

10. Actual pore volume evaporated, $V_p$, is then determined. Actual pore volume evaporated is composed of the volume evaporated out of the centre core plus the volume desorbed from the film left on the pore walls.

$$\Delta V_{aq} = \pi r_k^2 L + \Delta t \Sigma S$$

For a pore of length $L$,

$$V_p = \frac{r - r_k^2}{r_k} \left[ \Delta V_{aq} - (\Delta t \Sigma S \times 10^{-4}) \right] \text{ cm}^3 / \text{g}$$

Now, $V_p = \pi r_k^2 L$ By combining

11. The surface area of the pores walls can be calculated from pore volume by:

$$S = \frac{2V_p}{r_p} \times 10^4 \text{ m}^2$$

$r_p$ in cm$^3$/g and $r$ in A$^0$

An elaborate example of pore size distribution work table can be seen in Lowell et al. for more understanding.

Fig. 4. Pore volume distribution of titania samples calcined at 400$^\circ$C

(a) differential (b) cumulative

Pore size distribution can be represented both in differential and cumulative ways. The Fig. 4(a) shows the differential BJH pore distribution of titania sample calcined at 400$^\circ$C. The figure shows that for the given sample pores were in the range of 2-10 nm. The corresponding cumulative pore distribution is shown in Fig. 4(b).

(b) By mercury intrusion
For macropores materials with pore diameter greater than 50 nm, the mercury intrusion method is preferred. Due to non-wetting nature of mercury on oxide supports, intrusion is met with resistance and mercury is forced to enter the pores of material under pressure. The pore radius ‘r’ is related to the applied pressure P as

\[ P = \frac{-2\gamma \cos \theta}{r} \]

The wetting or contact \( \theta \) angle between mercury and solid is on average lies in the range 130-140° and surface tension of mercury is 0.48 N/m². \( p \) is in atm and \( r \) in nanometers.

As can be observed from equation (5) smaller the pore radius higher is the pressure needed for mercury to intrude in the pore. At low pressure of 0-2 atm, mercury penetrates voids between particles. At moderate pressure range of 3-500 atm large macro pores are filled. At further higher pressure range of 500-2000 atm, smaller macro pores and large mesopores are progressively filled. This technique is satisfactory for pores down to 3-5 nm dia. Maximum diameter that can be measured is usually \( 10^5 \) nm. Mercury intrusion method is carried out in the instrument known as mercury porosimeter. In a typical mercury porosimeter data, volume of mercury penetrating into pores is plotted as a function of applied pressures.

![Mercury intrusion](image)

**Fig. 5. Intrusion of mercury into pores of various sizes. Here ‘r’ represents the radius of pores.**

The pressure required for filling up the pores as a function of pore size is schematically shown in Fig.5. As pore radius decreases in the order \( r_1 > r_2 > r_3 \), required pressure for filling the pores increases in order of Pressure 1 < Pressure 2 < Pressure 3. The available instruments can measure pore size up to 2 nm using a maximum operating pressure of about 400 MPa.

**Table 1. Typical pore volume values of different support and catalyst.**

<table>
<thead>
<tr>
<th>Support/catalyst</th>
<th>Pore volume cm³/g</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>0.6-0.8</td>
<td>Used as support for various process</td>
</tr>
<tr>
<td>Zeolites</td>
<td>0.5-0.8</td>
<td>Used as catalyst and support</td>
</tr>
<tr>
<td>Al₂O₃-SiO₂-Zeolites</td>
<td>0.1-0.9</td>
<td>Fluid catalytic cracking catalysts</td>
</tr>
</tbody>
</table>

2. (i) Explain the nature of catalytic surface with suitable examples.

(ii) Discuss in detail about different types of adsorption.
A catalyst is effective in increasing the rate of reaction because it makes possible an alternative mechanism, each step of which has a lower free energy of activation than that for an un-catalyzed process.

- The combination of reactant and the catalyst is a widely accepted basis for explaining the catalysis.
- A relatively small amount of catalyst can cause conversion of a large amount of reactant.
- The position of equilibrium in a reversible reaction is not changed by the presence of the catalyst.

(ii) Types of Adsorption:

Depending on the nature of interaction, the adsorption can be of two types:

1. Physisorption
2. Chemisorption

The phenomenon of adsorbate molecules attaching themselves to adsorbent surface under the influence of van der Waals forces is called physisorption or physical adsorption. The van der Waals forces mainly consist of dipole–dipole interactions. This is an exothermic process with a low enthalpy change known as heat of adsorption. This process resembles liquefaction and heat of adsorption for physisorption is also known as heat of liquefaction.

At higher temperature, the adsorbed molecules can undergo electronic rearrangement with the surface molecules. This phenomenon is called chemisorption. The electronic rearrangement may include formation and breaking of chemical bonds. The electronic rearrangement occurs only when there is significant interaction between adsorbate and the adsorbent molecules. Hence all adsorbate will not be chemisorbed on all adsorbent surfaces. Chemisorption process is selective and an adsorbate molecule will chemisorbed only on selected adsorbent. The adsorption processes are shown in Fig 2. The Fig. 2(a) depicts the situation when the adsorbate molecule approach any adsorbent surface under the influence of attractive forces created by the unbalanced molecular forces on adsorbent surfaces. The Fig. 2(b) represents the phenomenon, when any molecule is physisorbed on surface by van der Waals forces. No bond formation occurs in this situation. A chemisorption situation is represented in Fig. 2(c) when there is a weak bond formation between adsorbate and adsorbent molecule. As discussed above, the adsorbate molecule will be chemisorbed only on selected adsorbent surface with which it can interact significantly.
Physisorption versus Chemisorption

1. Since physisorption involves only weak molecular interaction, the associated enthalpy changes are small (in the range of 10 to 40 kJ/mol). On the other hand, in case of chemisorption, enthalpy change is quite large and can range from 80-400 kJ/mol.

2. The Fig. 3 compares the volume of gas adsorbed as a function of temperature under physisorbed and chemisorbed conditions. In physisorption, the molecules are adsorbed on surface by weak interaction. With increase in temperature, adsorbed molecules gain excess energy and their tendency to escape from the surface increases. Hence volume of gas adsorbed on the surface decreases with temperature as shown in Fig. 3. However, the chemisorption involves higher interaction energy between adsorbate and adsorbent molecules and hence is favored by temperature rise. Hence at low temperature range volume of adsorbed gas increases with temperature. However, at higher temperature range as the adsorbed molecules gains excess energy, rate of desorption becomes higher resulting in decrease in adsorbed gas volume as shown in Fig. 3.
3. In case of chemisorption, since there is electronic interaction between adsorbate and adsorbent molecules, only a monolayer of adsorbate can be formed on the adsorbent surface. In case of physisorption, the first monolayer formed on the surface of the adsorbent can act as adsorbing surface for formation of next layer of adsorbate and so on. This phenomenon is called multilayer adsorption. The formation of monolayer and multilayers of the adsorbed molecules on a surface is shown in Fig. 4. For the physisorption, volume of gas adsorbed increases with pressure due to increase in concentration of adsorbate and formation of multilayers. However for chemisorption process which corresponds to monolayer formation, the effect of pressure is not significant.

Fig. 3. Volume of gas adsorbed as a function of temperature for physisorption and chemisorption processes

4. Chemisorption is specific for adsorbate and adsorbent pair. Specific solid adsorbent can undergo electronic interaction only with specific adsorbate gas molecule.

5. Physisorption is highly reversible while chemisorption can be irreversible.

6. Physisorption is important for estimating the total surface area. It also provides a basis for estimating the pore volume and pore size distributions. On the other hand, chemisorption is important in estimation of area of catalytic active sites as well as its dispersion.

Examples:

Physisorption: Adsorption of nitrogen on carbon or alumina.
Chemisorption: Adsorption of hydrogen on active platinum sites on any support.
3. Describe in detail the Nitrogen adsorption method for the determination of Surface area of a catalyst.

By the application of Langmuir adsorption isotherm for mono-molecular layer of adsorption, Brunauer-Emmett-Teller (BET) extended the Langmuir isotherm to apply it for the multilayer adsorption. As a result, the BET equation is

\[
\frac{P}{v (p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1)/(c \ v_m)}{p/p_0}
\]

Where $p$ - partial pressure of adsorbed gaseous molecule $p_0$ - saturation or vapor pressure
$v$ - volume of gas adsorbed
$v_m$ - volume adsorbed when all the active sites are covered
$c$ - Constant for the particular temperature and gas-solid system

- The above equation will give a linear plot with $v_m = 1/(\text{Slope} + \text{Y-int})$
- For the $N_2$ adsorption at $-195.5^\circ\text{C}$, the surface area

\[S_g = 4.3653 \ v_m \ (\text{m}^2/\text{g-cat})\]

3. Discuss the determination of Pore volume and Pore-volume distribution. [Dec 2102]

The pore volume of a catalyst particle can be estimated by boiling a weighed sample immersed in a liquid such as water. After the air in the pores has been displaced, the sample is superficially dried and weighed. The increase in weight divided by the density of the liquid gives the pore volume.
Since the effectiveness of the internal surface for catalytic reactions depends not only on the volume of void spaces but also on the radius of the void regions, it is necessary to know the distribution of void volume in a catalyst according to size of the pore.

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

- Mercury-penetration method
- Nitrogen-desorption method

- 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

\[ \pi a^2 p = -2\pi a \sigma \cos \theta \]
\[ a = -\frac{2\pi \sigma \cos \theta}{p} \]

- Where \( \theta \) is the contact angle between the mercury and pore wall (figure).

- Then the working equation for evaluating the radius corresponding to a given pressure is

\[ a(\text{Å}) = 8.75 \times 10^5 \frac{\text{p}(\text{lb/in.}^2)}{\text{p}(\text{lb/in.}^2)} \]

(or) Discuss in detail the catalyst preparation. (Nov/Dec 2015) (10 marks)
(or) Explain in detail about the Preparation of Catalyst.

Preparation of solid catalyst

The catalyst preparation methods can broadly categorized as follows:

1. Bulk preparation process:

Bulk catalysts and supports are prepared by this method. Bulk preparation is mainly done by the following methods:

   a. \textit{Precipitation process}

   b. \textit{Solgel process}

2. Impregnation process:

Supports are first prepared by bulk preparation methods and then impregnated with the catalytically active material. The active materials can be deposited on the supports by various methods. Most of the methods involve aqueous solutions and liquid solid interface. In some cases, deposition is done from the gas phase and involve gas-solid interface.

3. Physical mixing:

Mixed agglomerated catalysts are prepared by this method. These catalysts are prepared by physically mixing the active substances with a powdered support or precursors of support in ball mill. The final mixture is then agglomerated and activated.
Basic unit operations involved in preparation of solid catalyst is shown in Fig 11. Each step is discussed in details in the following sections.

(a) Precipitation and co-precipitation

In this process the desired component is precipitated from the solution. Co precipitation is used for simultaneous precipitation of more than one component. Catalysts based on more than one component can be prepared easily by co-precipitation. The precipitation process is used for preparation of bulk catalysts and support material such as Al₂O₃, SiO₂, TiO₂, ZrO₂ etc.

**Process**

In general, the metal hydroxides are precipitated from their precursor salt solution because of their low solubility. The precipitation of hydroxides can be performed either by starting from an alkaline solution which is acidified or from acidic solution by raising the pH. However, most hydroxides for technical application are precipitated from an acidic solution by the addition of an alkaline precipitating agent. Usually, ammonia or sodium bicarbonate is used as the precipitating agent. Highly soluble inorganic salts such as nitrates, carbonates or chlorides are generally used as metal precursors. For example, preparation of
alumina is done by precipitating aluminium hydroxide from aluminium nitrate solution by addition of ammonium hydroxide.

\[
\text{Al(NO}_3\text{)}_3 + \text{NH}_4\text{OH} \rightarrow \text{Al(OH)}_3 + \text{NH}_4\text{NO}_3
\]

During precipitation, several processes occurs and the major steps are:

1. liquid mixing/supersaturation
2. nucleation
3. crystal growth to form primary products
4. aggregation of the primary particles

Initial mixing or interdispersing of components in the solution has a significant effect on the precipitation. Good mixing result in a more homogeneous product particularly in case of co-precipitation. Rate of stirring primarily affects the nucleation whereas growth rate is much less influenced by this factor. Stirring rate also affect the aggregation. Aggregate size can be influenced by changing the stirring rate and the manner of mixing.

For nucleation to occur the solution must be super saturated with respect to the components which is to be precipitated. Parameters affecting supersaturation is shown in Fig. 1. In supersaturated region the system is unstable and precipitation occurs with any small disturbance. The supersaturaton region is approached either by increasing the concentration through evaporation, lowering the temperature or by increasing pH. The solubility of a component increases with temperature as shown in Fig. 1. The solubility curve is also function of pH. As pH increases solubility decrease and curve shift from 1 to position 2. Then the point which was initially in solution region becomes in supersatured region. The increase in pH is the most convenient method for precipitation. The reaction during precipitation, \(\text{M}^{n+} + \text{nOH}^- \rightleftharpoons \text{M(OH)}_n\), is controlled by increasing the pH through addition of a basic solution. Hence by raising the pH value of a solution by addition of alkaline or ammonium hydroxide the corresponding metallic hydroxide compounds can be made insoluble and precipitated from solution. Commonly used reagents are NaOH, KOH, NH\(_4\)OH, carbonates and bicarbonates. Particles within supersaturated region develop in two steps: nucleation and growth.
Fig 1. Parameters affecting supersaturation

If nucleation is faster than growth, the system produces a narrow distribution of small particles. Fast growth results in narrow distribution of large particles.

Several equations are proposed for nucleation rate and the most used is:

$$\frac{dN}{dt} = \beta \exp \left[ \frac{-16\pi\sigma^3V^2}{3(kT)^3 \ln^2 s} \right]$$

where $\beta$ is the pre-exponential term, $\sigma$ is solid–fluid interfacial energy, $V$ is solid molecular volume and $T$ is the temperature. The super saturation ‘s’ is defined as the ratio of actual concentration to solubility:

$$s = \frac{\text{actual concentration}}{\text{solubility}}$$

The equation can be simplified as

$$\frac{dN}{dt} = \beta \exp \left[ \frac{-A}{\ln^2 s} \right] \quad A = \frac{16\pi\sigma^3V^2}{3(kT)^3}$$

Thus nucleation depends strongly both on concentration and temperature. There is a critical super saturation concentration below which nucleation is very slow and above which nucleation is very fast.
Advantages and disadvantages: The main advantages of the precipitation process is the possibility of creating pure and homogenous material. However the major disadvantages include necessity of the product separation after precipitation and generation of the large volume of salt containing solutions. There is also difficulty in maintaining a constant product quality throughout the whole precipitation process if the precipitation is carried out discontinuously.

Process parameters

In addition to the process variations discussed above there are many other parameters that affect the final product properties as shown in Fig.2. The properties of the final product that are affected include phase formation, chemical composition, purity, particle size, surface area, pore size and pore volumes. It is necessary to optimize the parameters to produce desired products.
The sol gel method

In sol gel process initially a stable colloidal solution called sol is formed. The sol is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron. It can be obtained by hydrolysis and partial condensation of precursors such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three dimensional network produces a gel material. The gel is a diphasic material in which the solids encapsulate the solvent. The molecular weight of the oxide species produced continuously increases. The materials are referred to aqua sol or aqua gels when water is used as a solvent and aquosol or alcogel when alcohol is used.

The encapsulated liquid can be removed from a gel by either evaporative drying or with supercritical drying /extraction. The resulting solid products are known as xerogel and aerogel respectively. When gels are dried by evaporation, the dried product is called xerogel. When the gels are dried by supercritical drying, the dried gel is called aerogels. The aerogel retains high porosity and has very high pore volume.

![General scheme of preparation by solgel method](image)

**Fig. 1. General scheme of preparation by solgel method**

The sol gel method is distinguished from other routes of material preparation from solutions or melts such as precipitation and crystallization by two main characteristics:

1. Formation of clear colloidal solution due to primary condensation of dissolved molecular precursors.
2. These colloidal particles merge during subsequent gelation stage into polymeric chain by chemical bonding between local reactive groups at their surface.

Both stages are controlled by condensation chemistry that can include as a first step, hydrolysis of hydrated metal ions or metal alkoxides molecules. The condensation chemistry in this case is based on olation/oxolation reactions between hydroxylated species. Olation is a condensation process in which a hydroxyl bridge “–OH–” bridge is formed between two metal centers.

The oxolation is a condensation reaction in which an oxo bridge “-O-” is formed between two metal centers.
Parameters affecting any of the two reactions will affect the properties of the final product. Two of the main parameters that affect are (1) amount and rate of water addition and (2) pH of the solution. The amount of water added is expressed in terms of hydrolysis ratio ‘h’ and defined as

\[
h = \frac{\text{moles of water}}{\text{moles of metal alkoxide M(OR)\textsubscript{m}}}\]
Fig. 3. Schematic diagram showing effect of relative rates of hydrolysis and condensations reactions on gel structure.

**Gelation:** After a period of time the sol experiences a transition from liquid solution to a cross-linked gel state where it can support an elastic stress. This period of time is known as gel time or gelation time, and during this time the viscosity of the solution undergoes a rapid increase corresponding to the transition from a viscous fluid to an elastic gel.

The gel structure is determined by the ionic character of the M-O bond and the relationship between the hydrolysis and condensation rate.

![Diagram showing effect of relative rates of hydrolysis and condensation on gel structure](image)

**Effect of zeta potential on gelation:** The particle surface may be positively or negatively charged depending on the pH. With an acidic solution, that is low pH, the equilibrium is driven towards positive surfaces. As pH increases, the surfaces become less positively charged and finally negatively charged. However, the effective charge on the surface is partially neutralized by the counter-ions in the solution that may originate from the bases used during precipitation or electrolytes added during aging. These counter-ions form a space charge, part of which is held sufficiently strongly to be carried along as the particles move with Brownian motion.

![Double layer structure for particles](image)
The result is an effective charge called Zeta potential. Both the original charge and the neutralizing counter-ions respond to pH changes. This zeta potential determines the rate of gelation. If the charge is high, particles effectively repel one another and avoid contact. If it is low, then thermal motion leads to collision and coalescence. These rates are highest at the isoelectric point where the zeta potential is zero. The variation of zetapotential with pH for alumina is shown in Fig. 5.

![Fig. 5. Effect of pH on zeta potential of alumina](image)

Two other important parameters are temperature and solvent. Varying temperature is most effective when it can alter the relative rate of the competing reactions. Solvent can change the nature of an alkoxide through solvent exchange or affect the condensation reaction directly.

**Aging:** After visible formation of gel, processing proceeds to the aging step where the structure and the properties of the formed network continue to change up to the point that yields the target density. It represents the time between the formation of the gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel is not static and can undergo many transformations. This step includes four processes: polycondensation, syneresis, coarsening, and phase transformation.

Zirconium propoxide is used as precursor for zirconium. The sol prepared from precursor solution is aged for 2h and then supercritically dried. In this example calcination is done in two steps.
5. Explain the support Catalyst components in detail?

Supported catalysts

Supported catalysts are prepared by deposition of the active metal on the support materials. The main purpose of using a support is to achieve an optimal dispersion of the catalytically active component and to stabilize it against sintering. But in many reactions the support is not inert and the overall process consists of two catalytic functions both for active components and support.

Supported catalysts are prepared in two main steps:

1. Deposition of the precursor of the active component on the support.
2. Transformation of this deposited precursors to catalytically active site.

The final active component can be in metallic state, oxide form or reduced from depending on the requirements.

There are various deposition methods. Most of these involve aqueous solutions and liquid solid interface. In some cases deposition is also done from the gas phase and involve gas-solid interface. The methods most frequently used are:

a. impregnation
b. ion exchange
Impregnation

Impregnation can be classified in two categories according to the volume of solution used.

**Dry or incipient impregnation**

In this method a previously dried support is contacted with volume of solution equal to its pore volume. The solution contains the required amount of the precursors of the active phase. As soon as the support is placed in contact with the solution, the solution is drawn into the pores by capillary suction. In case of proper wetting no excess of solution remains outside the pore space. Part of the air present in the pores is imprisoned and compressed under the effect of capillary forces. The pressure developed inside the imprisoned gas bubbles depend on the radius, $r$, of the curve of the liquid-gas meniscus and may reach several MPa when $r<100$ nm as a result of young Laplace law, $\Delta P = P - P' = \frac{2\gamma}{r}$, where $\gamma$ is the liquid gas interfacial tension. Considerable forces will thus be exerted on the portions of the pore walls in contact with these bubbles. The walls that are not strong enough may break down causing a degradation of the mechanical properties. Occasionally, even bursting of the catalyst grains occurs. However, the development of the high pressure is a transitory phenomenon. Under highly compressed conditions, air dissolves and progressively escapes from the solid.

**Wet / diffusional impregnation**

In this method the pore space of the support is first filled with the same solvent as used in the impregnating precursor solution. The wetted support is then treated with the impregnating precursor solution. Here the actual impregnation takes place in diffusional condition when solvent filled support is dipped in the precursor solution.

The first phase of saturation of the support by solvent involves the characteristics of the dry impregnation. But in the second phase, when solvent saturated support is added to the impregnating solution, high pressure is not developed within the pores. The precursor salt migrates progressively from the solution into the pores of the support. The driving force at all times is the concentration gradients between the bulk solution and the solution with in the pores. The impregnation time is much longer than for dry impregnation. Wet impregnation should be avoided when the interaction between the precursors and the support is too weak to guarantee the deposition of the former.

**Mechanism of impregnations:** The mechanism of wet impregnation is simpler compared to dry impregnation. In wet impregnation the distribution of the solute inside the pores is assumed to be governed by two phenomena (Fig. 1):

1. Diffusion of the solutes within the pores. It is described by Fick’s law
2. Adsorption of the solute onto the support. This depends on the adsorption capacity of the surface and on the adsorption equilibrium constant.
The distribution of the precursors within the pellets depends on the balance between these diffusion and adsorption phenomenon.

(a) Wet impregnation
(b) Dry impregnation

Fig. 1. Schematic representation of basic processes involved during impregnation of precursors on porous support.

Drying

Impregnation is followed by elimination of the solvent. The impregnated sample is heated in an oven in flow of gas as discussed earlier. The gas may be air, oxygen, nitrogen or any other gas depending on the requirement. The temperature is generally maintained slightly higher than the boiling point of the solvent e.g 110-120°C for water. The elimination of water from the pores leads to the increase of precursor concentration up to saturation and consequent crystallization, preferably on the seeds resulting from the interaction with the support. Apart from temperature, heating rate affects the drying process.

(a) Constant rate period of drying
(b) Falling rate period of drying

Fig. 2. Schematic representation of drying process during impregnation method

Table: Distribution of precursors at different conditions of impregnation and drying.
6. **Explain the solid Catalyst components in detail?**

A solid catalyst consists of mainly three components:

1. Catalytic agent
2. Support /carrier
3. Promoters and Inhibitors

**Catalytic agent:**
These are the catalytically active component in the catalyst. These components generate the active sites that participate in the chemical reaction. Activity of any catalyst is proportional to the concentration of these active sites. Though concentration of the active sites depends on the amount of catalytically active component, however, it is not always directly proportional. Availability of active sites depends mainly on the dispersion of catalytic agent. The dispersion is defined as ratio of total number of exposed atoms/molecules of catalytic agent available for reaction to total number of atoms/molecules of catalytic agent present in the catalyst sample.

Catalytic agents may be broadly divided in the following categories:

i. Metallic conductors (e.g. Fe, Pt, Ag, etc.)
ii. Semiconductors (e.g. NiO, ZnO, etc.)
iii. Insulators (e.g. Al₂O₃, SiO₂, etc.)

**Metallic conductors:** The metals that have strong electronic interaction with the adsorbates are included in this category. The metals are used in various catalytic reactions such as methanol synthesis, oxidation, hydrogenation and dehydrogenation processes.

Examples of metal catalysts:
Cu for water gas shift reaction and methanol synthesis; Ag for oxidation of ethylene to ethylene oxide, Au for oxidation of methanol to formaldehyde; Fe for ammonia synthesis; Pd and Pt for hydrogenation of
olefins, dienes, aniline or nitriles as well as dehydrogenation of alkanes, alcohols, cyclohexanes, cyclohexanols etc.

**Semiconductors:**
The oxides and sulfides of transition metals that have catalytic activity are included in this category. Similar to conducting metals, they are also capable of electronic interaction with adsorbed species and catalyze the same type of reactions. Usually the lower valence band electrons participate in bonding. The upper conduction band separated by band gap energy is empty unless electrons are promoted by heat or radiation. Semiconductor characteristics may be intrinsic or induced by addition of foreign ion, creating cationic or anionic vacancies. Common transition oxides and sulfides such as CuO, AgO, NiO CoO, Fe₂O₃, MnO, Cr₂O₃, FeS, V₂O₅ show conductivity. These materials participate in catalytic reactions and reaction occurs through acceptation or donation of electrons between the reactant material and catalysts. Few applications of semiconductor catalysts are: CuO for oxidation of nitric oxides, NiO for dehydrogenation of alkanes, MnO₂ for oxidation of alcohols, and V₂O₅ for oxidation of hydrocarbons.

**Insulators:** Catalytic functions of insulators are different from that of conductor and semiconductor materials. Insulators have large values of band gap energy and very low concentration of impurity levels. The electrons remain localized in valence bonds and redox type reactions involving electronic interaction as observed for metal or semiconductor catalysts does not occur. However, insulators have sites that generate protons, thereby, promote carbonium ion based reactions such as cracking, isomerization or polymerization. Al₂O₃, SiO₂, SiO₂-Al₂O₃, zeolites, MgO, CaO, MgAl₂O₄, SiO-MgO are few examples of the insulators used as catalysts.

**Support or carrier**
Support or carrier provides large surface area for dispersion of small amount of catalytically active agent. This is particularly important when expensive metals, such as platinum, ruthenium, palladium or silver are used as the active agent. Supports give the catalysts its physical form, texture, mechanical resistance and certain activity particularly for bifunctional catalysts. Area of the support can range from 1 - 1000 m²/gm. Common supports are alumina, silica, silica-alumina, molecular sieves etc. The surface area of α-alumina is in the range 1-10 m²/gm whereas the surface area for γ or η-alumina can be in the range 100 – 300 m²/gm. Support may be inert or interact with the active component. This interaction may result in change in surface structure of the active agent and thereby affect the catalyst activity and selectivity. The support may also exhibit ability to adsorb reactant and contribute to the reaction process.

**Promoters:**
Promoters are generally defined as substances added during preparation of catalysts that improve the activity or selectivity or stabilize the catalytic agents. The promoter is present in a small amount and by itself has little or no activity.
Promoters are termed as physical or chemical promoter depending on the manner they improve the catalyst performance.

The additives that maintain physical integrity of the support and/or deposited catalytic agents are termed as physical promoters. For example, addition of small quantities of alumina to an iron catalyst employed in ammonia synthesis prevents sintering of the iron crystallites. Thus, for this catalyst, alumina is a physical promoter. The addition of K\textsubscript{2}O to the same catalyst increases the intrinsic activity of the iron crystallites and therefore acts as a chemical promoter. The promoter can be added during catalyst preparation or during reaction.

**Negative promoters or inhibitors:** Inhibitors act opposite to promoters. When added in small amount it can reduce catalysts activity, selectivity or stability. Inhibitor is particular useful to prevent or reduce the activity of a catalyst for undesirable side reactions. In oxidation of ethylene, ethylene dichloride is added to inhibit CO\textsubscript{2} formation thus acting as an inhibitor.

7. **Explain the Characterization of catalyst in detail?**

Characterization of heterogeneous catalyst refers to the determination of its physical and chemical characteristics, which are responsible for its performance in a reaction. Characteristics of catalysts include:

- Chemical composition of the bulk and surface of the solids
- Surface area and porosity (micro, meso and macro)
- Bulk solid structure, phase composition, crystallite size
- Surface morphology
- Surface chemical properties such as:
  - location and oxidation state of active metals
  - acid-base property
  - reducible – oxidizable property

- Aggregate properties such as aggregate or particle size, density, mechanical strength and attrition resistance
- Catalytic properties: activity, selectivity, stability

**Objectives of characterizations**

The primary objective of catalyst characterization is to understand the relationship among physical, chemical and catalytic properties. For this purpose, the physical and chemical properties are determined by various characterization techniques and related to its activity and selectivity. This is essential for design and process optimization. The characterization is also done to monitor the changes in physical and chemical properties of the catalyst during preparation, activation and reaction stages for better understanding and quality control. Determination of the extent of deactivation of catalysts during the reaction process is also important.

Characterization of used catalysts can help to determine the causes of deactivation and minimize it. It also helps to design procedures for catalysts regeneration.
Characterization Techniques

In this section some of the characterization techniques that are most commonly used will be discussed. These techniques are summarized below.

1. **Structural analysis**
   a. **Surface area**
      - widely accepted BET (Brunauer, Emmet and Teller) method used for analyzing multilayer physisorption isotherms of inert gases to determine the surface area
   b. **pore analysis by**
      - BJH method
      - mercury intrusion method
   c. **X-Ray Diffraction (XRD):**
      - can detect crystalline materials having crystal domains greater than 3-5 nm.
      - characterization of bulk crystal structure and chemical phase composition.

2. **Chemisorption technique**
   o determines dispersion of metal in catalysts
   o determination of surface metal area

3. **Thermal analysis**
   a. temperature programmed reduction (TPR):
      - measures the rate of reduction of active metals as function of temperature.
      - can be correlated with activity of catalysts
   a. temperature programmed desorption (TPD):
      - measurement of rate of desorption of adsorbed molecules as function of temperature
      - mainly used to of study acid – base property of catalysts
   b. Thermo Gravimetric Analysis (TGA):
      - measurement of weight loss (or gain) as a function of temperature in a controlled gaseous atmosphere;
      - process associated with mass change can be detected and analyzed
   c. Differential Thermal Analysis (DTA):
      - monitoring the temperature difference between sample and reference
      - process associated with latent heat of transition can be detected and analyzed

4. **Spectroscopic techniques**
   a. Infrared spectroscopy
      - identify compounds and investigate sample composition
      - Study of structure and bonds
   a. Raman spectroscopy:
- study of oxidation state and interaction of metal oxides

5. Microscopic technique
   - Scanning electron microscopy (SEM):
     - image the topography of solid surface
     - resolution better than 5 nm.
   a. transmission electron microscopy (TEM):
     - determines the micro-texture and micro structure
     - resolution better than 0.2 nm

8. What is catalyst deactivation? How and why it occurs? What are the factors that are responsible for deactivating a porous catalyst pellet? (May 2014)

**Types of catalyst deactivation:**
Catalyst deactivation can be divided into the following three categories:

(i) Deactivation by sintering (also called as aging),
(ii) Deactivation by fouling or coking,
(iii) Deactivation by poisoning.

(i) **Deactivation by sintering (aging)**: It is the loss of activity of the catalyst due to a loss of active surface area resulting from the prolonged exposure to high temperatures in the reacting atmosphere.
   The active surface area of the catalyst may be lost either by crystal agglomeration and growth of metals deposited on the surface or by narrowing or closing of the catalyst pores (i.e., by a change in the surface structure of the catalyst).

(ii) **Deactivation by fouling or coking**: It is caused by a physical deposition of carbonaceous (coke) material on the surface of a catalyst. This deactivation is rapid and common to reactions involving hydrocarbons. Removal of a deposited material from the catalyst surface is called regeneration. Carbon deposition on cracking catalyst is a common example of deactivation by fouling. Catalysts deactivated by coking can be regenerated by burning off the carbon with air and/or steam.

(iii) **Deactivation by poisoning**: It is caused by reversible or irreversible chemisorption of the poisoning material on the active sites. The chemisorption of
Mechanism of catalyst Deactivation:

Mechanisms of Catalyst Deactivation:

Although many factors affect the observed deactivation of a porous catalyst, here we consider only two factors: the actual decay reactions and pore diffusion.

Decay Reactions:

- Catalyst decay can occur by the following ways:
- (i) Parallel deactivation,
- (ii) Series deactivation,
- (iii) Side-by-side deactivation and
- (iv) Independent deactivation.

Parallel Deactivation:

In this case, the reactant may produce a side product which deposits on and deactivates the catalyst surface.

Let \( P \) be the material which deposits on and deactivates the surface. Then, this decay reaction can be represented by

\[
A \rightarrow R + P
\]

or

\[
A \rightarrow R
\]

\[
A \rightarrow P
\]

Here the deposition depends on the concentration of reactant.

Series Deactivation:

In this case, the reaction product may decompose or react further to produce a material which then deposits on and deactivates the surface. This decay reaction can be represented by

\[
A \rightarrow R \rightarrow P
\]

Here the deposition depends on the concentration of product.
Side-by-Side Deactivation:

In this case, an impurity in the feed may deposit and deactivate the surface. This decay reaction can be represented by

\[ A \rightarrow R \]
\[ P \rightarrow P \downarrow \]

Here the deposition depends on the concentration of impurity in the feed.

Independent Deactivation:

In this case, decay is caused by sintering of the surface resulting from the prolonged exposure of the catalyst to high temperatures. This type of decay is concentration independent (independent of concentration of any species present in the gas stream) and it is dependent on the time spent by the catalyst in the high temperature environment.
1. What are heterogeneous reactions?

Heterogeneous reactions are those in which more than one phase is involved to proceed. Accordingly, there may be two phase and three phase reaction systems.

A heterogeneous reaction involves substances which exist in different phases and reaction usually takes place at an interface between the phases or in one of the phases.

Heterogeneous reactions may be catalytic or non-catalytic. In catalytic heterogeneous reactions usually the catalyst is a solid.

2. Give some examples of catalytic heterogeneous reactions.

(i) Gas-solid reactions:

- Synthesis of ammonia, catalytic cracking of crude oil, oxidation of SO2 to SO3 using V2O5 catalyst in manufacture of sulphuric acid.

(ii) Gas-liquid-solid reactions:

- Catalytic oxidation of liquid hydrocarbons (e.g. ethanol) using air or oxygen to acetic acid, catalytic hydrogenation of acetone to propanal.

A heterogeneous catalytic reaction occurs at the interface (between the phases) which is the surface of a solid catalyst immersed in a gaseous or liquid reaction mixture.

3. Give some examples of Gas-solid and liquid solid heterogeneous reaction?

**Gas-solid reactions:** Roasting of sulphide ores, combustion of coal.

**Liquid-solid reactions:** production of acetylene by the action of water on calcium carbide.


**Gas-liquid reactions:** chlorination of liquid aromatic hydrocarbons using chlorine gas, purification of gas mixtures, manufacture of ammonium nitrate by absorption of ammonia in aqueous nitric acid.

**Liquid-liquid reactions:** nitration of organic compounds with aqueous nitric acid, formation of soaps by the action of aqueous alkalies on fats or fatty acids.

5. What are the factors to be considered for heterogeneous reaction system?

For a heterogeneous systems we have to consider the following factors in addition to those, normally considered in homogeneous systems:

(i) The modification of the rate equation resulting from the mass transfer between phases,

(ii) The contacting patterns for the reacting phases.

6. What is the overall rate of the heterogeneous reaction of the reaction consists of parallel steps.

If a heterogeneous reaction consists of parallel steps, then the overall rate is equal to the sum of all the individual rates:

$$r_{overall} = \sum_{i=1}^{n} r_i$$

7. What is the overall rate of the heterogeneous reaction consists of steps in series.
If, on the other hand, a heterogeneous reaction consists of several consecutive steps (i.e., if the overall change results from a number of steps that take place in series), then at steady-state conditions, the rate of the individual steps in series are all the same and equal to the overall rate of reaction:

\[ r_{\text{overall}} = r_1 = r_2 = \ldots = r_n \]

8. Give the various expression for rate of a chemical reaction?

Based on unit volume of reacting fluid:

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

Based on unit mass of solid:

\[ -r_A' = -\frac{1}{W} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{mass of solid} \cdot \text{time}} \]

Based on unit interfacial surface / unit surface of solid:

\[ -r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{interfacial surface} \cdot \text{time}} \]

9. How are various rates of the reaction related to each other?

These rates are related by

\[ \frac{\text{mol A reacted}}{\text{time}} = (-r_A)V = (-r_A')W = (-r_A'')S \]

\[ \therefore \quad -r_A = \frac{W}{V} r_A' \]

\[ -r_A' = \frac{S}{W} r_A'' \]

\[ -r_A'' = \frac{V}{S} r_A' \]

10. Give the expression for overall rate equation for a heterogeneous reaction.

\[ -r_A'' = \left( \frac{1}{\text{kg}} + \frac{1}{k''} \right) \]

11. What are the various contacting patterns for heterogeneous reaction?

In heterogeneous reactions, contacting patterns affect both physical and chemical rate processes. There are many ways in which two phases can be contacted. Each of the contacting pattern is having unique design equation. In ideal contacting of the phases, each phase may be in one of the two ideal flow patterns,
12. What do you mean by rate controlling step in heterogeneous reactions?

The slowest possible step in the sequence of steps involved in heterogeneous processes is said to be rate controlling step. Note: The sequence of steps involved in heterogeneous processes is;

- Transport of reactants from the bulk fluid to the fluid-solid interface.
- Intraparticle transport of reactants into the catalyst particle (if it is porous).
- Adsorption of reactants at interior sites of the catalyst.
- Chemical reaction of adsorbed reactants to adsorbed products (surface reaction - the intrinsic chemical step).
- Desorption of adsorbed products.
- Transport of products from the interior sites to the outer surface of the catalyst particle.
- Transport of products from the fluid-solid interface into the bulk-fluid stream. (Mostly the reaction step is the rate controlling one)


It is a surface phenomenon, in which accumulation of any substance (Adsorbate) on the surface of another substance (Adsorbent) takes place. Two types of adsorption may occur;

- Physical adsorption: It is non-specific and somewhat similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak.
- Chemisorption: It is specific and involves forces much stronger than in physical adsorption.

14. What is Chemisorption?

a. It is specific and involves forces much stronger than in physical adsorption.

b. The process is often irreversible.

c. The energy of activation is low for non-activated adsorption and high for activated adsorption.

15. Explain two characteristics of physical adsorption. [Dec 2012]

Some of the important characteristics of physisorption are as follows;

(i) **Deficient of specificity**: since the van der Waal forces are universal, a given surface of adsorbent does not show any preference for any specific gas. It can adsorb all the gases but to a different extent.

(ii) **Reversible nature**: physical adsorption of a gas by the solid is reversible and thus equilibrium is reached rapidly. **Solid + Gas gas/solid + Heat** Thus, according to Le-chatelier's principle, - Increase of pressure pushes the equilibrium in forward direction leading to more adsorption of gas and decrease of pressure cause desorption to occur. - Since process is exothermic, therefore, lowering of temperature favors more adsorption and increase of temperature leads to desorption.

16. What do you mean by adsorption isotherm.

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.

17. Write about Freundlich adsorption isotherm.

Freundlich Adsorption Isotherm It is an empirical relation between the amount of an adsorbate adsorbed per unit weight (x/m, mg g⁻¹) of adsorbent and the adsorbate equilibrium concentration (Ce, moles L⁻¹) in the fluid. The relation is given below x/m = K Ceⁿ


The assumptions made over Langmuir treatment of adsorption are;

- All the surface of the catalyst has the same activity for adsorption.
- There is no interaction between adsorbed molecules (or) the amount adsorbed has no effect on the rate of adsorption per site.
- All the adsorption occurs by the same mechanism, and each adsorbed complex has the same structure.
- The extent of adsorption is less than on complete monomolecular layer on the surface.

Since the adsorption is limited to complete coverage by a monomolecular layer, the surface may be divide into two parts; the fraction ‘θ’ covered by the adsorbed molecule and the fraction \((1 – θ)\), 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 \((1 – θ)\);

that is \(r_{ad} = k \ p \ (1 – θ)\)

The rate of Desorption will be proportional to the fraction of covered surface. That is \(r_{de} = k \ θ\) At equilibrium, \(r_{ad} = r_{de}\) or \(k \ p \ (1 – θ) = k^1 \ θ\)

Solving for ‘θ’, we get \(θ = k^1 \ p / (k^1 + k \ p) = K \ p/(1 + K \ p) = v/v_m\)

The above equation is called ‘Langmuir isotherm’. Where \(K = k^1/k^I\) is the adsorption equilibrium constant, expressed in units of \((\text{pressure})^{-1}\).

20. Write the B E T equation for multilayer adsorption.

The Brunauer-Emmett-Teller (B E T) equation is \(P / [v (p_o – p)] = [1 / (v_m \ c)] + \{(c – 1) p \} / (c \ v_m \ p_o)\)

Where \(p\) - partial pressure of adsorbed gaseous molecule \(p_o\) - saturation or vapor pressure \(v\) - volume of gas adsorbed \(v_m\) - volume adsorbed when all the active sites are covered \(c\) - a constant for the particular temperature and gas-solid system

21. A non-porous catalyst particle is of size 2 microns and density is 2 g/cm³. Calculate the external surface area per gram of the particle.

The external surface area per gram of the particle, \(S_g = 6 / [(\text{Size of the particle, } d_p) \ (\text{Density of the particle, } \rho_p)]\)

\(= 6 / \{[2 \times 10^{-4} \text{ (cm)}] \ [2 \ (\text{g/cm}^3)]\}\)

Or \(S_g = 1.5 \times 10^4 \text{ cm}^2/\text{g}\)


The mercury-penetration method for the determination of pore size distribution in a catalyst particle depends on the fact that mercury has a significant surface tension and does not wet most catalytic surfaces. This means that the pressure required to force mercury into the pores depends on the pore radius.


The advantages of the Langmuir-Hinshelwood method are;

✓ The resultant rate equation may be extrapolated more accurately to concentrations beyond the range of experimental measurements used.
✓ The method does take into account adsorption and surface reactions (which must occur) in a consistent manner.

24. What do you mean by desorption?

**Desorption** is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (that is, either adsorption or absorption). This occurs in a system being in the state of sorption equilibrium between bulk phase (fluid, i.e. gas or liquid solution) and an adsorbing surface (solid or boundary separating two fluids).

25. What is heterogeneous reaction?

**Heterogeneous reaction**, any of a class of chemical reactions in which the reactants are components of two or more phases (solid and gas, solid and liquid, two immiscible liquids) or in which one or more reactants undergo chemical change at an interface, e.g., on the surface of a solid catalyst.

27. Write the Freundlich Isotherm.
Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.
\[
x/m = K P^{1/n}
\]
Where \( x \) is the mass of the gas adsorbed on mass \( m \) of the adsorbent at pressure \( p \) and \( k, n \) are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

Langmuir isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

\[
\text{A(g) + B(S)} \xrightarrow{\text{Adsorption}} \text{AB} \quad \xrightarrow{\text{desorption}} \text{A(g)} + \text{B(S)}
\]

Where \( \text{A(g)} \) is unadsorbed gaseous molecule, \( \text{B(s)} \) is unoccupied metal surface and \( \text{AB} \) is Adsorbed gaseous molecule. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

\[
\theta = \frac{KP}{1 + KP}
\]

Where \( \theta \) the number of sites of the surface which are covered with gaseous molecule, \( P \) represents pressure and \( K \) is the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

29. Brief the Langmuir Hinshelwood mechanism.
Langmuir-Hinshelwood mechanism. The two molecules \( \text{A} \) and \( \text{B} \) both adsorb to the surface. While adsorbed to the surface, the \( \text{A} \) and \( \text{B} \) "meet," bond, and then the new molecule \( \text{A-B} \) desorbs.

30. Write the steps involved in heterogeneous catalytic reactions.
First the reactants adsorb onto the surface. Through a series of bonds being formed and being broken, adsorbed intermediates are produced and destroyed. Then the final product(s) is produced and it desorbs from the solid.

31. Write about physical adsorption.
It is nonspecific (similar to the process of condensation) and forces attracting the fluid molecules to the solid surface are relatively weak. Equilibrium between the solid and the gas molecules is usually rapidly attained and easily reversible.
PART – B

1. The irreversible reaction.

\[ A(g) + B(s) \rightarrow R(g) \] first order with respect to and takes place on a flat surface as shown in figure below. Dilute A diffuses through stagnant gas film onto a plain surface consisting of B. On the surface A reacts with B to give R which diffuses back to surface. Develop a rate expression for above reaction.

\[ \text{Solution: } A(g) + B(s) \rightarrow R(g) \]

**Given:** Irreversible first order G/S reaction with respect to A.

This overall process comprises of two steps in series:

1. **Mass transfer step:** Diffusion of A through a gas film to the surface of B
2. **Reaction step:** The reaction of A and B on the surface of B.
3. **Diffusion:** The mass transfer step: The flux of A (by diffusion) to the surface is given by,
- \dot{r}_{A_1} = - \frac{1}{S} \frac{dN_{A_1}}{dt} = \frac{D}{\Delta X} (C_{A_g} - C_{A_s}) = k_g (C_{A_g} - C_{A_s})

- \dot{r}_{A_1} \text{ is in mole/m}^2.\text{h}, C_{A_g} \text{ is in mol/m}^3.
K_g \text{ is in m/s [m}^3\text{ gas/(m}^2\text{ surface . s)] – mass transfer coefficient of the gas film.}
C_{A_g} \text{ is the coefficient of A in the main gas stream, mol/m}^3.

(ii) Reaction step: The reaction is first order with respect to A. The rate of reaction
based on unit surface is given by,

- \dot{r}_{A_2} = - \frac{1}{S} \frac{dN_{A_2}}{dt} = k'' C_{A_s} -

- \dot{r}_{A_2} \text{ is in mol A/(m}^2\text{ surface . time), k'' is in m/s and C_{A_s} is in mol/m}^3.

Now, we will obtain the overall rate of reaction in terms of k_{Ag}, k'' and C_{Ag} (as
the concentration of A on the surface i.e. C_{As} cannot be measured).

As both steps – diffusion and reaction are taking place in series, at steady
state, these steps will proceed at the same rate. Thus

\dot{r}_{overall} = - \dot{r}_{A_1} = - \dot{r}_{A_2}
\quad
k_g (C_{A_g} - C_{A_s}) = k'' C_{A_s}
\quad
k_g C_{A_g} = C_{A_s} (k_g + k'')
\quad
C_{A_s} = \frac{k_g}{k_g + k''} C_{A_g}
\quad

Putting value of C_{As} from equation (1) into equation (2), we get

- \dot{r}_{A_2} = - \dot{r}_{A} = \left( \frac{k'' k_g}{k_g + k''} \right) C_{A_g}
\quad
- \dot{r}_{A_1} = - \dot{r}_{A_2} = - \dot{r}_{A} = \left( \frac{1}{\frac{1}{k_g} + \frac{1}{k''}} \right) C_{A_g}
\quad

Let,
\quad
k_{overall} = \frac{1}{\frac{1}{k_g} + \frac{1}{k''}}
This is the overall rate expression accounting for both the mass transfer and reaction steps.

2. Dilute A diffuses through a stagnant liquid film onto plane surface of solid B. On this plain surface A and B react to field liquid product B which diffuses leak. Develop the overall rate of expression.

\[ -r_{A_2} = -r_{A_1} = -r_A = \left( \frac{1}{k_g} + \frac{1}{k'} \right) C_A = k_{overall} C_{Ag} \]

Solution: \( A(g) + B(s) \rightarrow R(g) \) ............ Irreversible G/S reaction with second order rate.

**Diffusion-mass transfer step**: Diffusion of A to the surface through a gas film.

The diffusional flux of A to the surface is given by,

\[ -r_{A_1} = - \frac{1}{S} \frac{dN_A}{dt} = k_g (C_{Ag} - C_{As}) \]

**Reaction step**: The reaction at the surface is second order with respect to A.

The rate of reaction based on unit surface is given by,

\[ -r_{A_2} = - \frac{1}{S} \frac{dN_A}{dt} = k'' C_{As}^2 \]

As the processes – diffusion and reaction at the surface occur in series, at steady state, these two steps will proceed at the same rate. Thus,

\[ -r_A = -r_{A_1} = -r_{A_2} \]

\[ k_g (C_{Ag} - C_{As}) = k'' C_{As}^2 \]

\[ k'' C_{As}^2 + k_g C_{Ag} = 0 \]
This is a quadratic in $C_A$.

\[
C_A = \frac{-k_g \pm \sqrt{k_g^2 - 4k''(-k_g C_{Ag})}}{2k''}
\]

The positive root is

\[
C_A = \frac{-k_g + \sqrt{k_g^2 + 4k''k_g C_{Ag}}}{2k''}
\]

Putting the value of $C_A$ (as it cannot be measured from equation (3) into equation (1), we get the following overall rate expression:

\[
-r_{A1} = k_g \left[ C_A - \left( \frac{-k_g + \sqrt{k_g^2 + 4k''k_g C_{Ag}}}{2k''} \right) \right]
\]

\[
-r_{A1} = -r_{A2} = r_A = k_g \left[ C_{Ag} + \frac{k_g}{2k''} - \sqrt{k_g^2 + 4k''k_g C_{Ag}} \right]
\]

Taking $2k''$ common from denominator,

\[
-r_A = \frac{k_g}{2k''} \left[ 2k''C_{Ag} + k_g - \sqrt{k_g^2 + 4k''k_g C_{Ag}} \right]
\]

Equation is the desired overall rate expression that takes into account both the mass transfer and reaction steps.

3. The slurry reactors pure reactant gas is bubbled through liquid containing suspended catalyst particles. In term of the two-film theory, these kinetics can be viewed as shown in figure. Hence, to reach the surface of solid, the reactant must diffuse the catalyst particle. At the surface of the catalyst particle, reactant gives product according to first order kinetics. Develop an expression for the rate of reaction in terms of these resistances.
Solution: Here three resistances act in series – liquid film surrounding gas bubble, liquid film surrounding the catalyst particle and reaction. [As pure A is used there is no gas film resistance (and for this $C_{Ag} = C_{Ai}$)]

The rate of transfer of A from gas to the surface of the catalyst particle is given by the rate expressions:

(i) Liquid film-surrounding gas bubble:

$$-r_A^w = k_{Al} a_i (C_{Ai} - C_{Al})$$

Where $-r_A^w$ is in mol A/(m$^3$ reactor’s)

$$a_i = \frac{\text{gas – liquid interface}}{\text{volume of reactor}}, \text{m}^2/\text{m}^3$$

$k_{Al}$ – liquid film mass transfer coefficient in m$^3$ liquid/(m$^2$ surface . s) i.e. in m/s. $k_{Al} a_i$ is in m$^3$ liquid/(m$^3$ reactor’s)

(ii) Liquid film-surrounding the catalyst particle:

$$-r_A^c = k_{Ac} a_c (C_{Al} - C_{As})$$

Where $k_{Ac}$ is the film coefficient about catalyst particle in m$^3$ liquid/(m$^2$ cat.s)

$$a_c = \frac{\text{external surface of particle}}{\text{volume of reactor}}, \text{m}^2/\text{m}^3$$
(iii) The reaction step: The surface reaction is first order with respect to A.

The rate of reaction is given by,

\[-r_A^* = k_1 a_c C_{As}\]

\(C_{As}\) is in mol/m\(^3\) liquid, \(a_c\) is in m\(^2\)/m\(^3\) of reactor, \(k_1\) is in m\(^3\) of liquid/(m\(^2\) cat.s).

At steady state:

\[-r_A^* = k_1 a_i (C_Ai - C_{Al}) = k_{Ac} a_c (C_{Al} - C_{As}) = k_1 a_c C_{As}\]

\[-r_A^* = C_{Al} - C_{As}\]

\[-r_A^* = C_{Al} - C_{As}\]

\[-r_A^* = C_{As}\]

Summing equations (5), (6) and (7), we get

\[-r_A^* \frac{1}{k_{Al} a_i} + \frac{1}{k_{Ac} a_c} + \frac{1}{k_1 a_c} = C_{Al} - C_{Al} + C_{Al} - C_{As} + C_{As}\]

\[-r_A^* \left[ \frac{1}{k_{Al} a_i} + \frac{1}{k_{Ac} a_c} + \frac{1}{k_1 a_c} \right] = C_{Al}\]

\[\therefore -r_A^* = \frac{1}{k_{Al} a_i} + \frac{1}{k_{Ac} a_c} + \frac{1}{k_1 a_c} C_{Al}\]

Equation is the desired rate expression for the rate of reaction in terms of three resistances in series.

4. For the reaction

\[A(g) + B(s) \rightarrow R(g)\]

Mass transfer step \(-r_{1}^* = k_g (C_g - \dot{C})\)

\[-r_{1}^* = k^* C_g^2\]
(i) Linearise second order rate expression
(ii) With this approximation obtain a rate expression.

Hint: It is decided to operate at conditions such that the concentration of gaseous reactant at the surface is somewhere in the vicinity of $C_0 = 2.5$.

The Taylor expansion of any function $f(C)$ in the vicinity of $C_0$ is

$$f(C) = f(C_0) + \frac{C-C_0}{1!} f'(C_0) + \frac{(C-C_0)^2}{2!} f''(C_0) + ...........$$

Solution: $A(g) + B(s) \rightarrow R(g)$

Irreversible G/S reaction ..........second order with respect to $A$.

1. Mass transfer step:

$$-r_i^* = k_s (C_g - C_s)$$

2. Reaction step:

$$-r_2^* = k'' C_2^2$$

$$f(C) = -r_2^*$$

$$f(C_0) = k'' C_0^2$$

$$(-r_2^*)' = 2k'' C_s$$  ...................... first derivative

$$f'(C_0) = 2k'' C_0$$

$$(-r_2^*)'' = 2k''$$  ...................second derivative

$$f''(C_0) = 2k''$$

Now, we will make the Taylor expansion about $C_0$ and retain linear terms.

$$f(C) = f(C_0) + \frac{C-C_0}{1!} f'(C_0) + \frac{(C-C_0)^2}{2!} f''(C_0) + ...........$$

$$-r_2^* = k'' C_0^2 + \frac{C_s - C_0}{1} (2k'' C_0) + \frac{(C_s - C_0)^2}{1 \times 2} (2k'') + ...........$$

Ignoring the third term on the RHS of the above equation, we get the linear approximation to the non-linear rate expression.
\[-r_2^* = k''C_0^2 + 2k''C_o(C_s - C_o)\]
\[= k''C_0^2 + 2k''C_oC_s - 2k''C_o^2 = 2k''C_oC_s - k''C_o^2\]
\[-r_2^* = k''C_o(2C_s - C_o)\]

At steady state (as steps are in series) we have

\[-r_1^* = -r_2^*\]
\[k_8(C_8 - C_s) = k''C_o(2C_s - C_o)\]
\[k_8C_8 - k_8C_s = 2k''C_oC_s - k''C_o^2\]
\[C_s(k_8 + 2k''C_o) = k_8C_8 + k''C_o^2\]
\[C_s = \frac{k_8C_8 + k''C_o^2}{k_8 + 2k''C_o}\]

Combine equation (1) and (3) to eliminate \(C_s\)

\[-r_1^* = k_8\left(C_8 - \frac{(k_8C_8 + k''C_o^2)}{k_8 + 2k''C_o}\right)\]
\[= k_8\left[\frac{k_8C_8 + 2k''C_oC_s - k_8C_8 - k''C_o^2}{k_8 + 2k''C_o}\right]\]
\[= \frac{k_8k''C_o(2C_s - C_o)}{k_8 + 2k''C_o}\]

Dividing the numerator and denominator of the above equation by \(k_8k''C_o\) gives

\[-r_1^* = \frac{2C_s - C_o}{\frac{1}{k''C_o} + \frac{2}{k_8}}\]
\[\therefore -r_1^* = -r_2^* = -r'' = \left(\frac{1}{\frac{2}{k_8} + \frac{1}{k''C_o}}\right)(2C_s - C_o)\]
5. **What are the characteristics of catalyzed reaction?**

1. A catalyst remains unchanged in its amount and chemical composition at the end of the reaction.
2. A small amount of a catalyst is often sufficient to catalyse a reaction.
3. A catalyst does not change the state/position of chemical equilibrium (since it does not depend on the pathway of the reaction).
4. A catalyst is usually specific in nature.
5. A catalysed reaction generally has a lower activation energy than non-catalysed reaction. Consequently, the catalysed reaction proceeds at a faster rate.

6. **What is the mechanism of solid catalyzed reaction?**

The steps involved in solid catalysed fluid-phase reactions (in converting the reactants into products) are as follows:

1. Diffusion of the reactant(s) (e.g., species A) from the bulk fluid phase to the external surface of the catalyst through the fluid film \( \rightarrow \) external or surface diffusion step.
2. Diffusion of the reactant from the pore mouth into the catalyst pores.
   The greater proportion of reactant molecules diffuse inside the pores of the catalyst ........ The pore diffusion step.
3. Adsorption of reactant A onto the catalyst surface (external and pore surfaces).
4. Chemical reaction of the adsorbed reactant on the surface of the catalyst (e.g. \( A \rightarrow R \)) to form product (surface reaction).
5. Desorption of the products (e.g., R) from the surface (to the fluid phase near the surface)
6. Diffusion of the desorbed products from the interior of the catalyst (pores) to the pore mouth at the external surface, i.e., to the external surface ........ reverses pore diffusion.
7. Diffusion of the products from the external surface into the bulk fluid phase through the fluid film surrounding the catalyst ............... reverse external diffusion.

Steps 1, 2, 6 and 7 .............. diffusion steps.
Steps 3, 4, and 5 ............... reaction steps.

Collectively, steps 3, 4 and 5 may be regarded as surface chemical reaction.
The overall rate of reaction is equal to the rate of the slowest step in the mechanism. With porous catalyst diffusion within the catalyst pores may limit the rate of reaction.

When a porous catalyst particle is soaked by reactant A, the rate of reaction of A depends upon:

1. Surface kinetics
2. Pore (diffusion) resistance. This resistance may cause the interior of the particle to be starved for reactant. We can reduce the resistance to pore diffusion by reducing the catalyst particle size, which thus shortens the diffusion path.
3. Particle ΔT – temperature gradient within the catalyst particle (internal temperature gradient). This is caused by evolution or absorption of large amount of heat during reaction. It causes the reaction rate of vary inside the catalyst (i.e., with position).
4. Film ΔT – temperature differences between the outer surface of the catalyst particle and the bulk gas stream (external temperature gradient) – resistance to heat transfer is within the gas film enveloping the catalyst particle.
5. Film (diffusion) resistance – external diffusion resistance – concentration gradient across the gas film surrounding the catalyst particle.

In the majority of cases with porous catalyst particle the rate is influenced by surface reaction and pore diffusion. Therefore, here we will consider surface kinetics and pore diffusion resistance. Also, we will use a simple empirical rate expression – first order of nth – order rate expression, which adequately fits the data, to represent the surface reaction.

7. Describe about Langumir adsorption isotherm.

The langumir treatment of adsorption: The derivations may be carried out by using as a measure of the amount adsorbed either the fraction of the surface covered or the concentration of the gas adsorbed on the surface. Both procedures will be illustrated, although the second is the more useful for kinetic developments. The important assumptions are as follows:

- All the surface of the catalyst has the same activity for adsorption; i.e., it is energetically uniform. The concept of nonuniform surface with active centers can be employed if it is assumed that all the active centers have the same activity for adsorption and that the rest of the surface has none, or that an average activity can be used.
There is no interaction between adsorbed molecules. This means that the amount adsorbed has no effect on the rate of adsorption per site.

All the adsorption occurs by the same mechanism and each adsorbed complex has the same structure.

The extent of adsorption is less than one complete monomolecular layer on the surface.

In the system of solid surface and gas, the molecules of gas will be continually striking the surface and a fraction of these will adhere. However, because of their kinetic, rotational, and vibrational energy, the more energetic molecules will be continually leaving the surface. Equilibrium will be established such that the rate at which molecules strike the surface, and remain for an appreciable length of time, will be exactly balanced by the rate at which molecules leaves the surface.

The rate of adsorption $r_a$ will be equal to the rate of collision $r_c$ of molecules with the surface multiplied by a factor $F$ representing the fraction of the colliding molecules that adhere. At a fixed temperature the number of collisions will be proportional to the pressure $p$ of the gas (or its concentration), and the fraction $F$ will be constant. Hence the rate of adsorption per unit of bare surface will be $r_c F$. This is equal to $kp$, where $k$ is a constant involving the fraction $F$ and the proportionality between $r_c$ and $p$.

Since the adsorption is limited to complete coverage by a monomolecular layer, the surface may be divided into two parts: the fraction $\theta$ 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 absorbed, the rate of adsorption per unit of total surface will be proportional to $1 - \theta$; that is,

$$r_a = kp(1 - \theta)$$

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

$$r_d = k' \theta$$

The amount adsorbed at equilibrium is obtained by equating $r_a$ and $r_d$ and solving for $\theta$. The result, called the Langmuir isotherm, is

$$\theta = \frac{kp}{k' + kp} = \frac{kp}{1 + Kp} = \frac{V}{V_m}$$
Where $K = k/k'$ is the adsorption equilibrium constant, expressed in units of \((\text{pressure})^{-1}\). The fraction $\theta$ is proportional to volume of gas adsorbed, $v$, since the adsorption is less than a monomolecular layer. Hence equation may be regarded as a relationship between the pressure of the gas and the volume adsorbed. This is induced by writing $\theta = v/v_m$, where $v_m$ is the volume of adsorbed when all the active sites are covered, i.e., when there is a complete monomolecular layer.

The concentration form of equation 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, mol/(s)(g catalyst) is, by analogy with equation,

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

Where $k_c$ is the rate constant for the catalyst and $C_g$ is the concentration of adsorbable component in the gas. Similarly equation becomes.

$$r_a = k'_c \bar{C}$$

At equilibrium the rates given by equations are equal, so that

$$\bar{C} = \frac{k_c \bar{C}_m C_g}{1 + K_c C_g}$$

Where now the equilibrium constant $K_c$ is equal to $K_c/K'_c$ and is expressed in units of \((\text{concn})^{-1}\), centimeters per gram mole. Since $\bar{C}/\bar{C}_m = \theta$, equation may also be written

$$\theta = \frac{K_c C_g}{1 + K_c C_g}$$

Which is a form analogous to equation, since $C_g$ is proportional to $p$?

Equation predicts that adsorption data should have the general form shown in figure. Note that at low values of $C_g$ (or low surface coverages $\theta$) the expression becomes a straight line with a slope equal to $K_c \bar{C}_m$. The data points in figure are for the physical adsorption of n-butane on silica gels ($S_g = 832 \text{ m}^2/\text{g}$) at $50^\circ\text{C}$. The solid line represents equation, where

$$\bar{C}_m = 0.85 \times 10^{-3} \text{ g mol/g silica gel}$$
And the equilibrium constant of adsorption is

\[ K_c = 4.1 \times 10^5 \text{ cm}^3 / \text{g mol} \]

For this instance of physical adsorption equation fits the data rather well. The measurements were made on mixtures of n-butane in helium (at 1 atm total pressure) to vary \( C_g \). The percentage of n-butane in the gas corresponding to the concentration \( C_g \) is shown as a second abscissa in the figure. Also, \( \theta \) is shown as a second ordinate. This was calculated from \( \theta = \frac{\bar{C}}{\bar{C}_m} \). It is interesting to note that the isotherm is linear up to about \( \theta = \frac{\bar{C}}{\bar{C}_m} \). It is interesting to note that the isotherm is linear up to about \( \theta = 0.10 \), or a gas concentration of 1% n-butane in He. This means that the denominator in equation is nearly unity at low concentrations. The region of linearity depends upon the adsorbent-adsorbate system. For example, for the same silica gel at 50°C, the linear isotherm was applicable up to 2% for adsorption of propane and to more than 4% for ethane.

Chemisorption data often do not fit equation. However, the basic concepts on which the Langmuir isotherm is based (the ideas of a dynamic equilibrium, between rates of adsorption and desorption and a finite adsorption time) are sound and of great value in developing the kinetics of fluid-solid catalytic reactions. Equations form the basis for the rate equations presented.

8. **How will you determine the surface area of a catalyst pellet. Explain?**

The standard method for measuring catalyst areas is based on the physical adsorption of a gas on the solid surface. Usually the amount of nitrogen adsorbed at equilibrium at the normal boiling point (-195.8°C) is measured over a range of nitrogen pressures below 1 atm. Under these conditions several layers of molecules may be adsorbed on top of each other on the surface. The amount adsorbed when one molecular layer is attained must be identified in order to determine the area. The historical steps in the development of the Brunauer-Emmett-Teller whether the values given by this method correspond exactly to the surface area. However, this is relatively unimportant, since the procedure is standardized and the results are reproducible. It should be noted that the surface are is so measured may not be the area effective for catalysis. Only certain parts of the surface, the active centers, may be active for chemisorption of a reactant, while nitrogen may be physically adsorbed on much more of the surface. When the catalyst is dispersed on a large-area support, only part of the support area may be covered by catalytic active forms and this area may be several atoms in depth. Thus, the active atoms may be together in clusters so that the catalytic surface is less than if the atoms may be together in clusters so that
the catalytic surface is less than if the atoms were more completely dispersed or separated. For example a nickel-on-kieselguhr catalyst was found to have a surface of 205 m$^2$/s as measured by nitrogen adsorption. To determine the area covered by nickel atoms was calculated to be about 40 m$^2$/g. It would be useful to know surface areas for chemisorption of the reactant at reaction conditions. However this would require measurement of relatively small amounts of chemisorption at different, and often troublesome, conditions (high temperature and/or pressure), for each reaction system. In contrast, nitrogen can be absorbed easily and rapidly in a routine fashion with standard equipment.

In the classical method of determining surface area an all-glass apparatus is used to measure the volume of gas adsorbed on a sample of the solid material.

![Figure: Adsorption isotherms for various gases on a 0.606-g sample of silica gel](image)

The apparatus operates at a low pressure which can be varied from near zero up to about 1 atm. The operating temperature is in the range of the normal boiling point. The data obtained are gas volumes are normally corrected to cubic centimeters at 0°C and 1 atm (standard temperature and pressure) and plotted against the pressure in millimeters, or as the ratio of the pressure to the vapor pressure at the operating temperature. Typical results from Brunauer and Emmett’s work are shown in figure for the adsorption of several gases on a 0.606 – g sample of silica gel. To simplify the classical experimental procedure a flow method has been developed in which a mixture of helium (or other nonadsorbed gas) and the gas to be adsorbed is passed continuously over the sample of solid. The operating total
pressure is constant, and the partial pressure of adsorbable gas is varied by changing the composition of the mixture. The procedure is to pass a mixture of known composition over the sample until equilibrium is reached, that is, until the solid has adsorbed an amount of adsorbable component corresponding to equilibrium at its partial pressure in the mixture. Then the gas is desorbed by heating the sample while a stream of pure helium flows over it. The amount desorbed is measured with a thermal-conductivity cell or other detector. This gives one point on an isotherm, such as shown in figure. Then the process is repeated at successively different composition of the mixture until the whole isotherm is obtained.

The curves in figure are similar to the extent that at low pressures they rise more or less sleepy and then flatten out for a linear section at intermediate pressures. After careful analysis of much data it was concluded that the lower part of the linear section at intermediate pressures. After careful analysis of much data it was concluded that the lower part of the linear region corresponded to complete monomolecular adsorption. If this point could be located with precision, the volume of one monomolecular layer of gas, \( V_m \), could then be read from the curve and the surface area evaluated. The Brunauer-Emmett-Teller method locates this pint from an equation obtained by extending the Langmuir isotherm to apply to multilayer adsorption. The development is briefly summarized as follows: Equation can be rearranged to the form

\[
\frac{p}{v} = \frac{1}{Kv_m} + \frac{p}{v_m}
\]

Brunauer, Emmett, and Teller adapted this equation for multilayer adsorption and arrived at the result.

\[
\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c-1)p}{Cu_m p_0}
\]

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

According to equation a plot of \( p/v(p_0-p) \) vs. \( p/p_0 \) should give a straight line. The data of figure are replotted in this fashion in figure. Of additional significance is the fact that such straight lines can be accurately extrapolated to \( p/p_0 = 0 \). The intercept I obtained from this extrapolation, along with the slope \( s \) of the straight lines, gives two equations from which \( V_m \) can be obtained.
Solving these equations for the volume of adsorbed gas corresponding to a monomolecular layer gives

\[ V_m = \frac{1}{I + s} \]

The volume \( V_m \) can be readily converted to the number of molecules adsorbed. However, to determine the surface area it is necessary to select a value for the area covered by one adsorbed molecule. If this is \( \alpha \), the total surface area is given by

\[ S_g = \left[ \frac{V_m N_0}{V} \right] \alpha \]

Where \( N_0 \) is Avogadro’s number, \( 6.02 \times 10^{23} \) molecules/mol, and \( V \) is the volume per mole of gas at conditions of \( V_m \). Since \( V_m \) is recorded at standard temperature and pressure, \( V = 22,400 \text{ cm}^3/\text{g mol} \). The term in brackets represent the number of molecules adsorbed. If \( V_m \) is based on a 1.0 g sample, then \( S_g \) is the total surface per gram of solid adsorbent.
Emmett and Burnauer proposed that $\alpha$ 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

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

Where $M$ is the molecular weight and $\rho$ is the density of the adsorbed molecules. The term in brackets represents the volume of one adsorbed molecule. The density is normally taken as that of the pure liquid at the temperature of the adsorption experiment. For example, for $N_2$ at $-195.8^\circ C$, $\rho = 0.808 \text{ g/cm}^3$ and the area per molecule from equation is $16.2 \times 10^{-16} \text{ cm}^2$, or $16.2 \text{ Å}^2$. If this result is used in equation along with the known values of $N_0$ and $V$, the surface area per gram is $S_g = 4.35 \times 10^4 \nu_m \text{ cm}^2 / \text{g solid adsorbent}$.

9. How will you determine the pore volume distribution of a catalyst pellet? Explain.

We shall that the effectiveness of the internal surface for catalytic reactions can depend not only on the volume of the void spaces ($V_v$), but also on the radius of the void regions. Therefore it is desirable to know the distribution of void volume in a catalyst according to size of the pore. This is a difficult problem because the void spaces in a given particle are nonuniform in size, shape, and length and normally are interconnected. Further, these characteristics can change from one type of catalyst particle to another. Figure shows electron-microscope (Scanning type) photographs of porous silver particles ($S_g = 19.7 \text{ m}^2 / \text{g}$). The material was prepared by reducing a precipitate of silver fumarate by heating at $350^\circ C$ in a stream of nitrogen. The larger darker regions probably represent void space between individual particles, and the smaller dark spaces are intraparticle voids. The light portions are solid silver. The complex and random geometry shows that it is not realistic to describe the void spaces as pores. It is anticipated than other highly porous materials such as alumina and silica would have similar continuous and complex void phases. For a material such as Vycor, with its relatively low porosity and continuous solid phase, the concept of void spaces as pores is more reasonable.

In view of evidence such as that in figure, it is unlikely that detailed quantitative descriptions of the void structure of solid catalysts will become available. Therefore, to account quantitatively for the variations in rate of reaction
with location within a porous catalyst particle, a simplified model of the pore structure is necessary. The model must be such that diffusion rates of reactants through the void spaces into the interior surface can be evaluated. More is said about these models in chapter. It is sufficient here to note that in all the widely used models the void spaces are simulated as cylindrical pores. Hence the size of the void volume is defined in terms of this variable. However, as the example of the silver catalyst indicates, this does not mean that the void spaces are well-defined cylindrical pores.

There are two established methods for measuring the distribution of pore volumes. The mercury-penetration method depends on the fact that mercury has a significant surface tension and does not wet most catalytic surfaces. This means that the pressure required to force mercury into the pores depends on the pore required to fill pores for which \( a = 10,000 \text{ Å}, \) and 10,000 lb/in\(^2\) (approximately) is \( a = 100 \text{ Å}. \) Simple techniques and equipment are satisfactory for evaluating the pore-volume distribution down to 100 to 200 Å, but special high-pressure apparatus is necessary to go below \( a = 100 \text{ Å}, \) where much of the surface resides. In the second method, the nitrogen-adsorption experiment for surface area measurement) is continued until the nitrogen pressure approaches the saturation value (1 atm of the normal boiling point). At \( p/p_0 \rightarrow 1.0, \) where \( p_0 \) is the saturation pressure, all the void volume is filled with adsorbed and condensed nitrogen. Then the desorption isotherm is established by lowering the pressure in increment and measuring the amount of nitrogen evaporated and desorbed for each increment. Since the vapor pressure of a liquid evaporating from a capillary desorbed vs. pore radius. Thus this procedure also gives the distribution of pore volumes. The vapor pressure is not affected significantly by radii of curvature greater than about 200 Å. Hence, this method is not suitable for pores larger than 200 Å.

If a high pressure mercury porosimeter is not available a combination of the two methods is necessary to cover the entire range of ore radii (10 to 10,000 Å) which may exist in a bidisperse catalyst or support, such as alumina pellets. For a monodisperse pore distribution, such as that in silica gel, the nitrogen-desorption experiment is sufficient, since there are few pores of radius greater than 200 Å. In a bidisperse pore system the predominant part of the catalytic reaction occurs in the surface resides. However, the transport of reactants to these small pores occurs in primarily in pores of 200 to 10,000 Å (the macro pore region). Hence the complete
distribution of pore volume is required in order to establish the effectiveness of the interior surface, that is, the global rate of reaction. Calculation procedures and typical results are discussed briefly in the following paragraphs.

**Mercury-penetration method:** 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

\[ \pi a^2 p = -2\pi a \sigma \cos \theta \]

Or

\[ a = \frac{-2\sigma \cos \theta}{p} \]

**Figure: Mercury penetration in a pore of radius a.**

Where \( \theta \) is the contact angle between the mercury and pore wall. While \( \theta \) probably varies somewhat with the nature of the solid surface, \( 140^\circ \) appears to be a good average value. Then the working equation for evaluating the radius corresponding to a given pressure is

\[ a(\text{Å}) = \frac{8.75 \times 10^5}{p(\text{lb/in.}^2)}. \]
**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 vapor pressure decreases as the capillary size decreases, such condensation will occur first in the smaller pores. Condensation will be complete, as $p/p_0 \to 1.0$, 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 vapor pressure of nitrogen is greater than the chosen pressure. The Kelvin equation gives the relationship between vapor 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 $\delta$ of the adsorbed layers. With this correction, the pore radius is related to the saturation-pressure ratio (vapor pressure $p$ in the pore divided by the normal vapor pressure $p_0$) by

$$a - \delta = \frac{-2\sigma V_1 \cos \theta}{R_\text{g} T \ln(p/p_0)}$$

Where $V_1 =$ molal volume of the condensed liquid

$\sigma =$ Surface tension

$\theta =$ 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 $\delta$ depends on $p/p_0$. The exact relationship has been the subject of considerable study, but Wheeler’s form

$$\delta (\text{Å}) = 9.52 \left( \log \frac{P_0}{P} \right)^{-1} / n$$

Is generally used.

For nitrogen at -195.8°C (normal boiling point) equation, for $a - \delta$ in angstroms, becomes

$$a - \delta = 9.52 \left( \log \frac{P_0}{P} \right)^{-1}$$

With $\delta$ determined from equation.
For a chosen value of $p/p_0$, equations 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. Differentiation of the curve for cumulative pore volume vs. radius gives the distribution of volume as described in example. Descriptions of the method of computations are given by several investigators. As in the mercury-penetration method, errors will result unless each pore is connected to at least one larger pore.

Figure shows the result of applying the method to a sample of Vycor (porous glass). This material, which contained only microprocessor, had the properties:

\[
\begin{align*}
\rho_p &= 1.46 \text{ g/cm}^3 \\
V_g &= 0.208 \text{ cm}^3 / \text{g} \\
\varepsilon_p &= 0.304 \\
S_g &= 90 \text{ m}^2 / \text{g}
\end{align*}
\]

The surface area was determined from nitrogen-adsorption data in the low $p/p_0$ range, as described in section, while the distribution results in figure were established from the desorption curve in the capillary-condensation (high $p/p_0$) region.

**Figure:** Pore-volume distribution in Vycor; 
$\rho_p = 1.46 \text{g/cm}^3$, $V_g = 0.208 \text{cm}^3 / \text{g}$, $S_g = 90 \text{m}^2 / \text{g}$.
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. Figure shows the cumulative pore volume for two alumina pellets, each prepared by compressing porous particles of boehmite (Al₂O₃·H₂O). The properties of the two pellets are given in table. The only different in the two is the pelleting pressure. Increasing this pressure causes drastic reductions in the space between particles (macro pore volume) but does not greatly change the void volume within the particles or the surface area. The derivative of the volume curves in figure gives the pore volume distribution, and these results are shown in figure. In this figure the bidisperse pore system, characteristic of alumina pellets, is clearly indicated. The micropore range within the particles is narrow, with a most probable radius of 20 Å has been squeezed out, while the most probable radius for the low pressure pellet is 8000 Å. Pelting pressure seems to have little effect on the micropores, which suggests that the particles themselves are not crushed significantly during the pelleting process.

![Figure: Pore volume in alumina (boehmite) pellets](image)

Some models for quantitative treatment of the effectiveness of the internal catalyst surface require only the average pore radius $\bar{a}$

**Table – Properties of boehmite (Al₂O₃·H₂O) pellets**
<table>
<thead>
<tr>
<th>Pelleting pressure</th>
<th>Macropore volume, cm$^3$/g</th>
<th>Micropore volume, cm$^3$/g</th>
<th>Surface area, m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>1.08</td>
<td>0.56</td>
<td>389</td>
</tr>
<tr>
<td>High</td>
<td>0.265</td>
<td>0.49</td>
<td>381</td>
</tr>
</tbody>
</table>

**Notes:** Volume and surface area refer to mass of Al$_2$O$_3$ obtained by ignition of boehmite. The pore volume distribution is given in figure. Average particle size from which pellets were made was 85 microns.

![Figure: Pore-volume distribution in alumina pellets](image)

Which requires only surface-area and pore-volume measurement. Suppose, all the pores in a hypothetical particle are straight, cylindrical, not interconnected, and have the same radius $\bar{a}$ and length $\bar{L}$. 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.

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

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

$$\bar{a} = \frac{2V_g}{S_g}$$
This expression agrees well with volume-average values obtained from the distribution curve from monodisperse pore system. For example, from the data for the Vycor sample equation gives

\[ \bar{a} = \frac{2(0.208)}{90 \times 10^2} = 46 \times 10^{-8} \text{ cm} \text{ or } \bar{A} = \frac{90}{10} \]  

The volume-average value is calculated from the pore volume data used to obtain the distribution curve and the expression.

\[ \bar{a} = \int_0^{V_s} a \, dV \\ \frac{V_s}{V_s} \]

By this method \( \bar{a} = 45 \bar{A} \).

10. How will you prepare a catalyst pellet?

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. To begin with, a distinction should be drawn between preparations in which the entire material constitutes the catalyst and those in which the active ingredient is dispersed on a support or carrier having a large surface area. The first kind of catalyst is usually made by precipitation, gel formation, or simple mixing of the components.

Precipitation provides a method of obtaining the solid material in a porous form. It consists of adding a precipitating agent to solutions of the desired components. Washing, drying, and usually calcinations and activation (or pretreatment) are subsequent steps in the process. For example, a magnesium oxide catalyst can be prepared by precipitating the magnesium form nitrate solution by adding sodium carbonate. The precipitate 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, pore structure, and intrinsic activity 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 the 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. Detailed techniques for producing catalysts through gel formation or ordinary precipitation are given by Ciapetta and Plank.

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.

Catalyst carriers 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 palladium, ruthenium and silver are used. Berkman et al, have treated the subject of carriers in some detail.

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) calcinations 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 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 (activation), 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. In this case no precipitation of all the interior surface of the carrier particles is relatively simple. However, if the solution used to soak the carrier contains potential poisons such as chlorides or sulfates, it may be necessary to precipitate the required constituent and wash out the possible poison.

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 a 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 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 conversation 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 atoms were deposited from a much more concentrated Ni(NO₃)₃ solution to make the catalyst containing 5.0 wt% NiO. This may have led to larger clusters of nickel atoms. 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. It is interesting to note that a 5.0 wt% NiO catalyst prepared by 10 individual depositions of 0.5 wt% was much more active (by a factor of 11) than the 5.0 wt% added in a single treatment. The multiple deposition method presumably gave a much larger active nickel surface, because of better dispersion of the nickel atoms on the Al₂O₃ surface. Since the total amount of nickel was the same for the two preparations, one would conclude that the individual particles of nickel were smaller in the 10-application catalyst. These kinds of data indicate the importance of measuring surface areas for chemisorption of the reactants involved. A technique based on the chemisorption of H₂ and CO has been developed to study the effect of dispersion of a catalyst on its activities and the effect of interaction between catalyst and support on activity.

11. The mechanism of decomposition of cumene on catalyst surface is given by

\[
\text{C}_6\text{C}_5\text{CH}(\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_6 + \text{C}_3\text{H}_6
\]

\[
\text{C}(g) \rightarrow \text{B}(g) + \text{p}(g)
\]

**Mechanism:**

\[
\begin{align*}
\text{C} + \text{S} & \rightarrow \text{C.S (adsorption)} \\
\text{C.S} & \rightarrow \text{B.S} + \text{P (surface reaction) CC} \\
\text{B.S} & \rightarrow \text{B} + \text{S (adsorption)}
\end{align*}
\]

**Derive the rate of expression if surface reaction controls.**

**Solution:**

The catalytic decomposition of cumene is given by following overall reaction:

\[
\text{C}_6\text{C}_5\text{CH}(\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_6 + \text{C}_3\text{H}_6
\]

\[
\text{C}(g) \rightarrow \text{B}(g) + \text{p}(g)
\]
[The catalytic reaction is not diffusion limited.]

The mechanism of cumene decomposition (with no adsorbing inert in the feed) is

\[
\begin{align*}
C + S & \xrightleftharpoons[k_A]{k_A^S} C.S \\
C.S & \xrightleftharpoons[k_S]{k_S^C} B.S + P
\end{align*}
\]

…………… adsorption of cumene on the surface

…………… surface reaction

[surface reaction forms adsorbed benzene and propylene in the gas phase]

\[
B.S \xrightleftharpoons[k_B]{k_B^S} B + S \quad \text{……………desorption of benzene from surface}
\]

[while writing rate expressions for these steps we will consider each step as an elementary reaction and we will replace the species concentration in the gas phase by their respective partial pressures].

(1) **Adsorption of cumene on the surface:**

\[
C + S \xrightleftharpoons[k_A]{k_A^S} C.S, \quad [C(g) \text{......use } P_C]
\]

The rate of attachment of molecules (C) is proportional to (i) partial pressure of C in the gas phase, \(P_C\) and (ii) the concentration of vacant sites,

\[
\text{Rate of attachment} = k_A P_C C_V
\]

The rate of detachment of molecules from the surface is directly proportional to the concentration of sites occupied by the molecules, \(C_{C.S}\)

\[
\text{Rate of detachment} = k_A C_{C.S}
\]

The net rate of adsorption of cumene (the rate expression for the adsorption of cumene is)

\[
r_r = K_A P_C C_V - k_A C_{C.S}
\]

where \(k_A\) is the adsorption rate constant (the constant of proportionality for the attachment process). \(k_A\) is the desorption constant.

\[
K_C = \frac{K_A}{k_A} = \text{the adsorption equilibrium constant for C}
\]

\(S\) – represents active site.
C, S – means one unit of C is adsorbed on the site S
P, i – partial pressure of species I in the gas phase
C, i,s – surface concentration of sites occupied by species i in mol/g cat
C,CS – surface concentration of sites occupied by species C
K, C – (surface concentration of adsorbed species i) in mol/g cat.
C, V – molar concentration of vacant sites per unit mass of catalyst divided by Avogadro’s number (mol/g cat)

\[ r_{AD} = k_A \left( P_C C_V - \frac{k_{-A}}{k_A} C_{CS} \right) \]

If \( r_{AD} \) has units of mol/(g cat.s) and \( C_{CS} \) has units of mol cumene adsorbed/g cat then

- \( k_A \) has units of (kPa.s)\(^{-1}\)
- \( k_{-A} \) has units of s\(^{-1}\)
- \( K_C \) has units of (kPa)\(^{-1}\) or atm\(^{-1}\)

(2) Surface reaction: The rate expression for the surface reaction step yielding adsorbed benzene and propylene in the gas phase (surface reaction is a single site mechanism) is

\[ C, S \xrightarrow{k_s} B, S + P \]  
\[ r_s = k_s C_{CS} - k_{-s} P_C C_{BS} \]
\[ r_s = k_s \left[ C_{CS} - \frac{P_C C_{BS}}{K_s} \right] \]

[concentration of species P in the gas phase is replaced by its partial pressure]

\[ K_s = \frac{k_s}{k_{-s}} = \text{surface reaction equilibrium constant} \]

(3) Desorption:

\[ B, S \xrightarrow{k_D} B + S \]  
[B(g) ...... use P_B]

The rate of benzene desorption is
\[ R_D = k_D C_{BS} - k_D P_B C_V \]

and
\[ K_{DB} = \frac{k_D}{k_{-D}} \]

\( K_{DB} \) is the desorption equilibrium constant for benze

\[ r_D = k_D \left( C_{BS} - \frac{P_B C_V}{K_{DB}} \right) \]

Units of \( k_S \) (and \( k_D \)) and \( K_S \) and \( (K_{DB}) \) are s\(^{-1}\) and atm or kPa respectively.

The desorption of benzene is just the reverse of the adsorption of benzene.

\[ K_B = \frac{1}{K_{DB}} \]

Putting value of \( K_{DB} \) from equations we get

\[ r_D = k_D (C_{BS} - K_B P_B CV) \]

As we cannot measure \( C_{CS} \) and \( C_{BS} \) we have to replace these variables in terms of measurable quantities-partial pressures \( P_C \) and \( P_B \).

For doing this we have to make use of –

(i) Rate expressions for adsorption of C and desorption of B.
(ii) Fact – for surface reaction as rate limiting both \( k_A \) and \( k_D \) are very large compared with \( k_S \). So \( r_{AD}/k_A \approx 0 \) and \( r_D/k_D \approx 0 \).

Evaluation of the surface concentration of adsorbed cumene (\( C_{CS} \)) using rate expression for adsorption of cumene:

When surface reaction is controlling \( k_A \) is large (and \( k_S \) is small) and therefore the ratio \( r_{AD}/k_A \) is very small (approximately zero).

\[ C + S \xrightarrow{k_A/k_A} C_{SC} \]

The rate of adsorption of cumene is given by,
\[ r_{AD} = k_A \left( P_C C_V - \frac{C_{CS}}{K_C} \right) \]

\[ \frac{r_{AD}}{k_A} = P_C C_V - \frac{C_{CS}}{K_V} \approx 0 \]

\[ \therefore C_{CS} = KCP_CV \]

Evaluation of the surface concentration of adsorbed benzene (C_{BS}) using rate expression for desorption of benzene:

When surface reaction is rate controlling \( k_D \) is very large and therefore the ratio \( r_D/k_D \) is very small (approximately zero).

\[ B.S, \quad B+S \]

The rate expression for adsorption for desorption of benzene is

\[ r_D = k_D (C_{BS} - K_B P_B C_V) \]

\[ \frac{r_D}{k_D} = (C_{BS} - K_B P_B C_V) \approx 0 \]

\[ \therefore C_{BS} = K_B P_B C_V \]

Substituting \( C_{SS} \) and \( C_{BS} \) from equations

\[ r_s = k_s \left( K_C P_C C_V - \frac{P_P K_B P_B C_V}{K_s} \right) \]

\[ r_s = k_s \left( P_C K_C - \frac{K_B P_P P_B}{K_s} \right) C_V \]

For the reaction

\[ B+S \quad B+P \]

The overall partial pressure equilibrium constant \( K_P \) is
\[
K_p = \frac{P_B P_p}{P_C} = \frac{K_S K_C}{K_B}
\]

\[
r_s = k_s \left( K_C P_C - \frac{K_B P_p P_B}{K_S} \right) C_V
= k_s K_C \left( P_C - \frac{K_B P_p P_B}{K_S K_C} \right) C_V
= k_s K_C \left( P_C - \frac{P_p P_B}{K_p} \right) C_V
\]

We can not measure \( C_V \) so we will eliminate it from the above expression. In the present case a site balance is the total concentration of sites is

\[
C_t = C_v + C_{B:S} + C_{P:S}
C_t = C_v + K_C P_C C_V + K_B P_B C_V = C_V \left( 1 + K_C P_C + K_B P_B \right)
C_V = \frac{C_t}{1 + K_C P_C + K_B P_B}
\]

Substituting value of \( C_V \) from equations, we get

\[
r_s = k_s K_C C_t \left( P_C - \frac{P_p P_B}{K_p} \right)
\]

Let, \( k = k_s K_C C_t \)

\[\therefore \text{ The rate law for the catalytic decomposition of cumene, assuming the surface reaction as the rate limiting step, is} \]

\[
r'_C = r_s = \frac{k (P_C - P_p P_B / K_p)}{1 + K_C P_C + K_B P_B}
\]

Equation is the desired rate expression.

Where \( k = k_s K_C C_t \)
and \( C_t \) – total molar concentration of active sites per unit mass of catalyst and is equal to the number of active sites per unit mass divided by Avogadro’s number (mol/g.cat).
12. The mechanism of decomposition of cumene on the catalyst surface is given by,

Reaction:

\[
C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6 \\
C(g) \rightarrow B(g) + P(g)
\]

Mechanism:

1. \[C + S \overset{k_1}{\rightarrow} \text{C.S.} \rightarrow \text{adsorption}\]
2. \[\text{C.S.} \overset{k_2}{\rightarrow} \text{B.S} + P(g) \rightarrow \text{surface reaction}\]
3. \[\text{B.S} \overset{k_3}{\rightarrow} B(g) + S \rightarrow \text{desorption}\]
4. \[I + S \overset{k_4}{\rightarrow} \text{I.S.} \rightarrow \text{adsorption of inert of the surface}\]

Where the last step represents adsorption of an inhibitor I present along with reactant in the feed (I is an adsorbing inert in the feed that occupies sites on the catalyst surface). Find the rate expression if surface reaction controls.

Solution:

The overall reaction for decomposition of cumene on the catalyst surface is

\[
C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6 \\
C(g) \rightarrow B(g) + P(g)
\]

with adsorbing inert (I) in the feed the mechanism of decomposition is

1. \[C + S \overset{k_1}{\rightarrow} \text{C.S.} \rightarrow \text{adsorption of cumene on the surface}\]
2. \[\text{C.S.} \overset{k_2}{\rightarrow} \text{B.S} + P \rightarrow \text{surface reaction}\]
3. \[\text{B.S} \overset{k_3}{\rightarrow} B + S \rightarrow \text{desorption of benzene from surface}\]
4. \[I + S \overset{k_4}{\rightarrow} \text{I.S.} \rightarrow \text{adsorption of inert of the surface}\]

[While writing rate expressions for these steps we will consider each step as an elementary reaction and we will replace species concentrations in the gas phase by partial pressures of respective species].
1. Adsorption of benzene:

\[ C + S \xrightarrow{k_{A}} C.S \]

Rate expression for adsorption of cumene is

\[ r_{AD} = k_A P_C C_{v-A} C_{C.s} \quad \rightarrow (1) \]

The adsorption equilibrium constant for C is

\[ K_C = k_{A/A} \quad \rightarrow (2) \]

Combining Equation (1) and (2), we get

\[ r_{AD} = k_A \left( P_C C_v \frac{C_{C-S}}{K_C} \right) \]

Where

- \( r_{AD} \) – rate of adsorption of species C.
- \( P_C \) – partial pressure of species C in the gas phase
- \( P_i \) – partial pressure of species I in the gas phase
- \( C_{C.S} \) – surface concentration of sites occupied by species C (surface concentration of adsorbed C) in mol/g cat.
- \( C_v \) – molar concentration of vacant sites – number of vacant sites per unit mass of catalyst divided by Avogadro’s number (mol/g cat)
- \( S \) – active site and \( C.S \) – means one unit of C is adsorbed on the site S
- \( K_A \) – adsorption rate constant and \( k_{A} \) – desorption rate constant
- \( C_{i.S} \) – surface concentration of sites occupied by species I in mol/g cat

2. Surface reaction to form adsorbed benzene and propylene in the gas phase

\[ C.S \xrightarrow{k_{A}} BS + P \]

(After adsorption the adsorbed C decomposes on the site – surface reaction – single-site mechanism).

The rate of surface reaction is
\[ r_s = k_s C_{c,s} - k_s P_r C_{B,s} \]

and

\[ K_s = k_s / k_{-s} \]

\( K_s \) is the surface reaction equilibrium constant.

Combining Equation (4) and (5), we get

\[ r_s = k_s \left( C_{c,s} - \frac{P_r C_{B,s}}{K_s} \right) \]

\( P_r \) is the partial pressure of species P in the gas phase and \( C_{B,s} \) is the surface concentration of sites occupied by species B (surface concentration of adsorbed B) in mol/g cat.

3. Desorption of benzene from the surface:

\[ \text{B.S} \xrightarrow{k_{D}} \text{B + S} \]

The rate of desorption of benzene is

\[ r_D = k_D C_{B,s} - k_{-D} P_B C_v \]

And

\[ K_{DB} = k_D / k_{-D} \]

\( K_{DB} \) is the desorption equilibrium constant for benzene

Combining Equation (7) and (8), we get

\[ r_D = k_D \left( C_{B,s} - \frac{P_B C_v}{K_{DB}} \right) \rightarrow (9) \]

\( P_B \) is the partial pressure of species B in the gas phase.

The desorption of benzene is just the reverse of the adsorption of benzene.

\[ \therefore \]

\( K_B = 1 / K_{DB}, K_B \) – adsorption equilibrium constant for benzene Equation (9) then becomes,
4. Adsorption of inert (I) on the surface:

\[ \text{I} + \text{S} \xrightarrow{k_{AI}} \text{I.S} \]

The rate of adsorption of I is given by

\[ r_{ADI} = k_{AI}P_{C} - k_{-AI}C_{I.S} \quad \rightarrow (11) \]

And \[ K_{I} = k_{AI}/k_{-AI} \quad \rightarrow (12) \]

\( K_{I} \) is the adsorption equilibrium constant for I.

Combining Equation (11) and (12), we get

\[ r_{ADI} = k_{AI} \left( P_{C} - \frac{C_{I.S}}{K_{I}} \right) \quad \rightarrow (13) \]

**Given:** Surface reaction is the rate controlling step.

Now we will obtain rate equation for decomposition of cumene for the case of – surface reaction controls.

The rate expressions for the surface reaction is

\[ r_{s} = k_{s} \left( C_{C.S} - \frac{P_{C}C_{B,S}}{K_{S}} \right) \quad \rightarrow (14) \]

As we cannot measure \( C_{C.S} \) and \( C_{B.S} \) we have to replace these variables in terms of measurable quantities – partial pressure \( P_{C} \) and \( P_{B} \).

For doing this we have to make use of rate expressions for adsorption of C and desorption of B and the fact that for surface reaction as rate limiting step both \( k_{A} \) and \( k_{D} \) are very large compared with \( k_{S} \).

**Evaluation of \( C_{C.S} \) – surface concentration of adsorbed cumene:**
When surface reaction is the rate controlling step $k_A$ is large (and $k_s$ is small) and therefore the ratio $r_{AD} / k_A$ is very small (approximately zero).

$$\frac{r_A}{k_A} \approx 0 \ldots \text{if surface reaction controls.}$$

We have:

$$r_{AD} = k_A \left( P_C C_v - \frac{C_{CS}}{K_C} \right)$$

$$\frac{r_{AD}}{k_A} = P_C C_v - \frac{C_{CS}}{K_C} = 0 \ldots \text{when surface reaction controls}$$

$$\therefore \quad C_{B,S} = K_B P_B C_v \quad \rightarrow (16)$$

Substituting $C_{CS}$ and $C_{BS}$ from Equations (15) and (16) into Equation (14), we get

$$r_s = k_s \left( K_{PC} P_C C_v - \frac{P_P K_B P_B C_v}{K_s} \right)$$

$$r_s = k_s \left( P_C K_C - \frac{K_B P_P}{K_s} \right) C_v \quad \rightarrow (17)$$

For reaction: $\text{C} \rightarrow \text{B} + \text{P}$

The overall partial pressure equilibrium constant $K_P$ is

$$K_P = \frac{P_B P_P}{P_C} = \frac{K_B K_C}{K_B} \quad \rightarrow (18)$$

Equation (17) can be written as

$$r_s = k_s K_C \left( P_C - \frac{K_B P_P}{K_s K_C} \right) C_v$$

Using Equation (18) the above equation becomes

$$r_s = k_s K_C \left( P_C - \frac{P_P}{K_P} \right) C_v \quad \rightarrow (19)$$
We can not measure $C_v$ so we will eliminate it from the above expression by performing a site balance.

In the present case a site balance is (the total concentration of sites is)

$$C_t = C_v + C_{CS} + C_{BS} + C_{IS} \quad \rightarrow (20)$$

Where $C_t$ is the total molar concentration of active sites per unit mass of catalyst and is equal to the number of active sites per unit mass divided by Avogadro’s number (mol/g cat).

Now we will determine the concentration of sites occupied by the inert ($C_{IS}$) to make use of Equation (20) to eliminate $C_v$ from Equation (19).

We have,

$$r_{ADI} = k_{AI} \left( \frac{P_CP_v - C_{IS}}{K_i} \right)$$

When surface reaction is rate controlling $k_{AI}$ is very large compared to $k_A$ and therefore the ratio $r_{ADI}/k_{AI}$ is very small (approximately zero).

$$\frac{r_{ADI}}{k_{AI}} = \frac{P_CP_v - C_{IS}}{K_i} = 0$$

$$\therefore \quad C_{IS} = K_i P_CP_v \quad \rightarrow (21)$$

Putting values of $C_{CS}$, $C_{BS}$ and $C_{IS}$ from Equation (15), (16) and (21) into Equation (20), we get

$$C_t = C_v + K_CP_CC_v + K_BP_BC_v + K_IP_IC_v$$

$$C_t = (1 + K_CP_C + L_BP_B + K_IP_I)C_v$$

$$C_v = \frac{C_t}{1 + K_CP_C + K_BP_B + K_IP_I} \quad \rightarrow (22)$$

Putting value of $C_v$ from Equation (22) into Equation (19), we get

$$r_s = k_{K_CP_C} \left( \frac{P_CP_B - P_BP_B}{K_P} \right) \left( \frac{C_t}{1 + K_CP_C + K_BP_B + K_IP_I} \right)$$

$$r_s = \frac{kK_CP_CP_B}{1 + K_CP_C + K_BP_B + K_IP_I}$$
Let, \( k = k_s K_c C_t \)

\[ \therefore \text{The rate law (rate expression) for the catalytic decomposition of cumene (with an inhibitor in the feed), assuming the surface reaction as the rate controlling step, is} \]

\[ -r_c = r_s = \frac{k(P_c - P_B / K_p)}{1 + K_c P_c + K_B P_B + K_I P_I} \]

\( \rightarrow (23) \)

Where

Equation (23) is the desired rate expression for the catalytic decomposition of cumene.

Typical units of various constants are:

13. Derive the equation of rate of adsorption of cumene with adsorption of cumene as rate linking step?

To answer this question we shall assume that the adsorption of cumene is indeed rate-limiting, derive the corresponding rate law, and then check to see if it is consistent with experimental observation. By assuming that this (or any other) step is rate-limiting, we are considering that the reaction rate constant of this step (in the case \( k_A \)) is small with respect to the specific rates of the other steps (in this case \( k_s \) and \( k_D \)).

Strictly speaking one should compare the product \( K_A P_c \) with \( k_s \) and \( k_D \). (See Summary Notes for Lecture 19 on CD-ROM. The end result is the same however. The rate of adsorption is

Need to express \( C_v \) and \( C_c \) in terms of \( P_o \), \( P_B \) and \( P_p \)

\[ -r_c = r_{ad} = k_A \left( P_c C_v - \frac{C_c s}{K_c} \right) \]

Since we cannot measure either \( C_v \) or \( C_c s \). We must replace these variable in the rate law with measurable quantities for the equation to be meaningful.

For steady-state operation we have

\[ -r_c = r_{ad} = r_s = r_D \]
For adsorption limited reactions, $K_A$ is small and $k_s$ and $k_D$ are large. Consequently, the ratios $r_s/k_s$ and $r_D/k_D$ are very small (approximately zero), whereas the ratio $r_{AD}/k_A$ is relatively large. The surface reaction rate expression is

$$r_s = k_s \left( C_{c,s} - \frac{C_{B,s} P_p}{K_s} \right)$$

For adsorptions limited reactions the surface specific reaction rate $kg$ is large by comparison and we can set

$$\frac{r_s}{K_s} = 0$$

And solve Equations for $C_{c,s}$

$$C_{c,s} = \frac{C_{B,s} P_p}{K_s}$$

To be able to express $C_c$ solely in terms of the partial pressures of the species present, we must evaluate $C_{B,s}$. the rate of desorption of benzene is

$$r_D = k_D \left( C_{B,s} - K_B P_B C_v \right)$$

However, for adsorption limited reactions, $k_D$ is large by comparison and we can set.

Using $\frac{r_s}{k_s} = 0 = \frac{r_D}{K_D}$ to find $C_{B,s}$ and $C_{c,s}$ in terms of partial pressures.

$$\frac{r_D}{k_D} \neq 0$$

And then solve Equation for $C_{B,s}$:

$$C_{B,s} = K_B P_B C_v$$

After combining Equations, we have

$$C_{c,s} = K_B P_B \frac{P_p}{K_s} C_v$$

Replacing $C_{c,s}$ in the rate equation and then factoring $C_v$ We obtain

$$r_{AD} = k_A \left( P_C = \frac{K_B P_B P_p}{K_c K_c} \right) C_v = k_A \left( P_C - \frac{P_B P_p}{K_p} \right) C_v$$
Observe that by setting $r_{AD} = 0$, the term $(K_b K_c / K_b)$ is simply the overall partial pressure equilibrium constant, $K_p$ for the reaction

$$C \square B + P$$

$$\frac{K_s K_c}{K_b} = k_p$$

The equilibrium constant can be determined from thermodynamic data and is related to the change in the Gibbs free energy $\Delta G^\circ$, by the equation.

$$RT \ln K = \Delta G^\circ$$

Where $R$ is the ideal gas constant and $T$ is the absolute temperature.

The concentration of vacant sites, $C_v$, can now be eliminated from equation by utilizing the site balance to give the total concentration of sites $C_t$, which is assumed constant:

Total sites = vacant sites + occupied sites

Since cumene and benzene are adsorbed on the surface, the concentration of occupied sites is $(C_{cs} + C_{bs})$, and the total concentration of sites is

Site balance $C_i = C_v + C_{cs} + C_{bs}$

Substituting Equation into Equation, we have

$$C_i = C_v + \frac{K_b}{K_s} P_b P_v C_v + K_b P_b C_v$$

Solving for $C_v$, we have

$$C_v = \frac{C}{P_b P_v K_b / K_s + K_b P_b}$$

Combining Equations we find that the rate law for the catalytic decomposition of cumene, assuming that the adsorption of cumene is the rate-limiting step, is

Cumene reaction rate law if adsorption were limiting step

$$-r_C = r_{AD} = \frac{C_i k_s (P_c - P_b P_b / K_b)}{1 + K_b P_b / K_s + K_b P_b}$$
We now wish to sketch a plot of the initial rate as a function of the partial pressure of cumene, $P_{co}$. Initially, no product are present, consequently, $P_r = P_b = 0$. The initial rate is given by

$$-r_{co} = C_i K_c P_{co} = kP_{co}$$

In the cumene decomposition is adsorption limited, then the initial rate will be linear with the initial partial pressure of cumene as shown in figure.

Before checking to see if figure is consistent with experimental observation, we shall derive the corresponding rate laws and initial rate plots when the surface reaction is rate-limiting and then when the desorption of benzene is rate-limiting.

If adsorption were rate-limiting, the data should show $-r_0$ increasing linearly with $P_{co}$.

![Figure Uninhibited adsorption limited reaction](image)

14. Derive the equation of rate of adsorption of cumene with desorption of Benzene as rate limiting step?

The rate expression for the desorption of benzene is

$$r_D = k_D (C_{B,s} - K_B P_B C_v)$$

From the rate expression for surface reaction, equation we set

For desorption limited reactions, both $k_{AD}$ and $k_s$ are very large compared with $k_D$, which is small

$$\frac{r}{k_s} = 0$$

To obtain
\[ C_{B,s} = K_s \left( \frac{C_{c,t}}{P_p} \right) \]

Similarly, for the adsorption step, Equation we set

\[ \frac{r_{AD}}{k_A} = 0 \]

To obtain

\[ C_{c,s} - K_s P_v C_v \]

Then substitute for \( C_{c,s} \) in Equation

\[ C_{B,s} = \frac{K_c K_s P_v C_v}{P_p} \]

Combining Equation and gives us

\[ r_d = k_b K_s K_t \left( \frac{P_t}{P_p} - \frac{P_B}{K_p} \right) C_v \]

Where \( K_s \) is the cumene adsorption constant, \( K_t \) is the surface reaction equilibrium constant, and \( K_p \) is the gas-phase equilibrium constant for the reaction. To obtain an expression for \( C_v \), we again perform a site balance.

**Site balance**  \[ C_t = C_{c,s} + C_{B,s} + C_v \]

After substituting for the respective surface concentrations, we solve the site balance for \( C_v \)

\[ C_v = \frac{C_t}{1 + K_c K_s P_c / P_p + K_c P_c} \]

Replacing \( C_v \) in Equation by Equation and multiplying the numerator and denominator by obtain the rate expression for desorption control

**Cumene decomposition rate law if adsorption were limiting**

\[ -r_x = r_d = \frac{k B C_t K_s K_C \left( P_t - P_B P_p / K_p \right)}{P_p + P_c K_c K_s + K_c P_p P_c} \]
To determine the dependence of the initial rate on partial pressure of cumene, we again set \( P_r = P_b = 0 \); and the rate law reduces to

If desorption controls, the initial rate is independent of partial pressure of cumene

\[-r_{c_0} = k_D C_i\]

With the corresponding plot of \(-r_{c_0}\) shown in figure. If desorption were controlling, we would see that the initial would be independent of the initial partial pressure of cumene.

15. Derive the equation of rate of reaction of cumene with surface reaction as rate limiting step?

The rate of surface reaction is

\[ r_s = k_s \left( C_{c,s} - \frac{P_s C_{b,s}}{K_s} \right) \]

Since we cannot readily measure the concentration of the adsorbed species, we must utilize the adsorption and desorption steps to eliminate \( C_{c,s} \) and \( C_{b,s} \) from this equation.

From the adsorption rate expression in Equation and the conditions that \( k_A \) is large by comparison when surface reaction is controlling (i.e. \( r_{AD} / k_A \ll 0 \)). We obtain a relationship for the surface concentration for adsorbed cumene.

\[ C_{c,s} = K_c P_i C_v \]

In a similar manner, the surface concentration of adsorbed benzene can be evaluated from the desorption rate expression [Equation ] together with the approximation.

Using \( \frac{r_{AD}}{k_A} \approx 0 \approx \frac{r_D}{k_D} \) to find \( C_{b,s} \) and \( C_{c,s} \) in terms of partial pressures.

When \( \frac{r_D}{k_D} \approx 0 \) then \( C_{b,s} = K_b P_b C_v \)

Substituting for \( C_{b,s} \) and \( C_{c,s} \) in Equation gives us

\[ r_s = k_s \left( P_c K_c - \frac{K_b P_b P_p}{K_s} \right) C_v = k_s K_c \left( P_c - \frac{P_b P_p}{K_p} \right) C_v \]
The only variable left to eliminate is $C_v$:

**Site balance**

$$C_v = C_v + C_{B,s} + C_{c,s}$$

Substituting for concentrations of the adsorbed species, $C_{B,s}$ and $C_{c,s}$ yields

$$C_v = \frac{C}{1 + K_B P_B + K_c P_C}$$

**Cumene rate law for surface reaction-limiting**

$$-r_C = r_s = \frac{k}{k} \overline{C_B} \overline{C_C} \left( P_C - P_B K_B / K_P \right)$$

$$1 + P_B K_B + K_c P_C$$

The initial rate is

$$-r_{CO} = \frac{k}{k} \overline{C_C} \overline{K_C} P_{CO} = \frac{k P_{CO}}{1 + K_c P_{CO}}$$

At low partial pressure of cumene

$$1 \overline{K_C P_{CO}}$$

And we observe that the initial rate will increase linearly with the initial partial pressure of cumene.

$$-r_{CO} \approx k P_{CO}$$

At high partial pressures

$$K_c P_{CO} \approx 1$$

And Equation becomes

$$-r_{CO} \approx \frac{K_{PCO}}{K_c P_{CO}} = \frac{k}{K_c P_{CO}}$$

And the rate is independent of the partial pressure of cumene. Figure shows the initial rate of reaction as a function of initial partial pressure of cumene for the case of surface reaction controlling.
If surface reaction were rate-limiting, the data would show this behaviour.

Figure Surface-reaction limited.
1. Explain Knudsen diffusion. (NOV/DEC 2013)

If the pore size of a solid catalyst is small and as the gas is less dense, then in such cases, molecules collide more frequently with the catalyst pore walls as compared to collisions among each other. This type of diffusion phenomena is called Knudsen diffusion.

2. Distinguish between Knudsen diffusion and Bulk diffusion.

Bulk diffusion occurs when the pores of a solid catalyst are considerably large and the gas is relatively dense or if the pores are filled with liquid. If the pore size of a solid catalyst is small and as the gas is less dense, then in such cases, molecules collide more frequently with the catalyst pore walls as compared to collisions among each other. This type of diffusion phenomena is called Knudsen diffusion. When the reaction mixture in the pore is liquid, Knudsen diffusion does not occur.

3. Write short notes on surface diffusion.

The transport by movement of adsorbed molecules over the catalyst surface is called Surface Diffusion. The direction of diffusion is that of the increasing surface concentration. Surface diffusion contributes little to overall transport through a porous mass unless appreciable adsorption occurs.


In a porous catalyst, the pores in a catalyst are not straight and they follow tortuous (zig-zag), interconnecting paths having varying cross sectional area. To account this variation, effective diffusivity is considered. Effective diffusion coefficient accounts for the average diffusion taking place at any position in the catalyst pellet and it is the function of both bulk diffusivity and Knudsen diffusivity. It is denoted by ‘De’. Effective diffusivities in porous catalysts are usually measured under conditions where the pressure is maintained constant by external means.

5. What is a Parallel pore model?

This is a geometric model of the pore system, used to convert ‘D’ to ‘De’ for the porous pellet. It is the model based on the properties (ρs, Vg, εp), to represent the mono-disperse pore-size distribution in a catalyst pellet. By this model, the effective diffusivity is \( D_e = \varepsilon D / \delta \). Where ‘\( \delta \)’ is the tortuosity factor, ‘\( \varepsilon \)’ is the porosity of the pellet and ‘\( D \)’ is the diffusivity (in the absence of surface diffusion).

6. What is Random pore model?

This model was originally developed for pellets containing a bi-disperse pore system (considering both Macro and Micro pores) to convert ‘D’ to ‘De’. By this model, the effective diffusivity is
De = \([\varepsilon_M^2] D_M + [\varepsilon_\mu^2 (1 + 3 \varepsilon_M)/(1 - \varepsilon_M)] D_\mu\)

Where \(D_M\) & \(D_\mu\) are the diffusivities for macro and micro pore regimes and \(\varepsilon_M\) & \(\varepsilon_\mu\) are the porosities for the macro and micro pore regimes.

7. What are the resistances in porous catalyst?

The resistances in porous catalyst are;

- Resistance offered by the diffusion of reactants (gas or liquid) into the pores of the solid catalyst (Pore diffusion resistance or diffusional mass transfer resistance)
- Resistance offered by the resultant rate equation for the surface phenomena (Reaction resistance)


It is a dimensionless number (denoted by ‘\(M_T\) or \(\Phi\)’), defined as the ratio of the intrinsic chemical reaction rate in the absence of mass transfer limitation to the rate of diffusion through the particle. Thiele Modulus is useful in predicting the reactor behavior from known kinetic information.

The Thiele modulus was developed by Ernest Thiele in his paper ‘Relation between catalytic activity and size of particle’ in 1939. Thiele reasoned that with a large enough particle, the reaction rate is so rapid that diffusion forces are only able to carry product away from the surface of the catalyst particle. Therefore, only the surface of the catalyst would be experiencing any reaction. The Thiele Modulus was then developed to describe the relationship between diffusion and reaction rate in porous catalyst pellets with no mass transfer limitations. This value is generally used in determining the effectiveness factor for catalyst pellets.

\[\text{Thiele modulus} = \frac{\text{Reaction rate}}{\text{Diffusion rate}}\]


The effectiveness factor (denoted by ‘\(\eta\)’) is defined as the ratio of actual rate for the whole pellet to the rate evaluated at outer surface conditions. (OR) It is the ratio of reaction rate with diffusion to the rate without diffusion resistance.

The effectiveness factor \(\eta\) relates the diffusive reaction rate with the rate of reaction in the bulk stream. For a first order reaction in a slab geometry, this is:

\[\eta = \tanh \frac{h_T}{h_T}\]

10. Explain the significance of effectiveness factor.

For diffusion in single cylindrical pore, follows a first order kinetics, the effectiveness factor is \(\eta = \tanh (\Phi_L) / \Phi_L\) Where ‘\(\Phi_L\)’ is the Thiele modulus and is given by \(\Phi_L = L / (k \rho_p / D_e)^{1/2}\)

‘\(L\)’ is the thickness of cylindrical pore.

For small \(\Phi_L (\Phi_L < 0.4)\), \(\eta \approx 1\), the concentration of reactant does not drop appreciably within the pore; thus pore diffusion offers negligible resistance. For large \(\Phi_L (\Phi_L > 4)\), \(\eta = 1/\Phi_L\), the reactant concentration drops rapidly to zero on moving into the pore, hence diffusion strongly influences the rate of reaction.

11. What is the effect of catalyst pellet size on the effectiveness factor?
In the regime of strong diffusion resistance, the rate (thus the effectiveness factor) varies inversely proportional to the catalyst pellet size. So, increase in pellet size will decrease the value of effectiveness factor and vice-versa.

12. **Can effectiveness factor of a catalyst be greater than one? Explain.**

Yes. For exothermic reactions (only), where pore resistance just begins to intrude, the effectiveness factor can become greater than unity; because heat is released and catalyst particles are hotter than the surrounding fluid. (Hence, non-isothermal rate is always greater than the isothermal rate as measured by the bulk fluid stream conditions).

13. **‘In a catalyst pellet, if the rate of diffusion through the pores is much higher than the rate of reaction, then the value of Thiele modulus will approach unity’. Justify this statement.**

By the definition, we know that the Thiele modulus is the ratio of the intrinsic chemical reaction rate in the absence of mass transfer limitation to the rate of diffusion through the particle. If the rate of diffusion through the pores (denominator term) is much higher than the rate of reaction (numerator term), then the value of Thiele modulus will approach unity.

14. **Write short notes on ‘Non-isothermal effectiveness factor’.**

For an exothermic reaction, the temperature rises going into the pellet, the increase in rate of reaction accompanying the temperature rise can more than offset the decrease in rate due to drop in reactant concentration. Then \( \eta > 1 \) increase the rate per pellet, and therefore the production per unit mass of catalyst, there may also be some disadvantages. With larger \( \eta \) there will be a large increase in temperature toward the center of the pellet, resulting in sintering and catalyst deactivation. The desired product may be subject to further reaction of unwanted product or undesirable side reactions may occur. If these reactions have higher activation energies than the desired reaction, the rise in temperature would reduce selectivity. For an endothermic reaction, there is a decrease in temperature and rate into the pellet. Hence \( \eta \) is always less than unity. Since the rate decreases with drop in temperature, the effect of heat-transfer resistance is diminished.

15. **Explain ‘Wagner Modulus’.**

It is the modulus which accounts the pore resistance effects on the solid catalyzed reaction, which is given by \( M_w = M_T^2 \eta = L^2 (-r_A^\parallel / C_A)_{obs} / D_e \) Where \( M_T \) is the Thiele modulus, \( \eta \) is the effectiveness factor, \( L \) is the characteristic size of the catalyst, \( (-r_A^\parallel) \) is the reaction rate based on the volume of the catalyst pellet, \( C_A \) is the fluid concentration at absolute conditions and \( D_e \) is the effective diffusivity.

16. **When is it said that a reaction follows ideal mechanism in gas-solid catalytic reactions**

If \( \eta \rightarrow 1 \) (\( M_T \) or \( \Phi \) is large enough) then it is said that the gas solid catalytic reaction follows ideal mechanism. That is, this condition means that diffusion into the pellet is relatively slow, so that reaction occurs before the reactant has diffused far into the pellet.
17. **What is Channeling?**

When the gas is not evenly distributed in the catalyst bed cross section and is concentrated in channels through the catalyst bed, the phenomena is called as Channeling of fluidized bed.

18. **Define Effective thermal conductivity.** (NOV/DEC 2013)

The effective thermal conductivity (ke) is the energy transferred per unit of total area of pellet (perpendicular to the direction of heat transfer).

19. **Compare fixed and fluidized - bed reactors for gas-solid catalytic operation.**

- It is not possible to use fine size catalyst particles in fixed bed reactor. This results in plugging and high pressure drop. High pressure increases the operating cost.

- It is possible to use fine size catalyst particles in fluidized bed reactor. Fine size particles provide large interfacial / contact area.

- Catalyst regeneration can be a problem in fixed bed reactor. If the regeneration needs to be frequently done, this problem will be bottleneck in operation.

- Catalyst particle regeneration is quite easy in fluidized bed reactors. If the regeneration needs to be done frequently, the catalyst particles can be entrained with the product stream, separated in cyclone separator and then sent to the regenerator.

20. **List some of the problems that would be encountered in the operation of a fluidized catalytic reactor.**

In operation of a fluidized catalytic reactor, some difficulties can occur. They are;

- Slugging: When the gas passes up through the catalyst bed in the form of large gas bubbles, it is called as Slugging of fluidized bed.

- Channeling: When the gas is not evenly distributed in the catalyst bed cross section and is concentrated in channels through the catalyst bed, the phenomena is called as Channeling of fluidized bed.

21. **What is effective diffusivity?** (Nov/Dec 2016) (or) **Express the relationship between diffusion coefficient and effective diffusivity with units.** (Nov/Dec 2017)

The pores in the pellet are not straight and cylindrical; rather, they are a series of tortuous, interconnecting paths of pore bodies and pore throats with varying cross-sectional areas. It would not be fruitful to describe diffusion within each and every one of the tortuous pathways individually; consequently, we shall define an effective diffusion coefficient so as to describe the average diffusion taking place at any position r in the pellet. Consider only radial variations in the concentration; the radial flux $W_{Ar}$ will be based on the total area (voids and solid) normal to diffusion transport (i.e., $4\pi r^2$) rather than void area alone. This basis for $W_{Ar}$ is made possible by proper definition of the effective diffusivity $D_e$.

The effective diffusivity accounts for the fact that:

1. Not all of the area normal to the direction of the flux is available (i.e., the area occupied by solids) for the molecules to diffuse.
2. The paths are tortuous.

3. The pores are of varying cross-sectional areas. An equation that relates $D_e$ to either the bulk or the Knudsen diffusivity is

$$D_e = \frac{D_{AB} \phi_p \sigma_c}{\tau}$$

where

$$\tau = \text{tortuosity} = \frac{\text{Actual distance a molecule travels between two points}}{\text{Shortest distance between those two points}}$$

$$\phi_p = \text{pellet porosity} = \frac{\text{Volume of void space}}{\text{Total volume (voids and solids)}}$$

$$\sigma_c = \text{Constriction factor}$$

The constriction factor, accounts for the variation in the cross-sectional area that is normal to diffusion. It is a function of the ratio of maximum to minimum pore areas.

22. What is effective thermal conductivity? Explain. (Apr/May 2017)

The effective thermal conductivity of each layer is the weighted arithmetic mean of solid and fluid conductivities as follows:

$$K_{eff} = \varepsilon k_f + (1-\varepsilon) k_s$$

In order to simplify, $K_{eff}$ is formulated based on the following nondimensionless relationships:

$d = R/L$

$e = r/L$


<table>
<thead>
<tr>
<th>S.No.</th>
<th>Fluidized bed Reactor</th>
<th>Mixed flow Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fluidized bed reactor (FBR) is a type of reactor device that can be used to carry out a variety of multiphase chemical reactions.</td>
<td>MFR is also called CSTR and usually are equipped with an agitating device (stirrer, agitator) for mixing the reactants.</td>
</tr>
<tr>
<td>2</td>
<td>In this type of reactor, a fluid (gas or liquid) is passed through a granular solid material (usually a catalyst possibly shaped as tiny spheres) at high enough velocities to suspend the solid and cause it to behave as though it were a fluid.</td>
<td>MFR composition of the reactant mixture is uniform throughout the reactor and same as that in the exit line MFR can be both batch or continuous.</td>
</tr>
</tbody>
</table>
| 3     | **Advantages**  
The increase in fluidized bed reactor use in today's industrial world is largely due to the inherent advantages of the technology.  
   a) Uniform Particle Mixing  
   b) Uniform Temperature Gradients  
   c) Ability to Operate Reactor in Continuous State | **Advantages**  
a) Easy in controlling temperature in each stage since each operates in a stationary state  
b) This reactor can be readily adapted for automatic controlling general that allowing fast response to changes in operating conditions for examples, feed rate and its concentration. |
4 Disadvantages
   a) As in any design, the fluidized bed reactor does have its drawbacks, which any reactor designer must take into consideration.
   b) Increased Reactor Vessel Size:
   c) Particle Entrainment:
   d) Lack of Current Understanding:
   e) Erosion of Internal Components:
   f) Pressure Loss Scenarios:

Disadvantages
   a) For this reactor is its conversion per unit volume of the reactor is smallest compared to other flow reactors
   b) Principle stems from the fact that the outlet stream is the same as the contents of the vessel. This implies that all reaction takes place at the lowest concentration (of reactant A, say, cA) between inlet and outlet.
   c) For normal kinetics, in which reaction rate (rA) decreases as cA decreases, this means that a greater volume of reactor is needed to obtain a desired conversion.

25. Define effectiveness factor for diffusion through the catalyst pores.

The magnitude of the effectiveness factor (ranging from 0 to 1) indicates the relative importance of diffusion and reaction limitations. The internal effectiveness factor is defined as

\[
\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As}, T_s}
\]  

(12-28)

The overall rate, \(-r_A^\prime\), is also referred to as the observed rate of reaction \([-r_A^{\text{obs}}]\). In terms of symbols, the effectiveness factor is

\[
\eta = \frac{-r_A}{-r_{As}} = \frac{-r_A^\prime}{-r_{As}^\prime} = \frac{-r_A^{\text{obs}}}{-r_{As}^{\text{obs}}}
\]

To derive the effectiveness factor for a first-order reaction, it is easiest to work in reaction rates of (moles per unit time), \(M_A\), rather than in moles per unit time per volume of catalyst (i.e., \(-r_A\))

\[
\eta = \frac{-r_A}{-r_{As}} = \frac{-r_A \times \text{Volume of catalyst particle}}{-r_{As} \times \text{Volume of catalyst particle}} = \frac{M_A}{M_{As}}
\]

First we shall consider the denominator, \(M_{As}\). If the entire surface were exposed to the concentration at the external surface of the pellet, \(C_{As}\), the rate for a first-order reaction would be

\[
M_{As} = \frac{\text{Rate at external surface}}{\text{Volume}} \times \text{Volume of catalyst}
\]
PART – B

1. With a neat sketch explain how to obtain the diffusivity of a catalyst pellet?

Considerable experimental data has been accumulated for effective diffusivities in gas-filled pores. Since reactors normally are operated at steady state and nearly constant pressure, diffusivities have also been measured under these restraints. The usual apparatus is of the steady-flow type, illustrated in figure for studying diffusion rates of H₂ and N₂. The effective diffusivity is defined in terms of such rates (per unit of total cross-sectional area) by the equation.

\[
(N_A)_e = -D_e \frac{dC_A}{dr} = -\frac{\rho}{R_s T} D_e \frac{dy_A}{dr}
\]  

... (1)

Where the subscript e on \( N_A \) emphasizes that this is a diffusion flux in a porous catalyst rather than for a single pore, as given by Eq. (11-1). If we use the concentration-independent diffusivity \( D \) given by Eq. \( D_e \) for a porous pellet will also be constant. Then Eq. can be integrated to give

\[
(N_A)_e = -\frac{\rho}{R_s T} D_e \frac{(y_A)_2 - (y_A)_1}{\Delta r}
\]  

... (2)

Where \( \Delta r \) is the length of the pellet. If the flow rates and concentrations are measured for the experiment pictured in figure, \( (N_A)_e \) can be calculated. Then this flux and the measured concentrations and pellet length are substituted in eq. to obtain an experimental effective diffusivity.

A- Mixing chambers
C- Detector for determining composition of N₂, in H₂ stream
D- Detector for determining composition of H₂ in N₂ stream
E- Flow meters
P- Catalyst pellet
G- Pressure equalization gauge

**Figure: Constant pressure apparatus for measuring diffusion rates in porous catalysts.**

Dynamic methods have also been used to measure $D_e$. For example, a pulse input of diffusing component A can be inserted into a stream of helium flowing through the upper chamber as indicated in figure. Pure helium also flows through the lower chamber. Some of the pulse of A diffuses through the pellet and is measured as a response pulse at the detector in the lower stream. For high flow rates of a nonadsorbing component, the effective is given by

$$D_e = \frac{(\Delta r)^2 \epsilon_p}{6\mu_1} \quad \ldots(3)$$

Here, $\mu_1$ is the first moment (retention time) of the diffusing component in the pellet. It is obtained from the measured response pulse $C_A(t)$ by the equation.

$$\mu_1 = \frac{\int_0^\infty C_A(t) t \, dt}{\int_0^\infty C_A(t) \, dt} \quad \ldots(4)$$

Where $C_A(t)$ = Concentration (function of time, t) in the response pulse

$\epsilon_p$ = porosity of pellet

$\Delta r$ = length of pellet

Other equations have been developed, both for adsorbing components and for lower flow rates across the pellet faces.

Comparison of diffusivities from steady-state and dynamic experiments can, in principle, provide information about pore structure. For example, dead-end pores should not affect diffusion at steady state, but would influence the results in dynamic experiments. Actually, uncertainties of experimental results have prevented, as yet, meaningful comparisons. Another method of evaluating effective diffusivities, provided the rate equation for the chemical step is known, is the comparison of the observed and predicted global rates by combining the equation for the chemical step with the intraparticle mass-transport resistance (see example for a variation of this method).
In the absence of experimental data it is necessary to estimate $D_e$ from the physical properties of the catalyst. In this case the first step is to evaluate the diffusivity for a single cylindrical pore, that is, to evaluate $D$ from Equation. Then a geometric model of the pore system is used to convert $D$ to $D_e$ for the porous pellet. A model is necessary because of complexity of the geometry of the void spaces. The optimum model is a realistic representation of the geometry of the voids (with tractable mathematics) that can be described in terms of easily measurable physical properties of the catalyst pellet. As noted in Chapter, these properties are the surface area and pore volume per gram, the density of the solid phase, and the distribution of void volume according to pore size.

2. Describe the parallel pore and Random pore model?

The Parallel-pore Model Wheeler proposed a model, based on the first three of these properties, to represent the monodisperse pore-size distribution in the catalyst pellet. From $\rho_s$ and $V_0$ the porosity $\epsilon_p$ is obtained from equation. Then a mean pore radius $\bar{a}$ is evaluated by writing equations for the total pore volume and total pore surface in a pellet. The result, developed as Equation, is

$$\bar{a} = \frac{2V_0}{S_0} \quad \text{(1)}$$
By using $V_0$, $S_0$ and $\rho_0$, Wheeler replaced the complex porous pellet with an assembly (having a porosity, $\varepsilon_0$) of cylindrical pores of radius $\bar{a}$. To predict $D_e$ from the model the only other property necessary is the length $x_L$ of the diffusion path. If we assume that, on the average, the pore make an angle of 45° with the coordinate $r$ in the resultant direction of diffusion (for example, the radial direction in a spherical pellet), $x_L = \sqrt{2} r$. Owing to pore interconnections and non-cylindrical shape, this value of $x_L$ is not very satisfactory. Hence, it is customary to define $x_L$ in terms of an adjustable parameter, the tortuosity factor $\delta$, as follows:

$$X_L = \delta r$$

An effective diffusivity can now be predicted by combining Eq. for a single pore with this parallel-pore mode. To convert $D$, which is based on the cross-sectional area of the pore, to a diffusivity based upon the total area perpendicular to the direction of diffusion, $D$ should be multiplied by the porosity. In equation, $x$ is the length of a single, straight cylindrical pore. To convert this length to the diffusion path in a porous pellet $x_L$ from Equation should be substituted for $x$. With these modifications the diffusive flux in the porous pellet will be

$$(N)_e = -\frac{\rho}{R T} \frac{\varepsilon D}{\delta} \frac{\partial y}{\partial r} \quad \text{..(2)}$$

Comparison with Eq. shows that the effective diffusivity is

$$D_e = \frac{\varepsilon D}{\delta} \quad \text{..(3)}$$

Where $D$ is given (in the absence of surface diffusion) by Eq. The use of Equation to predict $D_e$ is somewhat limited because of the uncertainty about $\delta$. Comparison of $D_e$ from equation with values obtained from experimental data for various catalysts using Eq. shows that $\delta$ varies from less than unity to more than 6.

**The Random-Pore Model**

This model was originally developed for pellets containing a bidisperse pore system, such as the alumina described in chapter. It is supposed that the pellet consists of an assembly of small particles. When the particles themselves contain pores (micropores), there exists both a macro and a micro void-volume distribution. The voids are not imagined as capillaries, but more as an assembly of short void regions surrounding and between individual particles, as indicated in figure. The nature of the interconnection of macro and micro void regions is the essence of the
model. Transport in the pellet is assumed to occur by a combination of diffusion through the macro regions (of void fraction $\varepsilon_M$), the micro regions (of void fraction $\varepsilon_\mu$), and a series contribution involving both regions. It is supposed that both macro and micro regions can be represented as straight, short cylindrical pores of average radii $\bar{a}_M$ and $\bar{a}_\mu$. The magnitude of the individual contributions is dependent on their effective cross-sectional areas (perpendicular to the direction of diffusion). The details of the development are given elsewhere, but in general these areas are evaluated from the probability of pore interconnections. The resultant expression for $D_e$ may be written.

$$D_e = \bar{D}_M \varepsilon_M^2 + \varepsilon_\mu^2 \left(\frac{1 + 3\varepsilon_M}{1 - \varepsilon_M}\right) D_\mu \quad \text{...(4)}$$

Here $\bar{D}_M$ and $\bar{D}_\mu$ are obtained by applying Eq. to macro and micro regions. Thus

$$\frac{1}{D_M} = \frac{1}{D_{AB}} + \frac{1}{(D_K)_M} \quad \text{...(5)}$$

$$\frac{1}{D_\mu} = \frac{1}{D_{AB}} + \frac{1}{(D_K)_\mu} \quad \text{...(6)}$$

No tortuosity factor is involved in the mode. The actual path length is equal to the distance coordinate in the direction of diffusion. To apply Equation requires void fractions and mean pore radii for both macro and micro regions. The mean pore radii can be evaluated for the micro region by applying Equation to this region. However, $\bar{a}_M$ must be obtained from the pore-volume distribution as described in sec. The mean pore radii are necessary in order to calculate $(D_K)_M$ and $(D_K)_\mu$ from Equation. Thus the random-pore model does not involve an adjustable parameter.

Figure: Random-pore model.
The random-pore model can also be applied to monodisperse systems. For a pellet containing only macropores, $\varepsilon_\mu = 0$ and Equation becomes

$$D_\varepsilon = \bar{D}_M \varepsilon_M^2 \quad \ldots(7)$$

Similarly, for a material such as silica gel, where $\varepsilon_M = 0$, the effective diffusivity is

$$D_\varepsilon = \bar{D}_\mu \varepsilon_\mu^2 \quad \ldots(8)$$

Comparison of these last two equations with Eq. indicates that $\delta = 1/\varepsilon$. The significance of the random-pore model is that the effective diffusivity is proportional to the square of the porosity. This has also been proposed by Weisz and Schwartz. Johnson and Stewart have developed another method for predicing $D_e$ that utilizes the pore-volume distribution. Evaluation of their model and random-pore model with extensive experimental data has been carried out by Satterfield and Cadles and Brown et al.

3. Explain surface diffusion in a catalyst pellet?

Surface Diffusion

Surface migration is pertinent to a study of intrapellet mass transfer if its contribution is significant with respect to diffusion in the pore space at reaction temperature. When multimolecular layer adsorption occurs, surface diffusion has been explained as a flow of the outer layers as a condensed phase. However, surface transport of interest in relation to catalyst reaction occurs in the monomolecular layer. It is more appropriate to consider, as proposed by deBoer, that such transport is an activated process, dependent on surface characteristics as well as those of the adsorbed molecules. Imagine that a molecule in the gas phase strikes the pore wall and is adsorbed. Then two alternatives are possible: desorption into the gas or movement to an adjacent active site on the pore wall and is adsorbed. Then two alternatives are possible: desorption into the gas or movement to an adjacent active site on the pore wall (surface diffusion). If desorption occurs, the molecule can continue its journey in the void space of the pore or be readorsed by again striking the wall. In moving along the wall, the same molecule would be transported sometimes on the surface and sometimes in the gas phase. If this view is correct, the relative contribution of surface migration would increase as the surface area increases for the pore size decreases). There is evidence to indicate that such is the case.
Experimental verification of surface diffusion is usually indirect, since concentrations of adsorbed molecules on a surface are difficult to measure. When gas concentrations are obtained, the problem arises of separating the surface and pore-volume transport rates. One solution is to measure both $N_A$ and $N_B$ in the apparatus shown in figures, using a nonadsorbable gas for A. If the diffusion rate of B is greater than that calculated from $N_A$ by Equation, the excess is attributable to surface migration. Barrer and Barrier used this procedure with Vycor at room temperature and found surface migration significant for such gases as CO$_2$, CH$_4$, and C$_2$H$_4$ and negligible for helium and hydrogen. Rivarolas found that for CO$_2$ the surface contribution on an alumina pellet increased from 3.5 to 54% of the total mass-transfer rate as the macropore properties changed from $a_M = 1.710$ and $\varepsilon_M = 0.33$ to $a_M = 348$ and $\varepsilon_M = 0.12$

By analogy to Fick’s law, a surface diffusivity $D_s$ may be defined in terms of a surface concentration $C_s$ in moles of adsorbate per square centimeter of surface.

$$N_s = D_s \frac{dC_s}{dx} \quad ...(1)$$

Where $N_s$ is the molal rate per unit perimeter of pore surface. In order to combine surface and pore-volume contributions in a catalyst pellet, the surface flux should be based on the total area of the catalyst perpendicular to diffusion and on the coordinate $r$. If this flux is $(N_s)_e$, then

$$(N_s)_e = -D_s \rho_p \frac{dC}{dr} \quad ...(2)$$

Where $\rho_p$ is the density of the catalyst and $C$ now represents the moles adsorbed per gram of catalyst. To be useful, Equation must be expressed in terms of the concentrations in the gas phase. If the adsorption step is fast with respect to surface transfer from site to site on the catalyst, we may safely assume equilibrium between gas and surface concentration. Otherwise the relation between the two concentrations depends on the intrinsic rates of the two processes. If equilibrium is assumed, and if the isotherm is linear, then

$$\bar{C}_A = \left( K_A \bar{C}_m - C_s \right) = K' \frac{D_p \gamma_A}{R_g T} \quad ...(3)$$

Where the subscript A refers to the adsorbate and $K'$ is the linear form of the equilibrium constant, in cubic centimeters per gram. The latter is obtained from the
Langmuir isotherm. Equation, when adsorption is small enough that the linear form is valid. Now, applying Equation to component A.

\[
(N_A)_e = -\frac{D_s}{R_g T} \rho_p K'_A D_s \frac{dy_A}{dr} \quad \ldots(4)
\]

Equation gives the surface diffusion of A in the same form as Eq. applied earlier to transport in the gas phase of the pores. From these equations the total flux and total effective diffusivity are given by

\[
(N_A)_t = -\frac{D_e}{R_g T} (D_e + \rho_p K'_A D_s) \frac{dy_A}{dr} \quad \ldots(6)
\]

\[
(D_e)_t = D_e + \rho_p K'_A D_s \quad \ldots(7)
\]

If the density of the catalyst and the adsorption equilibrium constant are known. Equation permits the evaluation of a total effective diffusivity from \(D_s\). Data for \(D_s\) have been reported in the literature in a variety of ways, depending on the definitions of adsorbed concentrations and equilibrium constants. Schneider has summarized much of the information for light hydrocarbons on various catalysts in the form defined by Eq. such \(D_s\) values ranged from \(10^{-3}\) to \(10^{-6}\), depending on the nature of the adsorbent and the amount adsorbed. Most values were in the interval \(10^{-4}\) to \(10^{-5}\) cm\(^2\)/s. Data for other adsorbates have similar magnitudes and show that the variation with adsorbed concentration can be large.

The effect of temperature on \(D_s\), given an activated process, is described by an Arrhenius type expression.

\[
D_s = A e^{-E_s / R_g T}
\]

Where \(E_s\) is the activation energy for surface diffusion. The variation of \(K'_A\) with temperature is given by van't Hoff equation.

\[
\frac{d \ln K'_A}{dT} = \frac{\Delta H}{R_g T^2}
\]

or

\[
K'_A = A'_s - \Delta H / R_g T
\]

The observed rate of surface diffusion, according to Eq. will be proportional to the product \(K'_A D_s\). Substituting the above expression for \(K'_A\) and \(D_s\) in Equation.
\[
(N_s)_e = -\frac{\rho}{RT} \rho_p (AA') e^{-\left(\frac{1}{RT}\right)(\Delta H + E_s)} \frac{\rho}{dr}
\]

The exponential term express a much stronger temperature dependency than the coefficient \(1/T\). If we neglect the latter, we may express the temperature effect on the rate as

\[
(N_s)_e = -A'' e^{-\left(\frac{1}{RT}\right)(\Delta H + E_s)}
\]

where

\[
A'' = AA' \frac{\rho}{dr} \frac{\rho}{RT} \rho_p
\]

This equation shows that the observed or apparent activation energy for surface diffusion is related to \(E_s\) by

\[
E' = \Delta H + E_s \quad \text{(8)}
\]

From available data it appears that \(E_s\) is only a few kilocalories per mole. The heat of adsorption \(\Delta H\) is generally greater than this, particularly for chemisorption, and is always negative. Therefore the observed effect is a decrease in rate of surface diffusion with increase in temperature. Note that \(\Delta H\) is negative.

From the assumption and approximation presented, it is clear that surface diffusion is not well understood. It is hoped that improved interpretations of surface migration will permit a more accurate assessment of its effect on global rates of reaction. When we consider the effect of intraparticle resistances in secs. We shall suppose that the \(D_e\) used is the most appropriate value and includes, if necessary, a surface contribution.

4. Explain the concept of effective Thermal Conductivity

Concept of Effective Thermal Conductivity

The effective thermal conductivities of catalyst pellets are surprisingly low. Therefore significant intrapellet temperature gradients can exist, and the global rate may be influenced by thermal effects. The effective conductivity is the energy transferred per unit of total area of pellet (perpendicular to the direction of heat transfer). The defining equation, analogous to Eq. (11) for mass transfer, may be written.
\[ Q_e = -k_e \frac{dT}{dr} \quad \ldots(1) \]

Where \( Q_e \) is the rate of energy transfer per unit of total area.

A major factor contributing to small values of \( k_e \) is the numerous void spaces that hinder the transport of energy. In addition, the path through the solid phase offers considerable thermal resistance for many porous materials, particularly pellets made by compressing microporous particles. Such behavior is readily understood if these materials are viewed as an assembly of particles which contact each other only through adjacent points. There is strong experimental evidence that such point contacts are regions of high thermal resistance. For example, the thermal conductivity of the bulk solid (zero porosity) from which the particles are prepared does not have a large effect on \( k_e \). Masume found that the effective thermal conductivity of pellets of microporous particles of silver was only two to four times that of alumina pellets, at the same macropore void fraction, pressures and temperature. In contrast, the thermal conductivity of solid silver is about 200 times as large as that of solid alumina. Furthermore, \( K_e \) is a strong function of the void fraction, increasing as \( \varepsilon_p \) decreases. Materials such as alumina pellets may be regarded as a porous assembly within a second porous system. Each particle from which the pellet is made contains a microporous region. These particles are in point contact with like particles and are surrounded by macroporous regions. When viewed in the way, the thermal conductivity of the bulk solid should have little influence on \( k_e \).

The pressure and nature of the fluid in the pores has an effect on the effective thermal conductivity. With liquids the effect of pressure is negligible and \( k_e \) is of the same magnitude as the true conductivity of the liquid. For gases at low pressures, where the mean free path is the same or larger than the pore size free molecule conduction controls the energy transfer. In this region \( k_e \) increases with pressure. At higher pressures \( k_e \) is about independent of pressure. The transition pressure depends on the gas as well as on the pore size. For air the transition pressure is about 470 mm in a silver pellet with mean pore diameter of 1500 A. For helium the value would be above 760 mm. For alumina pellets, at 120°F and a macropore void fraction of \( \varepsilon_{M\%} = 0.40 \), \( k_e \) was 0.050 in vacuum, 0.082 with pores filled with air, and 0.104 Btu/(h)(ft)(°F) with helium, at atmospheric pressure. Temperature does not have a strong influence. The effect is about what would be expected for the combination of variations of thermal conductivity with temperature for the solid and fluid phases.
5. What are the reasons for not able to predict diffusion rates by correcting bulk phase diffusivities?

Intrapellet Mass Transfer

It is seldom possible to predict diffusion rates in porous materials by simply correction bulk-phase diffusivities for the reduction in cross-sectional area due to the solid phase. There are several reasons for this:

1. The tortuous, random, and interconnected arrangement of the porous regions makes the length of the diffusion path unknown.
2. The diffusion in the pore volume itself will be influenced by the pore walls, provided the diffusing molecule is likely to collide with a wall rather than another molecule. This often is the case for gaseous systems. Then the porevolume contribution to total mass transport is not dependent solely on the bulk diffusivity, but may be affected (or determined) by the Knudsen diffusivity.
3. A catalyst is characterized as a substance which adsorbs reactant. When it is adsorbed it may be transported either by adsorption into the pore space or by migration to an adjacent site on the surface. The contribution of surface diffusion probably is small in most cases, but it must be added to the diffusion in the pores volume to obtain the total mass transport.

6. Describe about gaseous diffusion in cylindrical pores?

Basic Equations: For many catalysts and reaction conditions (especially pressure) both bulk and Knudsen diffusion contribute to the mass-transport rate within the pore volume. For some years the proper combination of the two mechanisms was in doubt. About 1961 three independent investigations proposed identical equations for the rate of diffusion (in a binary mixture of A and B) in terms of bulk diffusivity $D_{AB}$ and Knudsen diffusivity $D_k$. If $N_A$ is the molal flux of A, it is convenient to represent the result as

$$N_A = \frac{\rho}{R_T} \frac{dy_A}{dx}$$

...(1)

Where $y_A$ is the mole fraction of A, x is the coordinate in the direction of diffusion and D is a combined diffusivity diffusivity given by

$$D = \frac{1}{(1-\alpha y_A)/D_{AB} + 1/(D_k)_A}$$

...(2)
The quantity \( \alpha \) is related to the ratio of the diffusion of A and B by

\[
\alpha = 1 + \frac{N_B}{N_A} \quad \ldots(3)
\]

For reactions at steady state, \( \alpha \) is determined by the stoichiometry of the reaction. For example, for the reaction \( \text{A} \rightarrow \text{B} \), reaction and diffusion in a pore would require equimolal counter diffusion; that is, \( N_B = -N_A \). Then \( \alpha = 0 \), and the effective diffusivity is

\[
D = \frac{1}{1/D_{ab} + 1/(D_K)_A} \quad \ldots(4)
\]

When the pore radius is large, Eqs reduce to the conventional constant-pressure form for bulk diffusion. For this condition \( (D_K)_A \rightarrow \infty \). Then combining Eqs. (1) and (3) gives

\[
N_A = -\frac{\rho_A}{R_g T} D_{ab} \frac{dy_A}{dx} + y_A (N_A + N_B) \quad \ldots(5)
\]

When the pore radius is large, Eqs. (1) and (2) reduce to the conventional constant-pressure form for bulk diffusion. For the condition \( (D_K)_A \rightarrow \infty \). Then combining Eqs. (1) and (3) gives

\[
N_A = -\frac{\rho_A}{R_g T} D_{ab} \frac{dy_A}{dx} + y_A (N_A + N_B) \quad \ldots(6)
\]

If, in addition, the diffusion is equimolal, \( N_B = -N_A \), Eq may be written

\[
N_A = -\frac{\rho_A}{R_g T} D_{ab} \frac{dy_A}{dx} \quad \ldots(7)
\]

If the pore radius is very small, collisions will occur primarily between gas molecules and pore wall, rather than between molecules. Then the Knudsen diffusivity becomes very low, and Equation (1) and (2) reduce to

\[
N_A = -\frac{\rho_A}{R_g T} (D_k)_A l_A \frac{dy_A}{dx} \quad \ldots(8)
\]

This equatinis the usual one expressing Knudsen diffusion in a lon capillary.
Although Equation is the proper one to use for regions where both Knudsen and bulk diffusion are important, it has a serious disadvantage: the combined diffusivity \( D \) is a function of gas composition \( y_A \) in the pore. This dependency on composition carries over to the effective diffusivity in porous catalysts and makes it difficult later to integrate the combined diffusion and transport equations. The variation of \( D \) with \( y_A \) is usually not strong (see example) Therefore it has been almost in assessing the importance of intrapellet resistances, to use a composition – independent form for \( D \), for example equation. In fact, the concept of a single effective diffusivity loses its value if the composition dependency must be retained. Note also that the problem disappear when the reaction stoichiometry is such that diffusion is countercurrent and equimolal.

Effective diffusivities in porous catalysis are usually measured under conditions where the pressure is maintained constant by external means (experimental methods are described in section) Under this condition, and for a binary counterdiffusing systems, the ratio \( N_B/N_A \) is the same regardless of the extent of Knudsen and bulk diffusion. Evans et al have shown this constant ratio be fat constant pressure).

\[
\frac{N_B}{N_A} = -\sqrt{\frac{M_A}{M_B}}
\]

or

\[
\alpha = 1 - \sqrt{\frac{M_A}{M_B}}
\]

Where \( M \) represents the molecular weight. Equations applies for nonreacting conditions. When reactions occurs, stoichiometry determines \( \alpha \).

7. Describe about liquid diffusion in cylindrical pores?

Diffusion in Liquids

The mean free path in liquids is to small that Knudsen diffusion is not significant, Thus the diffusion rate is unaffected by a pore diameter and pressure (in the absence or surface diffusion). The effective diffusivity is determined by the molecular diffusivity and the pore structure of the catalyst pellet. Since the molecules in liquids are close together, the diffusion of one component is strongly affected by the force fields of nearby molecules and at the pore wall. As a result, diffusivities are concentrations dependent and difficult to predict. As an approximation, we may express the diffusion flux of component A in a single cylindrical pore as:
\[ N_A = -D_{AB} \frac{dC_A}{dx} \] ...(1)

Where \( D_{AB} \) is the molecular diffusivity of liquid A in a solution of A and B and \( dC_A/dx \) is the concentration gradient in the direction of diffusion.

Values of \( D_{AB} \) are much less than those for gases and are, in general, of the order of \( 1 \times 10^{-5} \) cm\(^2\)/s. For gases (for example, hydrogen) dissolved in liquids the diffusivity can be an order of magnitude larger, as noted in Examples. Several correlations are available for estimating diffusivities in liquids at low concentrations (infinite dilution). These may be used as approximation values in reactor problems but the uncertain and sometimes large effect of concentrations on \( D_{AB} \) should not be forgotten.

The major need for liquid-phase diffusivities is in problems involving slurry or trickle-bed reactors. Even though a gas phase is present, the wetting of the catalyst particles by the liquid means that the pores will be essentially filled with liquid. Since diffusivities in liquids are lower than those in gases, internal transport resistances can have a large effect on the global rate for trickle-bed reactors than for gas-solid (two phase), fixed-bed reactors. The effect is illustrated in example. Even in slurry reactors employing catalyst particles of the order of 100 microns diameter, intraparticle diffusion can affect the global rate.

8. Write about Surface diffusion?

Surface Diffusion:

Surface migration is pertinent to a study of intrapellet mass transfer if its contribution is significant with respect to diffusion in the pore space at reaction temperature. When multimolecular-layer adsorption occurs, surface diffusion has been explained as flow of the outer layers as a condensed phase. However, surface transport of interest in relation to catalytic reaction occurs in the monomolecular layer. It is more appropriate to consider, as proposed by deBoer, that such transport is an activated process, dependent on surface characteristics as well as those of the adsorbed molecules. Imagine that a molecule in the gas phase strikes the pore wall and is absorbed. Then two alternatives are possible: desorption into the gas or movement to an adjacent active site on the pore wall (surface diffusion). If desorption occurs, the molecule can continue its journey in the void space of the pore or be readorsorbed by again striking the wall.
In moving along the wall, the same molecule would be transported sometimes on the surface and sometimes in the gas phase. If this view is correct, the relative contribution of surface migration would increase as the surface area increases (or the pore size decreases). There is evidence to indicate that such is the case.

Experimental verification of surface diffusion is usually indirect, since concentrations of adsorbed molecules on a surface are difficult to measure. When gas concentrations are obtained, the problem arises of separating the surface and pore-volume transport rates. One solution is to measure both \( N_A \) and \( N_B \) in the apparatus shown in figure using a nonadsorable gas for A. If the diffusion rate of B is greater than that calculated from \( N_A \) by Equation, the excess is attributal to surface migration. Barrer and Barrer used this procedure with vycor at room temperature and found surface migration significant for such gases as CO\(_2\), CH\(_4\) and C\(_2\)H\(_4\) and negligible for helium and hydrogen. Rivarolas found that for CO\(_2\), the surface contribution on an alumina pellet increased from 3.5 to 54% of the total mass-transfer rate as the macropore properties changed from \( \bar{a}_M = 1.710 \) A and \( \varepsilon_M = 0.33 \) to \( \bar{a}_M = 348 \) A and \( \varepsilon_M = 0.12 \).

By analogy to Fick’s law, a surface diffusivity \( D_s \) may be defined in terms of surface concentration \( C_s \) in moles of adsorbate per square centimeter of surface.

\[
N_s = D_s \frac{dC_s}{dx} \tag{1}
\]

Where \( N_s \) is the molal rate per unit perimeter of pores surface. In order to combine surface and pore-volume contributions in a catalyst pellet, the surface flux should be based on the total area of the catalyst perpendicular to diffusion and on the coordinate \( r \). If the flux is \( (N_s)_e \), then

\[
(N_s)_e = -D_s \rho_p \frac{dc}{dr} \tag{2}
\]

Where \( \rho_p \) is the density of the catalyst and \( \bar{C} \) now represents the moles adsorbed per gram of catalyst. To be useful, equation must be expressed in terms of the concentration in the gas phase. If the adsorption step is fast with respect to surface transfer from site to site to the catalyst. We may safely assume equilibrium between gas and surface concentration. Otherwise the relation between the two
concentrations depends on the intrinsic rates of the two processes. If equilibrium is assumed, and if the isotherm is linear, then

$$C_A = \left( K_A C_m \right) C_g = K' \frac{\rho y_A}{R_s T}$$  \hspace{1cm} (3)

Where the subscript $A$ refers to the adsorbate and $K'$ is the linear form for the equilibrium constant, in cubic centimeters per gram. The latter is obtained from the Langmuir isotherm. Equation, when adsorption is small enough that the linear form is valid. Now, applying Equation to component $A$.

$$\left( N_s \right)_e = \frac{\rho}{R_s T} \rho_p K'_A \frac{dy_A}{dr}$$ \hspace{1cm} (2)

Equation gives the surface diffusion of $A$ in the same form as Equation applied earlier to transport in the gas phase of the pores. From these equation the total flux and total effective diffusivity are given by

$$\left( N_A \right)_s = \frac{D_e}{R_s T} \left( D_e + \rho_p K'_A D_s \right) \frac{dy_A}{dr}$$ \hspace{1cm} (3)

$$\left( D_e \right)_s = D_e + \rho_p K'_A D_s$$ \hspace{1cm} (4)

If the density of the catalyst and the adsorption equilibrium constant are known, equation permits the evaluation of a total effective diffusivity from $D_s$, Data for $D_s$ have been reported in the literature in a variety of ways. Depending on the definition of adsorbed concentrations and equilibrium constants. Schneider’s has summarized much of the information for light hydrocarbons on various catalysts in the form defined by Equation. Such $D_s$ values ranged from $10^{-3}$ to $10^6$, depending on the nature of the adsorbent and the amount adsorbed. Most values were in the interval $10^{-4}$ to $10^{-5}$ cm$^2$/s. Data for other adsorbates have similar magnitudes and show that the variations with adsorbed concentration can be large.

The effect of temperature on $D_s$, given an activated process, is described by an Arhenius –type expression.

$$D_s = A e^{-E_s/R_s T}$$

Where $E_s$ is the activation energy for surface diffusion. The variation of $K'_A$ with temperature is given by van’t Hoff equation
\[
\frac{d \ln K'_A}{dT} = \frac{\Delta H}{R_s T^2}
\]

Or

\[
K'_A = A' e^{-\Delta H/R_s T}
\]

The observed rate of surface diffusion, according to Equation will be proportional to the product \(K'_A D_s\). Substituting the above expression for \(K'_A\) and \(D_s\) in equation

\[
(N_s)' = \frac{\rho}{R_s T} \rho_p (AA') e^{-(1/R_s T)(\Delta H+E_s)} \frac{dy_A}{dr}
\]

The exponential term expresses a much stronger temperature dependency than the coefficient \(1/T\). If we neglect the latter, we may express the temperature effect on the rate as

\[
(N_s)' = -A'' e^{-(1/R_s T)(\Delta H+E_s)}
\]

where

\[
A'' = AA' \frac{dy_A}{dr} \frac{\rho}{R_s T} \rho_p
\]

This equation shows that the observed or apparent activation energy for surface diffusion is related to \(E_s\) by

\[
E' = \Delta H + E_s
\]

From available data it appears that \(E_s\) is only a few kilocalories per mole. The heat of adsorption \(\Delta H\) is generally greater than this, particularly for chemisorption, and is always negative. Therefore the observed effect is a decrease in rate of surface diffusion with increase in temperature. Note that \(\Delta H\) is negative.

From the assumption and approximation presented, it is clear that surface diffusion is not well understood. It is hoped that improved interpretations of surface migration will permit a more accurate assessment of its effect on global rates of reaction. When we consider the effect of intraparticle resistance in secs. 11-7 to 11-12 we shall suppose that the \(D_s\) used in the most appropriate value and includes, if necessary, a surface contribution.
9. Derive the general expression for effectiveness factor

Effectiveness Factors

Suppose that an irreversible reaction $A \rightarrow B$ is first order, so that for isothermal conditions $r = f(C_A) = k_1 C_A$. Then Equation becomes

$$ r_p = \eta k_1 (C_A)_s $$

We want to evaluate $\eta$ in terms of $D_s$ and $k_1$. The first step is to determine the concentrations profile of $A$ in the pellet. This is shown schematically in figure for a spherical pellet (also shown is the external profile from $C_b$ to $C_s$). The differential equation expressing $C_A$ vs. $r$ is obtained by writing a mass balance over the spherical shell volume of thickness $\Delta r$. According to Equation at steady state the rate of diffusion into the element less the rate of diffusion out will equal the rate of disappearance of reactant within the element. This rate will be $\rho_p k_1 C_A$ per unit volume, where $\rho_p$ is the density of the pellet. Hence the balance may be written, omitting subscript $A$ on $C$.

$$ -\left(4\pi r^2 D_c \frac{dC}{dr}\right) - \left(-4\pi D_r \frac{dC}{dr}\right) = 4\pi r^2 \Delta r \rho_p k_1 C $$

The diffusive flux into the element is given by Equation. Note that for $A \rightarrow b$ there is equimolal counter diffusion of $A$ and $B$ ($\alpha = 0$). The rate of diffusion is the product of the flux and the area. $4\pi r^2$. If we take the limits as $\Delta r \rightarrow 0$ assume that the effective diffusivity in independent of the concentration of reactant (see sec), this difference equation becomes.

$$ \frac{d^2 C}{dr^2} + \frac{2dC}{rdr} - \frac{k_1 \rho_p}{D_c} C = 0 $$

At the center of the pellet symmetry requires

$$ \frac{dC}{dr} = 0 \text{ at } r=0 $$

And at the outer surface

$$ C=C_s \text{ at } r= r_s $$

Linear differential equation with boundary conditions (11-47) and (11-48) may be solved by conventional methods to yield
\[
\frac{C}{C_s} = \frac{r_s \sinh(3\Phi_s r / r_s)}{\sinh 3\Phi_s}
\]

Where \( \Phi_s \) is a dimensionless group (a Thiele-type modulus for a spherical pellet) defined by

\[
\Phi_s = \frac{r_s}{3} \sqrt{\frac{k_s \rho_p}{D_s}}
\]

The second step is to use the concentrations profile given by Equation, to evaluate the rate of reaction \( r_p \) for the whole pellet. We have two choices for doing this: calculating the diffusion rate of reactant into the pellet at \( r_s \), integrating the local rate over the whole pellet, Choosing the first approach.

\[
r_p = \frac{1}{m_p} 4\pi r_s^2 D_s \left( \frac{dC}{dr} \right)_{r=r_s} = \frac{3}{r_s \rho_p} D_s \left( \frac{dC}{dr} \right)_{r=r_s}
\]

Where the mass of the pellet is \( m_p = \frac{4}{3} \pi r_s^3 \rho_p \). Then from Equation

\[
\eta = \frac{3D_s}{r_s \rho_p k_s C_s} \left( \frac{dC}{dr} \right)_{r=r_s}
\]

Differentiating equation evaluating the derivative at \( r=r_s \), and substituting this into Eq. gives

\[
\eta = \frac{1}{\Phi_s} \left( \frac{1}{\tanh 3\Phi_s} - \frac{1}{3\Phi_s} \right)
\]

If this equation for the effectiveness factor is used in Equatin, the desired rate for the whole pellet in terms of the concentrations at the outer surface is

\[
r_p = \frac{1}{\Phi} \left( \frac{1}{\tanh 3\Phi_s} - \frac{1}{3\Phi_s} \right) k_s C_s
\]
10. Derive the equation for diffusion and reaction in a catalyst pellet?

We now perform a steady-state mole balance on species A as it enters, leaves and reacts in a spherical shell of inner radius r and outer radius r + Δr of the pellet (figure). Note that even though A is diffusing inward toward the center of the pellet, the convention of our shell balance dictates that the flux be in the direction of increasing r. We choose the flux of A to be positive in the direction of increasing r (i.e., the outward direction). Because A is actually diffusing inward, the flux of A will have some negative value, such as -10 mol/m², indicating that the flux is actually in the direction of decreasing r.

First we will drive the concentration profile of reactant A in the pellet

![Figure: Shell balance on catalyst pellet](image)

We now proceed to perform our shell balance on A. The area that appears in the balance equation is the total area (void and solids) normal to the direction of the molar flux.

Rate of A in at r = \( W_{A_r} \), area = \( W_A \times 4\pi r^2 \) \( |_r \)

Rate of R at \((r + \Delta r) = W_{A_{r+\Delta r}}\) area = \( W_{A_{r+\Delta r}} \times 4\pi r^2 \) \( |_{r+\Delta r} \)

\[
\frac{rate \ of \ generation \ of \ A \ withing \ a \ shell \ thickness \ of \ \Delta r}{mass \ of \ catalyst} = \frac{rate \ of \ reaction}{mass \ catalyst} \times \left( \frac{mass \ catalyst}{volume} \right) \times [volume \ of \ shell]
\]

\[
= r_A \times \rho_c \times 4\pi r_m^2 \Delta r
\]
Mole balance for diffusion and reaction inside the catalyst pellet

Where \( r_m \) is some mean radius between \( r \) and \( \Delta r \) that is used to approximate the volume \( \Delta V \) of the shell.

The mole balance over the shell thickness \( \Delta r \) is

\[
\text{in at } r - \text{out at } r + \Delta r + \text{generation within } \Delta r = 0
\]

\[
\left( W_a A, \times 4 \pi r^2 \right) \left|_r \right. - \left. \left( W_a A, \times 4 \pi (r + \Delta r)^2 \right|_{r, \Delta r} \right) + \left( r_m \times \rho_e \times 4 \pi r^2 \Delta r \right) = 0
\]

After dividing by \((-4 \pi \Delta r)\) and taking the limit as \( \Delta r \to 0 \), we obtain the following differential equation.

\[
\frac{d(W_a A, r^2)}{dr} - r_m \rho_e r^2 = 0
\]

Because 1 mole of \( A \) reacts under conditions of constant temperature and pressure to form 1 mol of \( B \), we have EMCD at constant total concentrations.

The flux equation

\[
W_a = cD_e \frac{dy_A}{dr} = -D_e \frac{dC_A}{dr}
\]

Where \( C_A \) is the number of moles of \( A \) per dm\(^3\) of open pore volume (i.e., volume of gas) as opposed to (mol/vol of gas and solids). In systems where we do not have EMCD in catalyst pores, it may still be possible to use Equation if the reactant gases are present in dilute concentration.

After substituting Equation into Equation, we arrive at the following differential equation describing diffusion with reaction in a catalyst pellet.

\[
\frac{d[-D_e (dC_A / dr) r^2]}{dr} r^2 \rho_e r_A = 0
\]

We now need to incorporate the rate law. In the past we have based the rate of reaction in terms of either per unit volume.
Inside the pellet

\[-r_A(\text{mol} / \text{dm}^3 \cdot \text{s})\]

or per unit mass of catalyst

\[-r_A'(\text{mol} / \text{g cat. s})\]

When we study reactions on the internal surface area of catalysts, the rate of reaction and rate law are often based on per unit surface area,

\[-r_A^*(\text{mol} / \text{m}^2 \cdot \text{s})\]

As a result, the surface area of the catalyst per unit mass of catalyst.

\[S_a(\text{m}^2 / \text{g cat.})\]

Is an important property of the catalyst. The rate of reaction per unit mass of catalyst \(-r_A\) and the rate of reaction per unit surface area of catalyst are related through the equation.

\[10 \text{ grams of catalyst may cover as much surface area as a football field}\]

\[-r_A' = r^* A S_a\]

A typical value of \(S_0\) might be 150 m²/g of catalyst.

The rate law- As mentioned previously at high temperature, the denominator of the catalytic rate law approaches 1: Consequently, for the moment, it is reasonable to assume that the surface reaction is nth order in the gas-phase concentration of A within the pellet.

\[-r_A^* = k \cdot C_A^n\]

Where

\[-r_A^* : \quad k_n \left[ \frac{m^3}{kmol} \right]^{a-1} \quad \frac{m}{s}\]

Similarly,
For a first catalytic reaction

per unit surface Area: \( k_i = \left[ \frac{m}{s} \right] \)

Per unit Mass of catalyst \( k' = k_i S_a \left[ \frac{m^2}{kg \cdot s} \right] \)

Per unit volume \( k = k_i S_a \rho_c \left[ \frac{s^{-1}}{m} \right] \)

Substituting the rate law equation into equation gives

\[
\frac{d\left[r^2 \left(-D_e \frac{dc_A}{dr} \right)\right]}{dr} + r^2 k_n S_a \rho_c C_A^n = 0
\]

By differentiating the first terms and dividing through by \(-r^2 D_e\), Equation becomes

Differential equation and boundary conditions describing diffusion and reaction in catalyst pellet

\[
\frac{d^2 C_A}{dr^2} + \frac{2}{r} \left( \frac{dC_A}{dr} \right) - \frac{k_n S_a \rho_c}{D_e} C_A^n = 0
\]

11. Derive the equation for effectiveness factors for a first order reaction?

Single Cylindrical Pore + First Order Reaction: Consider a single cylindrical catalyst pore of length \( L \) as shown in figure. Further consider that reactant \( A \) diffuses into the pore, reacts on the surface (walls of pore) by a first order reaction and product diffuses out of the pore.

The reaction and rate based as unit surface are given by

\[
A \rightarrow \text{Product} \quad -r_A = -\frac{1}{S} \frac{dN_A}{dt} = k'' C_A
\]
Figure: A straight cylindrical pore and reactant concentration distribution along pore length

Figure: Elementary slice of catalyst pore

Figure: shows the elementary section of the catalyst pore of length \( \Delta x \). A steady state material balance for a reactant A across this elementary section is

\[
\text{Input of A} = \text{output of A} + \text{disappearance of A by reaction}
\]

Output of A – input of A + disappearance of A by reaction = 0

The individual terms in mol A/s are as follows:

Reactant A entering by diffusion (at \( x_{in} \), i.e. at \( x \)):

\[
\left( \frac{dN}{dt} \right)_{in} = -\pi r^2 \left( \frac{dC_A}{dx} \right)_{in} \pi r^2 = \text{cross-sectional area of the section}
\]
Reactant A leaving by diffusion (at \( x_{\text{out}} \), i.e., at \( x+\Delta x \)):

\[
\left( \frac{dN_A}{dt} \right)_{\text{out}} = -\pi r^2 D \left( \frac{dC_A}{dt} \right)_{\text{out}}
\]

Disappearance of reactant A on surface by reaction:

\[
\text{Disappearance of A by reaction} = \left( \frac{\text{rate of disappearance of A}}{\text{unit surface}} \right)_{\text{surface}} = \left( \frac{1}{S} \frac{dN_A}{dt} \right)_{\text{surface}} = k''C_A(2\pi r \Delta x)
\]

The surface on which reaction is occurring = \( S = \pi D \Delta x = 2\pi r \Delta x \)

Entering all these terms in Equation gives

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

Changing sign and dividing by \( \pi r^2 D \Delta x \) throughout gives

\[
\frac{dC_A}{dx} \bigg|_{\text{out}} - \frac{dC_A}{dx} \bigg|_{\text{in}} - 2k''C_A = 0
\]

[For any quantity \( Q \) which is a smooth continuous function of \( x \)]

\[
\lim_{\Delta x \to 0} x_2 \frac{Q_2 - Q_1}{x_2 - x_1} = \lim_{\Delta x \to 0} \frac{\Delta Q}{\Delta x} = \frac{dQ}{dx}
\]

So taking the limit as \( \Delta x \to 0 \), we obtain the following second order differential equation.

\[
\frac{d^2C_A}{dx^2} - \frac{2k''}{Dr} C_A = 0
\]

Here as the rate is based on unit surface area of the wall of the catalyst pore \( k'' \) has the unit of length per time (m/s)

The interrelation between rates on different bases is given by

\[
(-r_A) V = (-r_A') W = (-r_A'') S
\]

In terms of rate constant it becomes
\[ kV = k'W = k's \]

Therefore for cylindrical catalyst pore

\[ K = k'' \frac{S}{V} = k'' \left( \frac{\text{surface area}}{\text{volume}} \right) = k'' \left( \frac{2\pi rL}{\pi r^2 L} \right) = \frac{2k''}{r} \]

So in terms of volumetric units, Equation (6.3 becomes)

[substituting \( k \) for \( 2k''/r \) in Equation , we get]

\[
\frac{d^2C_A}{dx^2} - \frac{k}{D} C_A = 0
\]

Let \( k/D = m^2 \)

With this equation becomes

\[
\frac{d^2C_A}{dx^2} - m^2 C_A = 0
\]

We seek the particular solutions of the above equation in the form:

\[
C_A = e^{Ax}
\]

then \( \frac{dC_A}{dx} = Ae^{Ax} \) and \( \frac{d^2C_A}{dx^2} = A^2 e^{Ax} \)

So equation becomes

\[
A^2 e^{Ax} - m^2 e^{Ax} = 0
\]

Hence , \( A = \pm m \)

Thus, the particular solutions of Equation are:

\[
C_A = e^{mx} \quad \text{and} \quad C_A = e^{-mx}
\]

General solution of Equation is the linear combination of the particular solution

\[
C_A = M_1 e^{mx} + M_2 e^{-mx}
\]

(Where \( M_1 \) and \( M_2 \) are constant) of integration

General solution of the linear differential equation [Equation (6.7)] us

\[
C_A = M_1 e^{mx} + M_2 e^{-mx}
\]
Where, \( m = \sqrt{\frac{k}{D}} = \sqrt{2k''/Dr} \)

And where \( M_1 \) and \( M_2 \) are arbitrary constants of integration

Let us evaluate \( M_1 \) and \( M_2 \) using the boundary conditions

The boundary conditions are:

(i) At the pore entrance, the concentration is \( C_{As} \):

\[ C_A = C_{As} \text{ at } x=0 \]

(ii) There is no flux or movement of material through the interior end of the pore

\[ \frac{dC_A}{dx} = 0 \text{ at } x=L \]

With \( C_A = C_{As} \) as \( x=0 \) Equation becomes

\[ C_{As} = M_1 + M_2 \]

We have \( C_A = M_1 e^{mx} + M_2 e^{-mx} \)

\[ \frac{dC_A}{dx} = m M_1 e^{mx} - m M_2 e^{-mx} \]

With \( dC_A/dx = 0 \) at \( x=L \) the above becomes

\[ 0 = mM_1 e^{ml} - mM_2 e^{-ml} \]

\[ M_1 e^{ml} - M_2 e^{-ml} = 0 \]

Combining Equations gives

\[ M_1 e^{ml} - (C_A - M_1) e^{-ml} = 0 \]

\[ M_1 (e^{ml} + e^{-ml}) - C_A e^{-ml} = 0 \]

\[ \therefore M_1 = \frac{C_A e^{ml}}{e^{ml} + e^{-ml}} \]

Similarly, \( M_2 = \frac{C_A e^{-ml}}{e^{ml} + e^{-ml}} \)

Substituting \( M_1 \) and \( M_2 \) from Equation into Equation gives
The dimensionless concentration profile of reactant A within the pore is

\[
C_A = \frac{C_A}{C_{A_0}} = \frac{e^{-mL}e^{mx} + e^{mL}e^{-mx}}{e^{mL} + e^{-mL}}
\]

\[
C_A = C_{A_0} \left[ \frac{e^{-m(L-x)} + e^{m(L-x)}}{e^{mL} + e^{-mL}} \right]
\]

\[
C_A = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL}
\]

\[
\text{As} \quad \cosh mL = \frac{e^{mL} + e^{-mL}}{2}
\]

\[
\cosh x = \frac{e^x + e^{-x}}{2}
\]

Figure shows the concentration profile of reactant within the pore and it is seen to be dependent on the dimensionless quantity mL, or Mr, called the Thiele modulus.

Figure: Distribution and average concentration of reactant is a catalyst pore as a function of mL (Thiele modulus) for first order surface reaction.

Now, we define the quantity \( \eta \) called the effectiveness factor to measure how much the reaction rate is lowered due to the resistance of pore diffusion.
It is defined as the ratio of actual average reaction rate within the pore to the reaction rate in the absence of pore diffusion resistance.

\[ \eta = \frac{\text{actual average reaction rate within pore}}{\text{reaction rate in the absence of pore diffusion resistance}} \]

\[ \eta = \frac{\text{actual average reaction rate within pore}}{\text{reaction rate that would result of entire pore surface were exposed to condition at the external surface / pore mouth } C_{As}, T_s} \]

The rate of reaction in the absence of pore diffusion resistance is the maximum rate of reaction. The rate of reaction will be maximum when the concentration of reactant along the pore is the same as that at the external surface, \( C_{As} \)

\[ \eta = \frac{-r_A \text{ with diffusion}}{-r_A \text{ without diffusion}} \]

The actual rate is also referred to as the observed rate of reaction, \((-r_A)_{obs.}\).

The effectiveness factor ranges from 0 to 1.

For first order reactions as the rate is proportional to the concentration, the effectiveness factors is given by

\[ \eta_{\text{first order}} = \frac{\bar{C}_A}{C_{As}} \]

Evaluating the average rate in the pore from Equation yields the following relationship

\[ \eta_{\text{first order}} = \frac{\bar{C}_A}{C_{As}} = \frac{\tanh mL}{mL} \]

Let us obtain the realtionship given by Equations

For first-order reactions:

\[ \eta_{\text{first order}} = \frac{k\bar{C}_A}{kC_{As}} = \frac{\bar{C}_A}{C_{As}} \]
\( \bar{C}_A \) is given by

\[
\bar{C}_A = \frac{\int_0^L C_A \, dx}{L} = \frac{1}{L} \int_0^L C_A \, dx
\]

With this \( \bar{C}_A \), Equation becomes

\[
\eta_{\text{first order}} = \frac{1}{LC_{AS}} \int_0^L C_A \, dx
\]

We have,

\[
\frac{C_A}{C_{AS}} = \frac{\cosh m(L-x)}{\cosh mL}
\]

\[
\Rightarrow \quad C_A = C_{AS} \frac{\cosh m(L-x)}{\cosh mL}
\]

Substituting \( C_A \) into Equation in terms of \( C_{AS} \) gives

\[
\eta_{\text{first order}} = \frac{1}{LC_{AS}} \int_0^L C_{AS} \cosh m(L-x) \, dx
\]

\[
= \frac{C_{AS}}{LC_{AS}} \int_0^L \cosh m(L-x) \, dx
\]

\[
= \frac{1}{L \cosh mL} \left[ \cosh m(L-x) \right]_0^L
\]

\[
= \frac{1}{L \cosh mL} \left[ \frac{-1}{m} \sinh m(L-x) \right]_0^L
\]

\[
= \frac{-1}{mL \cosh mL} \left[ 0 - \sinh mL \right]
\]

\[
= -\frac{\sinh mL}{mL \cosh mL}
\]

\[
\Rightarrow \quad \eta_{\text{first order}} = \frac{-\tanh mL}{mL}
\]
12. What is the effect of heat transfer during reaction for a catalyst pellet?

Heat Effects (Exothermicity/ endothermicity) During reaction:

In faster reactions, there heat released (or absorbed) in the pellet can not be removed rapidly enough to keep the pellet close to the temperature of the surrounding fluid and consequently non-thermal conditions prevail. In such cases, the following types of temperature effects may be encountered.

(i) particle $\Delta T$: A temperature gradient may exist within the pellet – temperature varies within the catalyst pellet.

(ii) Film $\Delta T$: A temperature gradient may exist across the fluid film (between the outer surface of pellet and main gas stream). The whole pellet may be hotter (or colder) than the surrounding fluid, though uniform in temperature.

In case of exothermic reactions, heat is generated and particles are hotter than the surrounding fluid. Consequently, the non-isothermal rate (of reaction) is higher than the isothermal rate which is based on the bulk stream condition conditions. On the other hand, in case of endothermic reactions, heat is absorbed and the particles are cooler than the surrounding fluid. Consequently, the non-isothermal rate is lower than the isothermal rate.

Thus we would encourage nonisothermal behaviour in exothermic reactions provide no harmful effects of thermal shock, or sintering of the catalyst, or drop in selectivity occur with hot particles. On the other hand, we would like to depress nonisothermal behaviour in endothermic reactions.

The following simple calculation will give us idea regarding the form of non-thermal effect that may present if at all.

(i) Film $\Delta T$: To find maximum $\Delta T$ across the film, the rate of heat generation by reaction within the pellet is set equal to the rate of heat removal through the film.
\[
= Q_{\text{generated}} = V_{\text{pellet}} \left(-r_{\text{obs}}^w\right)(-\Delta H_r)
\]
\[
[V_{\text{pellet}} \left(-r_{\text{obs}}^w\right), (-\Delta H_r)] \Rightarrow \left(m^3 \text{ cat 's} \left(\frac{kJ}{mol \ A}\right)\right) = kJ/s
\]
\[
(-r_{\text{obs}}^w) - \text{observed reaction rate}
\]
\[
(-\Delta H_r) - \text{heat of reaction/enthalpy change resulting from reaction}
\]
\[
V_{\text{pellet}} - \text{Volume of pellet} = S_{\text{pellet}} \times L \left(\text{as} \ L = V_p / S_p\right)
\]
\[-L - \text{Characteristics size of the pellet}
\]
\[
Q_{\text{generated}} = S_{\text{pellet}} - L \left(-r_{\text{obs}}^w\right)(-\Delta H_r)
\]

Rate of heat removal through the film- \(Q_{\text{removed}} = h \times \text{Pellet} (T_g - T_s)\)

\(h = \text{film heat transfer coefficient}, \text{kJ} / (m^2 \cdot \text{s} \cdot \text{K})\)

\(T_g \) – temperature of main gas stream / bulk gas, K

\(T_s \) – temperature at the outer surface of the pellet, K

\(Q_{\text{removed}} = Q_{\text{generated}}\)

\(h \times \text{Pellet} (T_g - T_s) = S_{\text{pellet}} \cdot L \left(-r_{\text{obs}}^w\right)(-\Delta H_r)\)

\[
\Delta T_{\text{film}} = (T_g - T_s) = \frac{L \left(-r_{\text{obs}}^w\right)(-\Delta H_r)}{h} K
\]

(ii) Particle \(\Delta T\): In steady state, the heat flux within an elementary thickness of the particle is balanced by the heat generated by chemical reaction. At any point in the pellet,

\[
-K_{\text{eff}} \frac{dT}{dx} = D_e \frac{dC_A}{dx} (-\Delta H_r)
\]

For the pellet as a whole, integrating above equation from the exterior surface where \(T = T_B\) and \(C_a = C_{A_s}\) to the centre of the particle where say \(T = T_{\text{centre}}\) and \(C_A = C_{A_{\text{centre}}}\) we obtain.

\[
\Delta T_{\text{particle}} = (T_{\text{centre}} - T_s) = \frac{D_e \left(C_{A_s} - C_{A_{\text{centre}}}\right)(-\Delta H_r)}{k_{\text{eff}}}
\]
Where $k_{eff}$ is the effective thermal conductivity of the particle, J/s.m.cat.K).

When Thiele modulus is large, $C_{A_{centre}}$ is zero and consequently the maximum temperature difference between the centre and exterior surface of the particle is $D_E (-\Delta H_r) C_{As} / k_{eff}$.

13. The result of kinetic runs on the reaction $A \rightarrow R$ made in an experimental packed bed reactor using a fixed feed rate $F_{A0} = 10$ kmol/h are as follows

<table>
<thead>
<tr>
<th>$W$, kg catalyst</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_A$</td>
<td>0.12</td>
<td>0.20</td>
<td>0.27</td>
<td>0.33</td>
<td>0.37</td>
<td>0.41</td>
<td>0.44</td>
</tr>
</tbody>
</table>

(i) Find the reaction rate at 40% conversion
(ii) For a feed rate of 400 kmol/h to large scale packed bed reactor find the amount of catalyst needed for 40% conversion.
(iii) Find the amount of catalyst that would be needed in part (II) if the reactor employed a very large recycle of product stream.

Solution:

**A $\rightarrow$ R**

(i) Finding the reaction rate at 40% conversion in an experimental packed bed reactor.

The kinetic data provided at fixed feed rate ($F_{A0} = 10$ kmol/h) are:

The conversion as a function of the amount of catalyst used

For a packed bed reactor, the performance equation is

$$\frac{W}{F_{A0}} = \int \frac{dX_A}{-r_A}$$

In differential form, it becomes

$$\frac{dW}{dF_{A0}} = \frac{dX_A}{-r_A}$$
In differential form, it becomes

\[
\frac{dW}{dF_{A0}} = \frac{dx_A}{-r_A}
\]

\[
d\left(\frac{W}{R_{A0}}\right) = \frac{dx_A}{-r_A}
\]

\[-r_A' = \frac{dx_A}{d\left(\frac{W}{F_{A0}}\right)}
\]

If we construct a plot of \(X_A v/s \frac{W}{F_{A0}}\) from the given kinetic data then

\[-r_A' = \frac{dx_A}{d\left(\frac{W}{F_{A0}}\right)}\] is the slope of the curve

So plot \(X_A v/s \frac{W}{F_{A0}}\) and find the slope of the curve at 40% conversion to get the reaction rate \((-r_A')\) at 40% conversion

For' \(F_{A0} = 10\) kmol/h

<table>
<thead>
<tr>
<th>(W)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{W}{F_{Ac}})</td>
<td>0.10</td>
<td>0.20</td>
<td>0.30</td>
<td>0.40</td>
<td>0.50</td>
<td>0.60</td>
<td>0.70</td>
</tr>
</tbody>
</table>

\(X_A\) | 0.12 | 0.20 | 0.27 | 0.33 | 0.37 | 0.41 | 0.44 |

Draw tangent to the curve at a point P i.e. at \(X_A = 0.40\) and measure the slope

From figure.

\[-r_A' = \text{slope at a point P=0.38} \frac{\text{kmol converted}}{\text{kg catalyst.h}}\]

\[The \ \text{reaction rate=}-r_A' \text{at 40\% conversion} = \frac{0.38 \text{ kmol (converted)}}{\text{kg catalyst.h}} \ldots(i)\]

(ii) Determination of amount of catalyst needed in a packed bed reactor for \(F_{A0} = 400\) kmol/h to achieve 40% conversion.

Refer fig (b)
Read x-coordinate of a point P i.e. \( \frac{W}{F_{A0}} \) for \( X_A = 0.40 \) [40% conversion]

\[
\frac{W}{F_{A0}} = 0.57 \text{ at } 40\% \text{ conversion}
\]

\[
F_{A0} = 400 \text{ kmol/h}
\]

\[
W = 0.57 \times F_{A0} = 0.57 \times 400 = 228 \text{ kg}
\]

\[
\therefore \text{Amount of catalyst needed in the large scale packed bed reactor} = 228 \text{ kg} \quad \text{(ii)}
\]

(iii) Find the amount of catalyst needed in a packed bed reactor employing a very large recycle of product stream.

With a very large recycle of product stream (i.e. large recycle ratio) mixed flow is approached so here we will use the performance equation for mixed flow.

\[
\therefore \frac{W}{F_{A0}} = \frac{X_A}{r_{A_{out}}}
\]

\[
-r_A'_{out} \quad (at \ X_A = 0.40) = 0.38 \frac{\text{kmol}}{\text{kg catalyst.h}}
\]

\[
X_A = 0.40
\]

\[
F_{A0} = 400 \text{ kmol/h}
\]

\[
W = \frac{F_{A0} \cdot X_A}{-r_A'_{out}} = \frac{400 \times 0.40}{0.38} = 421 \text{ kg}
\]

\[
\therefore \text{Amount of catalyst needed in a packed bed reactor employing a very large recycle of product stream} = 421 \text{ kg} \quad \text{(iii)}
\]
14. The following kinetic data are obtained in a basket type mixed reactor. The catalyst is porous. Assuming isothermal behaviours interpret the data in terms of controlling resistances.

Data:

<table>
<thead>
<tr>
<th>Pellet diameter</th>
<th>Concentration in reactant in the exit stream</th>
<th>Spinning rate of baskets</th>
<th>Measured reactions rate $-r_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>High</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>Low</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>High</td>
<td>1</td>
</tr>
</tbody>
</table>

Solution:

<table>
<thead>
<tr>
<th>Run</th>
<th>dp</th>
<th>$C_A$</th>
<th>RPM</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>High</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1</td>
<td>Low</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1</td>
<td>High</td>
<td>1</td>
</tr>
</tbody>
</table>

Examine the data for its interpretation in terms of controlling resistances

Look at run -2 and run-3 (for large particles)

These two runs use different spinning rates but have the same reaction rate.

For diffusion to control higher the spinning rate higher will be the $k_e$ and hence rate. But for run-3 though the spinning rate is higher compared to run-2 the measured reaction rate is same as that for run-2 (not higher than that for run-2). Therefore, film diffusion is not controlling resistance for large particles.

Since the film diffusion is not controlling for a large pellets, it will not controlling in case of small pellets (run-1)

First conclusion: Film diffusion resistance is not controlling i.e. film diffusion resistance does not influence the rate.

Now we will check for pore diffusion resistance (to be controlling resistance)
In the regime of strong pore diffusion resistance

\[-r_A \propto \frac{1}{R}\]

i.e.

\[-\frac{r_{A1}}{r_{A2}} = \frac{R_2}{R_1} \ldots \ldots \text{should be satisfied for particles of sizes } R_1 \text{ and } R_2\]

Compare run-1 with either run -2 or -3

Run -1 and -2:

\[-r_{A1} = 3 \quad R_1 = \frac{1}{2}\]

\[-r_{A2} = 1 \quad R_2 = \frac{3}{2}\]

\[-\frac{r_{A1}}{r_{A2}} = \frac{3}{1} = 3\]

And

\[\frac{R_2}{R_1} = \frac{3}{1} = 3\]

\[\therefore \quad \frac{r_{A1}}{r_{A2}} = \frac{R_2}{R_1} \ldots \ldots \text{is satisfied}\]

Same result in obtained by comparing run - \(\frac{1}{3}\) with run -3

\[-\frac{r_{A1}}{r_{A3}} = \frac{3}{1} = 3 \quad \text{and} \quad \frac{R_3}{R_1} = \frac{3}{1} = 3\]

As the rate is inversely proportional to particle size, the pore diffusion resistance is controlling the rate. Therefore, the runs are conducted in the regime of strong pore resistance.

Final conclusion/final interpretation of data:

- Negligible film diffusion resistance
- Strong pore diffusion resistance.
15. The observed rate using a cube of 2 cm catalyst pellet is $10^{-3}$ mol/ (s.cm$^3$ cat). Calculate the value of first order reaction rate constant. The effective diffusivity is 0.1 cm$^2$/s and concentration of reactant at the exterior surface of pellet is $2 \times 10^{-4}$ mol/cm$^3$.

Solution:

The characteristic size of cube of side 2 cm is

$$L = \frac{Volume \text{ of \ particle \ pellet}}{Exterior \text{ surface available for reactant penetration}}$$

$$= \frac{a^3}{6a} = \frac{3}{6} \cdot a - \text{side of cube}$$

Given: Side of cube = $a$ = 2 cm

$\therefore \quad L = \frac{2}{6} = 0.333 cm$

For first order reaction $A \rightarrow R$

$$-r_A = k''C_A \eta$$

where

$$\eta = \frac{\tanh M_T}{M_T}$$

$$-r_A = k''C_A \tanh \frac{M_T}{M_T}$$

We have $M_T = L \left( \frac{K''}{D_e} \right)^{0.5}$ ...	ext{first order reaction}

$$\therefore -r_A'' = \frac{k''C_A \tanh \left[ L \left( \frac{K''}{D_e} \right)^{0.5} \right]}{L \left( \frac{K''}{D_e} \right)^{0.5}}$$

Given:
\[-r'_A = 10^{-3} \text{mol/}(s \cdot \text{cm}^3 \text{ cat})\]

\[L = 0.333 \text{ cm, } D_e = 0.01 \text{ cm}^2 / s\]

\[C_{As} = 2 \times 10^{-4} \text{ mol/cm}^3\]

\[2 \times 10^{-4} k''' \tanh \left[ 0.333 \left( \frac{k'''}{0.01} \right)^{0.5} \right] = 10^{-3}\]

\[5 = \frac{k''' \tanh \left[ 3.33 (k''')^{0.5} \right]}{3.33 (k''')^{0.5}}\]

\[(k''')^{0.5} \tanh \left[ 3.33 (k''')^{0.5} \right] = 16.65\]

We can obtain value of $k'''$ by trial and error procedure. Assume $k'''$ and check for LHS = RHS

\[K''' = 200 \quad \text{LHS} = 14.14 \quad \text{RHS} = 16.65\]

\[K''' = 270 \quad \text{LHS} = 16.43 \quad \text{RHS} = 16.65\]

\[K''' = 278 \quad \text{LHS} = 16.67 \quad \text{RHS} = 16.65\]

\[K''' = 277.2 \quad \text{LHS} = 16.649 \quad \text{RHS} = 16.65\]

LHS = RHS for $k''' = 277.2 s^{-1}$

**First order rate constant = $k''' = 277.2 s^{-1}$**

... Ans

Units of $k''' \Rightarrow \text{cm}^3 \text{ gas/ (cm}^3 \text{ cat.s)} = s^{-1}$

As tanh $[3.33 (k''')^{0.5}$ for $k''' > 2.3$ is 1, we can use easy approach (for getting $k'''$) as given below

A $\rightarrow$ R ……. First order reaction

\[-r_A'' = k''' C_{As} \eta\]

Assume strong pore resistance

For strong pore resistance
\[ \eta = \frac{1}{M_T} \]

\[-r_A^* = \frac{k'' C_{Ae}}{M_T} \]

\[ M_T = L \left( \frac{k''}{D_e} \right)^{0.50} \]

\[-r_A^* = \frac{k'' C_{Ae}}{L \left( \frac{k''}{D_e} \right)^{0.50}} \]

\[ (k'')^{0.50} = \left( \frac{-r_A^*}{C_{Ae} D_e^{0.50}} \right) \]

\[ k''' = \left[ \frac{-r_A L}{C_{Ae}} \right]^2 \times \frac{1}{D_e} \]

\[ = \left[ \frac{10^3 \times 0.333}{2 \times 10^{-1}} \right]^2 \times \frac{1}{0.01} \]

\[ = 277.2 \text{ s}^{-1} \]

First order rate constant = \( k''' = 277.2 \text{ s}^{-1} \)

Units of \( k''' \Rightarrow \text{cm}^3 \text{ gas/cm}^3 \cdot \text{cat. s} \)
1. Give the industrial importance of Gas-Solid non-catalytic reactions.
Gas-Solid non-catalytic reactions are employed in; (Solids does not appreciably change in size during the reaction)
- Roasting of ores.
- The preparation of metals from their oxides in reducing atmospheres.
- The platting of metals.
- Reactions of carbonaceous materials.
- Reactions in which solids change in size
- Manufacture of carbon disulfide \([\text{CS}_2 (\text{gas})]\)
- Manufacture of sodium cyanide \([\text{NaCN (liquid)}]\)
- Manufacture of sodium thio sulfate \([\text{Na}_2\text{S}_2\text{O}_3 (\text{solution})]\)
- Dissolution reactions
- Attack of metal chips by acids
- Rusting of iron

2. Give two examples of fluid-solid reaction in which the particles do not change their size on reaction.
- Iron is prepared form crushed and sized magnetic ore in continuous-countercurrent, three stage, fluidized bed reactors according to the reaction
  \[
  \text{Fe}_3\text{O}_4 (s) + 4 \text{H}_2 (g) \rightarrow 3 \text{Fe} (s) + 4 \text{H}_2\text{O} (g)
  \]
- With steam, water gas is obtained by the reactions
  \[
  \text{C} (s) + \text{H}_2\text{O} (g) \rightarrow \text{CO} (g) + \text{H}_2 (g)
  \]
  \[
  \text{C} (s) + 2 \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + 2 \text{H}_2 (g)
  \]

3. Name the models used in gas-solid non-catalytic reactions. (NOV/DEC 2013)
For the Gas-Solid non-catalytic reactions, two idealized models are available; (i) Progressive-conversion model [PCM] (ii) Shrinking-core model [SCM]

4. Briefly explain the Progressive Conversion Model for the gas-solid non-catalytic reactions.
- Solid reactant is converted continuously and progressively throughout the particle.
- The reaction rates are different at different locations within the particle.
- This model does not match with the real situations.

5. Explain Progressive Conversion Model. [Dec 2012]
- Solid reactant is converted continuously and progressively throughout the particle.
- The reaction rates are different at different locations within the particle.
- This model does not match with the real situations.

6. In the ‘Shrinking Core Model’ for gas-solid non-catalytic reactions, explain the term ‘Shrinking Core’.
Shrinking Core means, at any time, there exists an unreacted core of material which shrinks in size during reaction.

7. Explain the mechanism of Shrinking Core Model.
- At any time there exists an unreacted core of material which shrinks in size during reaction.
1. The reaction rate depends on the movement of unreacted core and the resistances involved in it.
2. Most of the practical situations (burning of coal, wood, briquettes, etc.) show that this model approximately matches with reality.

8. What are the limitations of Shrinking Core Model? (May 2015) (NOV/DEC 2014) (May June 2014)
It is the best simple representation for the majority of reacting gas-solid systems. However, there are two broad exceptions to this statement:
- First, Slow reaction of a gas with a very porous solid will not fit to the reality.
- Second, when solid is converted by the action of heat and without needing contact with gas – Such as baking bread, roasting chickens are mouth watering examples of such reactions.

9. What are the advantages of FBR? (NOV/DEC 2013)
**Uniform Particle Mixing**: Due to the intrinsic fluid-like behavior of the solid material, fluidized beds do not experience poor mixing as in packed beds. This complete mixing allows for a uniform product that can often be hard to achieve in other reactor designs. The elimination of radial and axial concentration gradients also allows for better fluid-solid contact, which is essential for reaction efficiency and quality.
**Uniform Temperature Gradients**: Many chemical reactions require the addition or removal of heat. Local hot or cold spots within the reaction bed, often a problem in packed beds, are avoided in a fluidized situation such as an FBR. In other reactor types, these local temperature differences, especially hotspots, can result in product degradation. Thus FBRs are well suited to exothermic reactions. Researchers have also learned that the bed-to-surface heat transfer coefficients for FBRs are high. **Ability to Operate Reactor in Continuous State**: The fluidized bed nature of these reactors allows for the ability to continuously withdraw product and introduce new reactants into the reaction vessel. Operating at a continuous process state allows manufacturers to produce their various products more efficiently due to the removal of startup conditions in batch processes.

10. Bring out the differences between ‘Progressive Conversion Model’ and ‘Shrinking Core Model’ used in gas-solid non-catalytic reactions.
**Progressive-conversion model**:
- Solid reactant is converted continuously and progressively throughout the particle.
- The reaction rates are different at different locations within the particle.
- This model does not match with the real situations.
**Shrinking-core model**:
- At any time there exists an unreacted core of material which shrinks in size during reaction.
- The reaction rate depends on the movement of unreacted core and the resistances involved in it.
- Most of the practical situations (burning of coal, wood, briquettes, etc.) show that this model approximately matches with reality.

11. Explain the characteristics of Fluidized bed reactor. [Dec 2012]
A fluidized bed reactor (FBR) is a type of reactor device that can be used to carry out a variety of multiphase chemical reactions. In this type of reactor, a fluid (gas or liquid) is passed through a granular solid material (usually a catalyst possibly shaped as tiny spheres) at high enough velocities to suspend the solid and cause it to behave as though it were a fluid. This process, known as fluidization, imparts many important advantages to the FBR. As a result, the fluidized bed reactor is now used in many industrial applications. Today fluidized bed reactors are still used to produce gasoline and other fuels, along with many other chemicals. Many industrially produced polymers are made using FBR technology, such as rubber, vinyl chloride, polyethylene, styrenes, and polypropylene. Various utilities also use FBR's for coal gasification, nuclear power plants, and water and waste treatment settings. Used in these applications, fluidized bed reactors allow for a cleaner, more efficient process than previous standard reactor technologies.
12. What are the three rate controlling steps assumed in the Shrinking Core Model for gas-solid non-catalytic reactions?
The three rate controlling steps assumed in the Shrinking Core Model for gas-solid non-catalytic reactions are:
- Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.
- Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.
- Reaction of gaseous A with solid at this reaction surface.

13. State all the assumptions made in the Shrinking Core Model used for gas-solid non-catalytic reactions.
The assumptions made in the Shrinking Core Model used for gas-solid non-catalytic reactions are;
- The pellet retains its shape during reaction.
- There is no gaseous region between the pellet and the product layer.
- The temperature is uniform throughout the heterogeneous region.
- The densities of the porous product and the reactant (solid) are the same, so that the total radius of the pellet does not change with time.

14. Explain the resistances that would encountered during the burning of coal.
The resistances that would be encountered during the burning of coal are;
- Diffusion resistance offered by the gas film surrounding the surface of the solid (coal) particle.
- Diffusion resistance offered by the blanket of ash surrounding the unreacted core of the (coal) particle.
- Reaction resistance on the surface of the unreacted core (coal).

15. Explain how the rate determining step is calculated in gas-solid non-catalytic reactions.
The kinetic runs with different sizes of particles can distinguish between reactions in the chemical and physical steps control (for gas-solid non-catalytic reactions) as,
\[ t \propto R^{1.5\text{ to } 2.0} \text{ for film diffusion controlling} \]
\[ t \propto R^2 \text{ for ash layer diffusion controlling} \]
\[ t \propto R \text{ chemical reaction controlling.} \]

16. In a gas-solid non-catalytic reaction, a 4mm solid is 7/8th converted. What is the diameter of the shrinking core?
Solution: Given \( D = 4 \text{ mm} \) and \( X_B = 7/8 \) or 0.875.
We know, the fraction unconverted is \( 1 - X_B = (dc/D)^3 \)
Where ‘dc’ & ‘D’ are the diameters of the unreacted (shrinking) core and the original diameter of the solid particle. Substituting the given data into the above equation,
we get \( 1 - 0.875 = (dc/4)^3 \)
On solving the above, we get \( dc = 2 \text{ mm} \)

17. Sketch the concentration profile for the gas-solid non-catalytic reaction in which the resistance through the ash layer is rate controlling.
18. Find the rate controlling mechanism, form the following data

<table>
<thead>
<tr>
<th>dp, cm</th>
<th>X_B</th>
<th>t, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>0.75</td>
<td>5</td>
</tr>
</tbody>
</table>

Solution: Since ‘dp’ is same for the two given data’s, we try to find the rate controlling mechanism by considering the time ‘t’ and conversion ‘X_B’. By assuming G-film surrounding the particles is rate controlling, we have \( \frac{t}{T} = X_B \). Where ‘T’ is the time for complete conversion. Sub. the given first data into the above, we get \( T_1 = \frac{2}{0.3} = 6.6667 \) hr Sub. the given second data into the above, we get \( T_2 = \frac{5}{0.75} = 6.6667 \) hr Since \( T_1 = T_2 \), our assumption is correct. That is, G-film surrounding the particles controls this reaction.

19. A gas-solid non-catalytic reaction taking place in a constant environment. It was found that the time for complete conversion of 2mm particle is four times the time for complete conversion of 1mm particle. What resistance is rate controlling?

Solution: Given \( D_1 = 1 \text{mm} \), \( D_2 = 2 \text{mm} \) and \( T_2 = 4T_1 \). From the given data, it was observed that

\[
\frac{T_2}{T_1} = \left( \frac{D_2}{D_1} \right)^2 = \left( \frac{R_2}{R_1} \right)^2
\]

(Or) \( T \propto R^2 \).

Thus, Diffusion through ash layer controls this reaction.

20. State how to reduce the gas film resistance for non-catalytic chemical reaction.

By increasing the mass transfer coefficient (kg), the gas film resistance (1/kg) can be reduced for non-catalytic chemical reaction.

21. How can the fluid solid reaction are represented.

A (fluid) + bB (solid) \( \rightarrow \) Fluid products

Solid products

Fluid and solid products

22. What are the 2 cases to be considered for fluid particle reactions?

The particle size remains unchanged during reaction. In fluid-solid reactions this will happen when.
23. Give examples of fluid-solid reaction in which solid does not appreciably change during reaction?
   (i) The roasting of sulphide ores in air to yield metal oxides.
   \[
   \text{ZnS(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{ZnO(s)} + \text{SO}_2(g)
   \]
   (ii) The reduction of metal oxides to corresponding metals. The reduction of magnetite, by hydrogen.
   \[
   \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g) \rightarrow 3\text{Fe(s)} + 4\text{H}_2\text{O(g)}
   \]

24. Give some examples of fluid solid reaction in which particle size changes.
   Example of fluid-solid reactions in which the size of solid changes are:
   (i) The production of carbon disulphide from the elements
   \[
   \text{C(s)} + 2\text{S}_2(g) \rightarrow \text{CS}_2(g)
   \]
   (ii) The production of water gas by the action of steam on coal (with low ash content).
   \[
   \text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(g)
   \]
   (iii) The burning of pure carbon in air.
   \[
   \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g)
   \]

25. When will the particle size change in the case of fluid solid reaction?
   In fluid-particle reactions this will happen when-
   (a) a flaking ash or product material is formed or
   (b) pure B is used in the reaction

26. What are the factors one has to consider before selecting a kinetic model?
   Every conceptual picture of model describing the progress of reaction has its own mathematical
   representation, its rate equation. Therefore, if we select a model we have to accept its rate equation and vice versa.

27. What are the two models to describe kinetics of non catalytic reaction of particles with surrounding
   fluid?
   Progressive conversion model, surrounding model.

28. Briefly describe progressive conversion model.
   This model assumes that the reactant gas enters and reacts throughout the particle at all times (reaction proceeds
   continuously throughout the particle). The rate of reaction is different at different locations within the particle.

29. Briefly describe SCM?
   This model assumes that the reaction first begins at the outer surface of the solid particle and the deeper
   layers do not take part in the reaction until all the outer layer has transformed into solid or gaseous product.
   Gradually, the reaction zone then moves inward (into the solid), constantly reducing the size of core of unreacted
   solid and leaving behind completely converted solid (solid product) and inert material (inert constituent of the
   solid reactant).

30. Sketch the concentration profile for a solid reactant according to SCM.
31. What are the rate controlling steps according to SCM?
   I. Diffusion through the gas film
   II. Diffusion through the ash (converted solid and inert material) / ash layer.
   III. Chemical reaction.

32. What is the expression for time taken for the product size to reach \( r_c \) according to SCM when diffusion through gas film controls?

\[
t = \frac{e_B R}{3b k g C_{Ag}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right]
\]

33. What is the expression for conversion for the above case?

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

34. What is the expression for time for time taken for complete conversion when diffusion through ash layer controls?

\[
\tau = \frac{\ell_B R^2}{6b D_e C_{Ag}}
\]

35. Give the expression for conversion in the above case.

\[
\frac{t}{\tau} = 1 - 3 \left( 1 - x_3 \right)^{\frac{2}{3}} + 2 \left( 1 - x_B \right)
\]

36. What is the expression for time required for complete conversion when chemical reaction controls?
\[ \tau = \frac{e_B R}{bk u C_A g} \]

37. Give the expression for conversion in the above case.

\[ \frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - \left(1 - X_B\right)^{1/3} \]

38. When does the particle size shrink according to SCM?
When no ash forms

39. What steps occur in reactions when no ash layer for SCM?
In case of such reactions as no ash layer is present, the following three steps occur in succession:
I. Diffusion of gaseous reactant A through the gas film to the surface of the solid from the main body of gas.
II. Reaction on the surface between gaseous reactant A and solid reactant B.
III. Diffusion of reaction products from the surface of the solid back into the main body of gas through the gas film.
Here the rate controlling step may be gas film diffusion or chemical reaction.

40. Give the expression for conversion when chemical reaction controls for particles of changing size.

\[ \tau = \frac{\ell_B R}{bk u C_A g}, \quad t = \frac{\ell_B (R - r_c)}{bk u C_A g} \]

\[ \frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - \left(1 - X_B\right)^{1/3} \]

41. One what parameters does the film resistance of a particle depend.
I. Size of particle,
II. Properties of fluid,
III. Relative velocity between particle and solid.

42. What is the correlation for mass transfer of a component?
With made function of in a fluid to freely falling solids is:

\[ \frac{k_g d p y}{D} = 2 + 0.6 N_{el}^{1/2} N_{sc}^{1/3} \]

43. How does \( k_g \) vary with particle size.
\[ k_g \alpha \frac{1}{d_p} \text{ for small } d_p \text{ and less } U. \]
\[ k_g \alpha \frac{U^{1/2}}{d_p^{1/2}} \text{ large } d_p \text{ and high } U. \]
44. What is the expression for time for small particle of changing size?

\[ t = \frac{e_B R o^2}{2bC_{Ag}D} \left[ 1 - \left( \frac{R}{R_o} \right)^2 \right] \]

\[ \tau = \frac{e_B R}{2bkgC_{Ag}} \left[ 1 - \left( \frac{r_c}{R} \right)^2 \right] \]

\[ \frac{t}{\tau} = X_B. \]

45. Give expression SCM, for cylindrical particles of unchanging size/fired size for diffusion through gas film controls.

46. Give expression for cylindrical particles under chemical reaction controls.

47. Give expression under diffusion through ash layer controls.

48. What is the overall late expression for the reaction when all the resistance act together?

\[ \frac{1}{S_{ex}} \frac{dN_B}{dt} = \frac{bC_A}{1 + \frac{R(R-r_C)}{r_cD_e} + \frac{R^2}{r_c^2K^{11}}} \]

Film resistance ash resistance reaction resistance

49. What are the various contacting patterns for non catalytic fluid-solid reaction?
Solid and gas both in plug flow, solids in mixed flow, plug flow of gas and stationary phase.

50. How will the plug flow of contacting phases be achieved?
I. Counter current flow of phases
II. Counter flow of phases.
III. Cross flow of phases.

51. What is the assumption for designing of fluid-solid systems?
Uniform composition of fluid through the reaction.

52. Draw the bar diagram showing size distribution of feed rate for mixture of particles.
53. What is the mean value of fraction of B uncounted?
Mean value for the fraction of reactant B uncounted

\[
= \sum_{\text{all sizes}} \left( \text{Fraction of reactant B unconverted in particles of size } R_i^c \right) \times \\
\left( \text{Fraction of feed which is of } 1 - X_B = \sum_{R=0, R \approx \infty}^{R_m} \left[ 1 - x_B(R_i) \frac{f(R_i)}{f} \text{ size } R_i \right] \right)
\]

54. What is the conversion in case of mixed flow of solids?

\[1 - \overline{X}_B = \int_0^\infty (1 - X_B) \cdot E \, dt \quad X_B \leq 1.\]

\[1 - \overline{X}_B = \int_0^{\tau} (1 - X_B) \cdot E \, dt, \quad E \text{ is exit age destruction of solids.}\]

55. What is the conversion in case of under fluid film resistance controls?

\[1 - \overline{X}_B = \frac{1}{2} \frac{\tau}{t} - \frac{1}{3!} \left( \frac{\tau}{t} \right)^2 + \frac{1}{4!} \left( \frac{\tau}{t} \right)^3 + \ldots.
\]

56. Give the expression for conversion when chemical reaction control the rate of reaction.

\[1 - \overline{X}_B = \frac{1}{4} \frac{\tau}{t} - \frac{1}{2!} \left( \frac{\tau}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau}{t} \right)^3\]

57. Give the expression for conversion under ash layer resistance controls.
58. Give the expression for conversion for mixed flow of solids under diffusion through gas film controls.

\[ 1 - \frac{\bar{X}_B}{f_i} = \sum_{R_m} \left\{ \frac{1}{2} \frac{\tau(R_i)}{t} - \frac{1}{3!} \left( \frac{\tau(R_i)}{t} \right)^2 + \frac{1}{4!} \left( \frac{\tau(R_i)}{t} \right)^3 \right\} \frac{f(R_i)}{f} \]

59. Give expression for conversion under chemical reaction controls.

\[ 1 - \frac{\bar{X}_B}{f_i} = \sum_{R_m} \left\{ \frac{1}{4} \frac{\tau(R_i)}{t} - \frac{1}{20} \left( \frac{\tau(R_i)}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau(R_i)}{t} \right)^3 \right\} \frac{f(R_i)}{f} \]

60. When does the carryover of solids f occur?
When the feed to a fluidized bed consists of a wide size distillation of solids carry over of sines may occur.

61. Give the expression for mean residence time of particle of given size.

\[ \bar{t}(R_i) = \frac{W(R_i)}{f_0(R_i)} = \frac{W(R_i)}{f_1(R_i) + f_2(R_i)} = \frac{1}{F_1 + \frac{f_2(R_i)}{W(R_i)}} \]

62. Give the expression for mean conversion under chemical reaction controls for the above case.

\[ 1 - \frac{\bar{X}_B}{f_i} = \sum_{R_m} \left\{ \frac{1}{4} \frac{\tau(R_i)}{t(R_i)} - \frac{1}{20} \left( \frac{\tau(R_i)}{t(R_i)} \right)^2 + \frac{1}{120} \left( \frac{\tau(R_i)}{t(R_i)} \right)^3 \right\} \frac{f_0(R_i)}{f_0} \]

63. Give the expression under ash diffusion is controlling resistance.

\[ 1 - \frac{\bar{X}_B}{f_i} = \sum_{R_m} \left\{ \frac{1}{5} \frac{\tau(R_i)}{t(R_i)} - \frac{19}{420} \left( \frac{\tau(R_i)}{t(R_i)} \right)^2 + \frac{41}{4620} \left( \frac{\tau(R_i)}{t(R_i)} \right)^3 \right\} \frac{f_0(R_i)}{f_0} \]

64. Obtain the expression for \( f_1 \) for case of elutriation.

\[ f_1 = \sum_{R_m} \frac{f_0(R_i)}{1 + \frac{W}{f_1} k(R_i)} \]

65. Give examples of process under fixed bed reactors are used.
Consider first a fixed bed in which the solid particles constitute or contain one of the reactants, while a second reactant is in the fluid phase. In the general case the reactant concentration in the bulk fluid will decrease along the reactor length z.
1. When the heterogeneous fluid-fluid reactions take place?
   Heterogeneous fluid-fluid reactions are made to take place for one of the three reasons;
   - The product of reaction may be a desired material.
   - To facilitate the removal of an unwanted component from a fluid.
   - To obtain a vastly improved product distribution.

2. Give the importance of equilibrium solubility in gas-liquid operations.
   The solubility of the reacting components will limit their movement from one phase to other. This factor will certainly influence the form of the rate equation since it will determine whether the reaction takes place in one or both phases.

3. Define Enhancement factor. (NOV/DEC 2014)
   The liquid enhancement factor (E) is defined as the ratio of rate of take up of gaseous „A” when reaction occurs to the rate of take up of gaseous „A” for straight mass transfer, at same C_{Ai}, C_A, C_{Bi}, C_B in the two cases. Or Enhancement factor E is defined as the ratio between the Sherwood number with chemical reaction and that without reaction.

4. ‘Enhancement factor is always greater than or equal to one’. Justify this statement.
   Since the rate of take up of „A” when reaction occurs is greater than or equal to the rate of take up of „A” for straight mass transfer, the enhancement factor is always greater than or equal to one.

5. Define Hatta number. (NOV/DEC 2013)
   Hatta number (M_H) is defined as the square root of the ratio of maximum possible conversion in the liquid film to maximum diffusion transport through the liquid film.

6. Explain the significance of Hatta number.
   The significance of Hatta number (M_H) is;
   - If M_H > 2, reaction occurs in the liquid film and are fast enough.
   - If 0.02 < M_H < 2, reaction is influenced by all the resistances.
   - If M_H < 0.02, reactions are infinitely slow.

7. Does the enhancement factor decrease or increase with Hatta number? Explain.
   Yes, Enhancement factor (E) decrease or increases with Hatta number (M_H). Because the evaluation of „E” depends on two quantities;
   - The enhancement factor for an infinitely fast reaction (E_i)
   - Maximum possible conversion in the film compared with maximum transport through the film (M_{He}).

8. How do you classify the kinetic regimes in gas-liquid reactions?
   The classification of kinetic regimes in a Gas-Liquid reaction based on the relative rates of reaction and mass transfer. According to two-film theory, the reaction may occur in liquid film or in both liquid film and main body of liquid or in main body of liquid. Based on the above three factors of reactions, we have eight special cases from infinitely fast to slow reaction as;
   - Instantaneous reaction - with low C_{liquid} & high C_{liquid}
   - Fast reaction - with low C_{liquid} & high C_{liquid}
   - Intermediate rate with reaction in the film and in the main body of the liquid.
9. What do you mean by instantaneous reactions in the gas-liquid operations?
In instantaneous reactions, the absorbing component of the gas and the liquid phase reactant cannot co-exist in the same region. In such reactions, the concentration of the liquid phase reactant at the gas-liquid interface is zero.

10. What do you mean by slow reactions in the gas-liquid operations?
In slow reactions, occurs in the main body of the liquid, mass transfer resistance is negligible and the composition of liquid phase and gas phase reactants are uniform. Thus, the rate is determined by chemical kinetics alone.

12. In a gas-liquid reaction, it was observed that the reaction occurs on a plane within the liquid film. Is the reaction slow, fast or instantaneous? Explain.
The reaction is either instantaneous or fast, with low concentration of liquid.
   □ For instantaneous reaction, the reaction plane exists where the two reactants interact in the liquid film.
   □ For fast reactions, the reaction zone exists where the two reactants completely reacted in the liquid film.

13. What are the advantages of surface renewal theory?
The biggest advantage arises from the square root dependence on the diffusion coefficient. This allows one to better predict the behavior of various solutes with different diffusion coefficients based on measured behavior of one particular solute. The square root dependence gives more accurate prediction than the linear dependence found with the two-film model. Recognize however that surface renewal is really most accurate when surface renewal rates are high.

This approach tries to apply the mathematics of the penetration theory to be more plausible physical picture. The liquid is pictured as two regions, a large well mixed bulk and an interfacial region that is renewed so fast that it behaves as a thick film. The surface renewal theory is caused by liquid flow.

15. What are the various resistances involved in developing rate equations for gas-liquid reactions?
The various resistances involved in developing rate equations for gas-liquid reactions are:
   □ Mass transfer resistances, to bring the reactants together.
   □ The resistance of the chemical reaction step.

16. Sketch the concentration profile for an instantaneous gas-liquid non-catalytic reaction.
17. Write short notes on slurry reactors.
- A slurry reactor is a multiphase flow reactor in which reactant gas is bubbled through a solution containing solid catalyst particles. The solution may be either a reactant or a product or an inert.
- Slurry reactors may be operated in a batch or continuous mode. One of the main advantages of slurry reactors is that temperature control and heat recovery are easily achieved. In addition, constant overall catalytic activity can be maintained by the addition of small amounts of catalyst with each reuse during batch operation or with constant feeding during continuous operation.
- These reactors are widely used in hydrogenation of fatty acids over a supported nickel catalyst, hydroformation of CO with high-molecular-weight olefins on either a cobalt or ruthenium complex bound to polymers, etc.

18. What are the advantages of slurry reactors over fixed beds?
The advantages of slurry reactors over fixed beds are
a. It usually has a higher rate
b. It holds good for fast reactions on porous catalyst
Note: Slurry reactors can use very fine particles, and this lead to problems of separating catalyst from liquid. (Only disadvantage of slurry reactor)

19. Explain Film penetration theory. (May 2015), [Dec 2012] (May/June 2014)
The penetration theory for mass transfer. Here the interfacial region is imagined to be very thick continuously generated by flow. Mass transfer now involves diffusion into this film. In this and other theories the interfacial concentration in the liquid is assumed to be in equilibrium with that in the gas.

20. **Write short notes on trickle bed reactors.**

c. A trickle bed reactor is a three-phase version in which gas and liquid reactants are brought into contact with solid catalyst particles.

d. In this gas and liquid flow counter-currently downward over a fixed-bed of catalyst particles contained in a tubular reactor.

e. These reactors are widely used for hydro-desulphurization of liquid petroleum fractions and hydro-treating of lubricating oils.

21. **List the types of flow regime that are possible in trickle bed reactors.**

In trickle bed reactor, four types of flow regimes are possible:

- **Trickle flow regime:** In this regime, gas flow is continuous.
- **Dispersed bubble regime:** In this regime, liquid phase is continuous and the gas moves into the bubbles.
- **Spray regime:** In this regime, gas flow rate is high while liquid rate is low. Liquid falls in droplets through the gas phase.
- **Pulsed flow regime:** In this regime, flow rates of both gas and liquid are high.
1. Describe progressive conversion model with diagram.

**Progressive-Conversion Model (PCM):**

This model assumes that the reactant gas enters and throughout the particle at all times (reaction proceeds continuously throughout the particle). The rate of reaction is different at different locations within the particle.

Hence, the whole particle is continuously and progressively converted into the product as shown in Fig. (which also shows (in diagrammatic form) how the concentration of the solid reactant changes throughout the solid particle at different instants after the onset of the reaction). [If the product is itself is a firm solid, the particle size remains unchanged, but if the product is volatile or flaking, the particle size decreases until it disappears.]

![Diagram of progressive conversion model](image_url)

**Figure:** Sketch of a solid particle and concentration profile of solid reactant (B) with progress of reaction – unchanging size – progressive-conversion model.
2. Describe shrinking core model with example.

Shrinking-Core Model (SCM)

This model assumes that the reaction first begins at the outer surface of the solid particle and the deeper layers do not take part in the reaction until all the outer layer has transformed into solid or gaseous product. Gradually, the reaction zone then moves inward (into the solid), constantly reducing the size of core of unreacted solid and leaving behind completely converted solid (solid product) and inert material (inert constituent of the solid reactant).

We refer to converted solid (i.e. solid product) and inert material as ash. An unreacted core of solid continuously decreases in size / shrinks in size during reaction until it is entirely consumed (Here the amount of solid material to be consumed by reaction is shrinking with the time).

At any given instant, the solid particle comprises of a core surrounded by an envelope. The core is the unreacted reactant (that shrinks with time) so this model is referred to as shrinking unreacted-core model. The envelope consists of a solid product and inert material.

The shrinking of size of unreacted core of solid with reaction time is shown in Fig.

Figure: Sketch of a solid particle and concentration profile of solid reactant – unchanging size – the shrinking – core model
3. What are the steps occurring accounting to SCM

Shrinking – Core Model (SCM) for Spherical of Unchanging Size / Fixed Size:

According to this model, the following five steps occur in succession during reaction:

i Diffusion of the gaseous reactant A through the gas film surrounding the particle to the surface of solid particle... reactant A diffuses to the external surface of the solid particle from the bulk gas phase through the gas film..... external diffusion.

ii Penetration of A by diffusion through pores and cracks in the blanket (layer) of ash to the surface of the unreacted core.... Pore or internal diffusion.

iii Reaction of gaseous A with solid B at the surface of the unreacted core (reaction surface).

iv Diffusion of any gaseous products back to the exterior surface of solid through the ash (ash layer).... Reverse internal diffusion.

v Diffusion of gaseous products through the gas film back into the body of gas .... Reverse external diffusion.

Fig. shows the concentration profile of a gaseous reactant A reacting with a solid particle-the concentration of reactant A at different points of the reaction space.

Figure: Concentration profile of a gaseous reactant A reacting with a solid particle-A(g)+bB(s) → solid product-particle of unchanging size-shrinking-core model
4. Derive the equation for SCM when diffusion through gas film controls.

Diffusion through Gas film Controls (Controlling resistance-gas film diffusion):

Whenever the resistance of the gas film controls the overall reaction rate, the concentration profile for gaseous reactant A will be as shown in Fig.

![Representation of a reacting particle when the controlling resistance is diffusion through the gas film](image)

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

It is clear from Fig. that no gaseous reactant A is present at the surface of particle and thus, the concentration driving force, \( C_{Ag} - C_{As} \), becomes \( C_{Ag} \) and is constant during the course of reaction.

As the rate of mass transfer is defined as the rate of flow of material normal to a unit surface, we base the rate on the unchanging exterior surface of a particle. The rate of reaction of A per unit surface is equal to the molar flux of A from the main body of gas (the bulk gas phase) to the surface of the particle.

\[
- \frac{1}{S_{ex}} \frac{dN_A}{dt} = - \frac{1}{4\pi R^2} \frac{dN_A}{dt} = k_g \left( C_{Ag} - C_{As} \right) = k_g C_{Ag} = \text{const} \ t \rightarrow (1)
\]

[as \( C_{Ag} \) and \( k_g \) both are constant for a given case]
From the stoichiometry of the reaction:

\[ \text{A(g) + bB(s) \rightarrow products} \]

\[
-\frac{dN_A}{dt} = -\left(\frac{1}{b}\right)dN_B = -\frac{1}{b}\frac{dN_B}{dt}
\]

\[
-\frac{dN_B}{dt} = -b\frac{dN_A}{dt} \quad \rightarrow (2)
\]

Combining Equations (1) and (2), we get

\[
-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}\frac{dN_B}{dt} = -\frac{b}{4\pi R^2}\frac{dN_A}{dt} = bk_g C_{Ag} = \text{const} \quad \rightarrow (3)
\]

The amount of B present in a particle is given by

\[ N_B = \rho_B V \quad \rightarrow (4) \]

When \( \rho_B \) is the molar density of B in solid in moles/m\(^3\) solid and V is the volume of a particle (m\(^3\) solid).

The decrease in volume or radius of unreacted core as a result of disappearance of \( dN_B \) moles of solid reactant is given by

\[
-dN_B = -bdN_A = -d(\rho_B V) = -\rho_B dV = -\rho_B d \left(\frac{4}{3}\pi r_c^3\right)
\]

\[
= -4\pi \rho_B r_c^2 dr_c \quad \rightarrow (5)
\]

Putting value of \( -dN_B \) from Equation (5) in Equation (3) we get an expression for the rate of reaction in terms of the shrinking radius of unreacted core:

\[
-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{4\pi \rho_B r_c^2}{4\pi R^2}\frac{dr_c}{dt} = \frac{-\rho_B r_c^2}{R^2}\frac{dr_c}{dt} = bk_g C_{Ag} \quad \rightarrow (6)
\]

where \( k_g \) is the mass transfer coefficient between fluid and particle, m\(^3\)/(m\(^2\).s.).

Rearranging Equation (6), gives

\[
\frac{\rho_B}{R^2} r_c^2 dr_c = bk_g C_{Ag} dt
\]
Integrate the above equation between the limits:

At \( t=0 \) ... \( r = R \), At \( t=t \), ... \( r = r_c \)

\[
- \frac{\rho_B}{R^2} \int_{R}^{r_c} r_c^2 \, dr_c = b k_b \int_{0}^{t} dt
\]

\[
- \frac{\rho_B}{R^2} \left[ \frac{r_c^3}{3} - \frac{R^3}{3} \right] = \frac{\rho_B R}{3 R^3} \left[ R^3 - r_c^3 \right]
\]

\[
= \frac{\rho_B R}{3} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] = b k_b C_{Ag} t
\]

\[ \therefore \quad t = \frac{\rho_B R}{3 b k_b C_{Ag}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad \to (7) \]

Equation (7) gives us an idea regarding how the unreacted core shrinks with time.

Let the time for complete conversion of a particle be \( \tau \). At complete conversion \( r_c = 0 \), so by putting \( r_c = 0 \) in Equation (7) we obtain an expression for \( \tau \) (replace \( t \) by \( \tau \)).

\[
\tau = \frac{\rho_B R}{3 b k_b C_{Ag}} \left[ 1 - \left( \frac{0}{R} \right)^3 \right]
\]

\[ \therefore \quad \tau = \frac{\rho_B R}{3 b k_b C_{Ag}} \quad \to (8) \]

Dividing Equation (7) by Equation (8), we get,

\[
\frac{t}{\tau} = 1 - \left( \frac{r_c}{R} \right)^3 \quad \to (9)
\]

Equation (9) expresses the radius of unreacted core in terms of fractional time for complete conversion.

The radius of unreacted core in terms of fractional conversion is given by
1 − X_B = fraction of B unreacted

\[ \frac{\text{Volume of unreacted core}}{\text{Total volume of particle}} = \frac{4}{3} \pi r_c^2 = \frac{104}{3} \pi R^3 \]

Combining Equation (9) and (10), we get,

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

→ (11)

Equation (11) expresses the relationship of time with the radius of unreacted core and fractional conversion of B.

5. Derive the equation for SCM under chemical reaction controls?

Diffusion through Ash Layer Controls (Controlling resistance-ash layer diffusion):

Whenever the resistance of the ash layer controls the overall rate of reaction, the concentration profile of the gaseous reactant A will be as shown in Fig.

![Diagram showing concentration profile](image)

Figure: Representation of a reacting particle when the controlling resistance is diffusion through the ash layer
Under this condition, the instantaneous rate of reaction of A at any time is given by the rate of diffusion of A to the reaction surface, that is,

\[- \frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{const} \tan t \quad \rightarrow (1)\]

Where $Q_A$ is the flux of A through a spherical surface of any radius $r$ in the ash layer, $Q_{As}$ is the flux of A through the exterior surface of particle and $Q_{Ac}$ is the flux of A to the reaction surface.

The flux of A through the ash layer may be represented by Fick’s law:

\[Q_A = D_e \frac{dC_A}{dr} \quad \rightarrow (2)\]

(Please note both $Q_A$ and $dC_A/dr$ are positive)

Where $D_e$ is the effective diffusion coefficient of A in the ash layer.

Combining Equations (1) and (2), we get for any $r$,

\[- \frac{dN_A}{dt} = 4\pi r^2 D_e \frac{dC_A}{dr} = \text{const} \tan t \quad \rightarrow (3)\]

Limits of integration:

At $r=R \ldots C_A = C_{As} = C_{Ag}$ and at $r=r_c \ldots C_A = C_{Ac} = 0$

Integrated Equation (3) across the ash layer.

\[- \frac{dN_A}{dt} \int_r^R \frac{dr}{r^2} = 4\pi D_e \int_{C_{Ag}}^0 dC_A\]

\[- \frac{dN_A}{dt} \left[ \frac{1}{R} - \frac{1}{r_c} \right] = -4\pi D_e C_{Ag}\]

\[- \frac{dN_A}{dt} \left[ \frac{1}{r_c} - \frac{1}{R} \right] = 4\pi D_e C_{Ag} \quad \rightarrow (4)\]

Equation (4) represents the condition of a reacting particle at any time.
We have \( \frac{dN_A}{dt} = -\frac{1}{b} \frac{dN_B}{dt} \) (from the stoichiometry of reaction)

Replacing \( \frac{dN_A}{dt} \) by \(-\frac{1}{b} \frac{dN_B}{dt}\) in Equation (4) we obtain

\[
-\frac{1}{b} \frac{dN_B}{dt} \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\rho D_e C_{Ag}
\]

\[
-dN_B \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\pi b D_e C_{Ag} dt \quad \rightarrow (5)
\]

We have \( -dN_B = -\rho_B dV = -\rho_B d \left( \frac{4}{3} \pi r_c^3 \right) = -4\pi r_c^2 dr_c \)

Replacing \( -dN_B \) in Equation (5) by its value given above, we get

\[
-4\rho_B r_c^2 dr_c \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\pi b D_e C_{Ag} dt \quad \rightarrow (6)
\]

\[
-\rho_B \int \left( \frac{1}{r_c} - \frac{1}{R} \right) r_c^2 dr_c = bD_e C_{Ag} \int dt
\]

\[
-\rho_B \int \left( \frac{r_c^2}{R} - \frac{R}{r_c} \right) dr_c = bD_e C_{Ag} \int dt
\]

Limits of integration: \( t=0 \rightarrow r_c = R \) and \( t=t \rightarrow r_c = r_c \)

\[
-\rho_B \int_R^{r_c} \left( \frac{r_c^2}{R} - \frac{R}{r_c} \right) dr_c = bD_e C_{Ag} \int_0^t dt
\]

\[
-\rho_B \left[ \frac{r_c^2}{2} - \frac{R^2}{2} \right] = bD_e C_{Ag} t
\]

\[
-\rho_B \left[ \frac{r_c^2}{3R} - \frac{R^3}{2} + \frac{R^3}{3R} \right] = bD_e C_{Ag} t
\]

\[
\rho_B \left[ \frac{R^2}{6} - \frac{r_c^2}{2} + \frac{r_c^3}{3R} \right] = bD_e C_{Ag} t
\]

\[
t = \frac{\rho_B}{bD_e C_{Ag}} \left[ \frac{R^2}{6} - \frac{r_c^2}{2} + \frac{r_c^3}{3R} \right]
\]

Taking \( R^2 / 6 \) common from RHS of the above equation, we get
Equation (7) relates the radius of unreacted core with time when the diffusion through ash layer controls the overall reaction rate.

The time required for the complete conversion of a particle \((\tau)\) is obtained by putting \(r_c = 0\) in Equation (7) as for the complete conversion of a particle \(r_c = 0\).

\[
\tau = \frac{\rho_B R^2}{6 b D_e C_{Ag}} \left[ 1 - 3 \left( \frac{r_c}{R} \right)^2 + 2 \left( \frac{r_c}{R} \right)^3 \right] \quad \rightarrow (8)
\]

Dividing Equation (7) by Equation (8), we get

\[
\frac{t}{\tau} = 1 - 3 \left( \frac{r_c}{R} \right)^2 + 2 \left( \frac{r_c}{R} \right)^3 \quad \rightarrow (9)
\]

Equation (8) gives idea regarding the progress of reaction in terms of the time required for complete conversion.

We have,

\[
1 - X_B = \left( \frac{r_c}{R} \right)^3
\]

\[
(1 - X_B)^{\frac{3}{2}} = \frac{r_c}{R}
\]

\[
\therefore \quad \text{Equation (9) in terms of fractional conversion becomes}
\]

\[
\frac{t}{\tau} = 1 - 3 (1 - X_B)^{\frac{3}{2}} + 2 (1 - X_B) \quad \rightarrow (10)
\]
6. Derive the equation for SCM under chemical reaction controls?

Chemical Reaction Controls (controlling resistance-chemical reaction step):

Whenever the resistance of chemical reaction step controls the overall rate of reaction, the concentration profile for gaseous reactant A will be as shown in Fig. In this case, diffusion steps – diffusion of A through the gas film and the ash layer – are rapid with respect to the surface reaction (slow reaction) and thus virtually no concentration gradients exit in the gas film and in the ash layer i.e. as neither the gas film nor the ash layer offers any significant resistance to mass transfer, the concentration of A at the reaction surface at the radial position $r_c$ will be $C_{Ag}$, the same as in the bulk of the gas.

![Diagram of a reacting particle when controlling resistance is chemical reaction](image)

**Figure:** Representation of a reacting particle when controlling resistance is chemical reaction $-A(g) + b \, B(s) \rightarrow \text{products.}$

Here the overall rate of reaction is proportional to the available surface of unreacted core. Thus, taking unit surface of unreacted core of radius $r_c$ as the basis for the reaction rate (i.e. to define the rate), the rate of reaction of A i.e. the rate at which moles of A are consumed in the reaction per unit surface is given by

$$-\frac{1}{4\pi r_c^2} \frac{dN_A}{dt} = k'' C_{Ag}$$

From the stoichiometry of the reactions represented by Equation and Equation,
\[
- \frac{dN_A}{dt} = - \frac{1}{b} \frac{dB}{dt} \quad \left[ A(g) + bB(s) \rightarrow \text{Products} \right]
\]

Combining Equation and

\[
- \frac{1}{4\pi r_c^2} \frac{dN_B}{dt} = - \frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = bk'' C_{Ag}
\]

Where \( k'' \) is the first order rate constant for the surface reaction, m/s.

Also we have

\[ N_B = \rho_B V \quad \text{... amount of B present in a particle} \]

\[
\frac{dN_B}{dt} = \rho_B \frac{dV}{dt} = \rho_B \left( \frac{4}{3} \pi r_c^3 \right) = 4\pi \rho_B r_c^2 dr_c
\]

\[ \therefore \quad \frac{dN_B}{dt} = 4\pi \rho_B r_c^2 \frac{dr_c}{dt} \]

Replacing \( \frac{dN_B}{dt} \) in Equation by its value in terms of the shrinking radius given by Equation, we get

\[
- \frac{1}{4\pi r_c^2} 4\pi \rho_B r_c^2 \frac{dr_c}{dt} - \rho_B \frac{dr_c}{dt} = bk'' C_{Ag}
\]

Integrate the above equation within limits:

\[ \text{Att} = 0 \ldots r_c = R \quad \text{and} \quad t = t \ldots r_c = r_c \]

\[
- \rho_B \int_{r_c}^R dr_c = bk'' C_{Ag} \int_0^1 dt
\]

\[ - \rho_B (r_c - R) = \rho_B (R - r_c) = bk'' C_{Ag} t \]

\[ \therefore \quad t = \frac{\rho_B}{bk'' C_{Ag}} (R - r_c) \]
The time $\tau$ required for complete conversion corresponds to $r_c = 0$ (zero radius of the unreacted core) and is obtained by replacing $t$ by $\tau$ and putting $r_c = 0$ in Equation.

$$\tau = \frac{\rho_B R}{b k'' C_{Ag}}$$

Dividing Equation by Equation we get

$$\frac{t}{\tau} = \frac{R - r_c}{R} = 1 - \frac{r_c}{R}$$

We have

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

$$\therefore \quad (1 - X_B)^{\frac{1}{3}} = \frac{r_c}{R}$$

Combining Equation and

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

Equation gives the time $t$ at which the core has a radius $r_c$ and the fractional conversion $X_B$ for the particle in terms of $\tau$.

7. Derive the expression for SCM for particle of varying size under diffusion through gas film controls.

**Diffusion through Gas Film Controls (Controlling resistance-film diffusion):**

When diffusion through the gas film controls, the situation becomes more involved because of the changing particle size in turn changing the film resistance. Film resistance at the surface of a particle depends upon the following parameters:

i. Size of particle.
ii. Properties of fluid,
iii. Relative velocity between particle and solid.
Figure: Concentration profile of a gaseous reactant A for the reaction between a shrinking solid particle and gaseous reactant A as per the stoichiometry: \( A (g) + bB (s) \rightarrow rR (g) \)

The parameters have been correlated for various ways of contacting fluid with solid. The correlation for mass transfer of a component with mole fraction \( y \) in a fluid to free falling solids is:

\[
\frac{k_g \cdot dpy}{D} = 2 + 0.6N_{Re}^{1/2}
\]

\[
N_{sc} = \frac{\mu}{\rho D} \quad \text{..... Schmidt number}
\]

\[
N_{Re} = \frac{dpup}{\mu} \quad \text{..... Reynolds number}
\]

\[
\frac{k_g \cdot dpy}{D} = 2 + 0.6 \left( \frac{\mu}{\rho D} \right)^{1/2} \left( \frac{dpup}{\mu} \right)^{1/2}
\]

This relationship is referred to as the Froessling correlation.

Since a particle changes in size with time, \( k_g \) varies during reaction. In general, \( k_g \) increases with increase in gas velocity and with smaller particles.

\[
k_g \propto \frac{1}{dp} \quad \text{... for small dp and low u}
\]

\[
k_g \propto u^{1/2} \quad \text{for large dp and high u}
\]
Equation represents particles in the Stokes law regime \[ \frac{d\rho_p}{\mu} < 0.3 \]

Let us derive conversion-time relationship for such particles.

**Stokes Regime-Small Particles:**

At the time when a particle of original size \( R_o \) has shrunk to size \( R \), we can write

\[
dN_B = d(\rho_B) = d(\rho_B V) = \rho_B dV = \rho_B d\left(\frac{4}{3} \pi R^3\right) = 4\pi \rho_B R^2 dR
\]

The rate of reaction in terms of size \( R \) of shrinking unreacted particle is given by an expression similar to Equation.

\[
\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\left(\frac{1}{4\pi R^2}\right) 4\pi \rho_B R^2 \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = bk_C A_B
\]

In the Stokes regime Equation reduces to

\[ k_c = \frac{2D}{dp} = \frac{D}{R} \]

Therefore, Equation becomes

\[-\rho_B \frac{dR}{dt} = \frac{bC_{A_B}}{R} \]

Integrating, we get

\[
\frac{dR}{dt} = -\frac{bC_{A_B} D}{\rho_B R} \quad \int R dR = -\frac{bC_{A_B} D}{\rho_B} \int dt
\]
Limits of integration:

At \( t=0 \)...R=R_0 and at \( t=t \) ... R=R

\[
\int_{0}^{R} R \, dR - \frac{bC_{Ag}D}{\rho_B} \int_{0}^{t} dt \\
= \left[ \frac{R^2}{2} - \frac{R_0^2}{2} \right] = -\frac{bC_{Ag}Dt}{\rho_B}
\]

\[
t = -\frac{\rho_B}{bC_{Ag}D} \left[ \frac{R^2}{2} - \frac{R_0^2}{2} \right]
\]

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

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

The time for complete disappearance of a particle (\( \tau \)) is obtained by putting \( t = \tau \) and \( R = 0 \) in Equation. Therefore,

\[
\tau = \frac{\rho_B R_0^2}{2bC_{Ag}D}
\]

Dividing Equation by Equation we get

\[
\frac{t}{\tau} = 1 - \left( \frac{R}{R_0} \right)^2
\]

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

\[
1 - X_B = \left( \frac{R}{R_0} \right)^3
\]

\[
\therefore \quad (1 - X_B)^{\frac{1}{3}} = \frac{R}{R_0}
\]

Therefore

\[
\frac{t}{\tau} = 1 - \left( \frac{R}{R_0} \right)^2 = 1 - (1 - X_B)^{\frac{1}{3}}
\]
Equation expresses the relationship of size with time for shrinking particles in the Stokes regime. The relationship is given by Equation well represents small burning solid particles as well as small burning liquid droplets.

9. A watch of spherical solids (of single size) is treated by gas in a uniform environment. Solid is connected to a firm non-faking product according to scm. The concession is 87.5% in a reaction time of 14 and concession is complete in 24. determine rate controlling mechanism.

For chemical reaction controls:

\[
\frac{1}{4\pi r_c^2} \frac{dN_B}{dt} = bk''C_{Ac}
\]

\[
C_{Ac} - C_{Ac} = C_{Ac} \text{ as } C_{Ac} = 0 \text{ for irreversible reaction}
\]

\[
- \frac{1}{S_{ex}} \frac{dN_B}{dt} = 4\pi r_c^2k''C_{Ac}
\]

\[
- \frac{1}{S_{ex}} \frac{dN_B}{dt} = 4\pi r_c^2k''C_{Ac} = \frac{bk''r_c^2C_{Ac}}{4\pi R^2} = \frac{bk''r_c^2C_{Ac}}{R^2}
\]

\[
- \frac{1}{r_c^2k''/R^2} = \frac{R^2}{r_c^2k''} = \frac{b}{1} \frac{dN_B}{S_{ex} \cdot dt}
\]

Adding Equations and, we get

\[
\frac{1}{k_g} + \frac{R(R-r_c)}{D_{ec}r_c} + \frac{R^2}{r_c^2k''} = \frac{b(C_A-C_{As})}{1 \frac{dN_B}{S_{ex} \cdot dt}} + \frac{b(C_{As}-C_{Ac})}{1 \frac{dN_B}{S_{ex} \cdot dt}} + \frac{bC_{Ac}}{-1 \frac{dN_B}{S_{ex} \cdot dt}} + \frac{bC_{Ac}}{-1 \frac{dN_B}{S_{ex} \cdot dt}}
\]

\[
\frac{1}{k_g} + \frac{R(R-r_c)}{D_{ec}r_c} + \frac{R^2}{r_c^2k''} = \frac{b(C_A-C_{As})}{1 \frac{dN_B}{S_{ex} \cdot dt}} + \frac{bC_{Ac}}{-1 \frac{dN_B}{S_{ex} \cdot dt}} + \frac{bC_{Ac}}{-1 \frac{dN_B}{S_{ex} \cdot dt}}
\]

\[
\frac{1}{k_g} + \frac{R(R-r_c)}{D_{ec}r_c} + \frac{R^2}{r_c^2k''} = \frac{b}{1} \frac{dN_B}{S_{ex} \cdot dt}
\]

\[
\frac{1}{k_g} + \frac{R(R-r_c)}{D_{ec}r_c} + \frac{R^2}{r_c^2k''} = \frac{bC_A}{1 \frac{dN_B}{S_{ex} \cdot dt}}
\]
Rearranging above equation, we get

\[ \frac{-1}{S_{ex}} \frac{dN_B}{dt} = \frac{bC_A}{\frac{1}{k_g}} + \frac{R(R-r_c)}{D_e r_c} + \frac{R^2}{r_c^2 k''} \]

10. Calculate the time required for complete burning of particles of graplute (size \( R_0 = 5 \text{mm} \), \( \epsilon_B = 2.2 \text{g/cm}^3 \)) in an 8% oxygen stream at 900°C and 1 atm for the high gas velocity used assume film diffusion does not offer any resistance to transfer and reaction. Data: \( k'' = 20 \text{cm/s} \).

Calculate the time required for complete burning of particles of graphite (size: \( R_0 = 5 \text{ mm} \), density: \( \rho_B = 2.2 \text{ g/cm}^3 \)) in an 8% oxygen stream at 900°C and 1 atm.

For the high gas velocity used assume film diffusion does not offer any resistance to transfer and reaction.

Data: Rate constant \( k'' = 20 \text{ cm/s} \)

Solution:

In burning of particles of graphite (pure C) there is no ash formation. The reacting particle shrinks in size as reaction progresses and finally disappears (no complete combustion).

As ash layer is absent there are only two possible resistances:

i. resistance offered by film diffusion.

ii. Resistance offered by chemical reaction

But we are provided with: film diffusion does not offer any resistance.

So in our case we have only one resistance: resistance offered by chemical reaction i.e. in our case chemical reaction controls the rate.

For small spherical particles when chemical reaction controls rate the time required for complete conversion (i.e. time required for complete burning of particle of graphite) is given by

\[ \tau = \frac{\rho_B R_0}{b k'' C_{Ag}} \]
Combustion Reaction:

\[ \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \text{....compare.....A(g)} + \text{bB(s)} \rightarrow \text{fluid product.} \]

\[ : \ b=1 \text{ (stoichiometric coefficient of C: Carbon)} \]

\[ R_0 = 5 \text{mm} = 0.5 \text{cm} \]

Density of graphite = \( \rho_b = 2.2 \text{g/cm}^3 \)
Rate constant = \( k^" = 20 \text{ cm/s} \)
Evaluate \( C_{Ag} \): bulk gas phase concentration of A.
Here A is \( \text{O}_2 \).

\[ C_{Ag} = \frac{P_{Ag}}{RT} \]

A in gas stream – 8% by volume, total pressure = 1 atm.

For an ideal gas : volume % A = pressure % A

Pressure % A = 8 = \( \frac{P_{Ag} \times 100}{P} \)

\[ \because \quad P_{Ag} = \frac{8 \times 1}{100} = 0.08 \text{ atm.} \]

\[ T = 900^\circ \text{C} = 1173 \text{K} \]

\[ R = 82.06 \text{(cm}^2\text{atm)/mol.K} \]

\[ C_{Ag} = \frac{0.08}{82.06 \times 1173} = 8.31 \times 10^{-7} \text{mol/cm}^3 \]

\[ \rho_B = 2.2 \text{ g/cm}^3 \text{ convert this mass density into molar density mol/cm}^3 \]

\[ \rho_B = \frac{2.2}{12} = 0.183 \text{ mol/cm}^3, (\text{At.Wt.C} = 12) \]

\[ \therefore \quad \tau = \frac{0.183 \times 0.50}{1 \times 20 \times 8.31 \times 10^{-7}} = 5505.4 \text{s} \]

**Time required for complete burning of particles of graphite = 5505.4 s or = 1.53 h....**
11. Two small samples of solids are kept in a constant environment over for 1hr under the conditions prevailing in a oven the 4mm particles are 57.8% converted & 2mm particles are 87.5% converted

(a) Find the rate controlling mechanism for conversion of solids.

(b) Find the time required for complete conversion of 1mm particle in this oven.

Solution:

For constant size spherical particles the possible mechanisms controlling the rate are:

(1) film diffusion
(2) ash diffusion and
(3) chemical reaction.

Data given:

<table>
<thead>
<tr>
<th>R, mm</th>
<th>t, h</th>
<th>X_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_1 = 4/2 = 2</td>
<td>1</td>
<td>X_B_1 = 0.578</td>
</tr>
<tr>
<td>R_2 = 2/2 = 1</td>
<td>1</td>
<td>X_B_2 = 0.875</td>
</tr>
</tbody>
</table>

(i) For film diffusion controlling we have for constant size spherical particles:

\[
\frac{t}{\tau} = X_B
\]

And

\[
\tau \propto R
\]

\[
\frac{t}{\tau_1} = X_B_1 \quad \ldots \ldots \text{(1) for 4 mm particle}
\]

\[
\frac{t}{\tau_2} = X_B_2 \quad \ldots \ldots \text{(2) for 2 mm particle}
\]

\[
\tau_1 \propto R_1 \quad \therefore \tau_1 = cR_1, \quad c = \text{constant}
\]

\[
\tau_2 \propto R_2 \quad \therefore \tau_2 = cR_2
\]

From equations (1) and (2) we get:

\[
t = X_B_1 \tau_1 = X_B_2 \tau_2
\]
\[ \therefore X_{B1} \cdot c \cdot R_1 = X_{B2} \cdot c \cdot R_2 \]
\[ X_{B1} \cdot R_1 = X_{B2} \cdot R_2 \text{......this should be satisfied} \]
\[ X_{B1} \cdot R_1 = 0.578 \times 2 = 1.158 \]
\[ X_{B2} \cdot R_2 = 0.875 \times 1 = 0.875 \]

\[ \therefore X_{B1} \cdot R_1 \neq X_{B2} \cdot R_2 \text{......} \]

----------so film diffusion does not control the rate.

OR:

We have:

\[ \frac{t}{\tau_1} = X_{B1} \]
\[ \frac{t}{\tau_2} = X_{B2} \]
\[ \frac{t}{\tau_2} = \frac{X_{B1}}{X_{B2}} \]

\[ \frac{t}{\tau_1} = \frac{cR_1}{cR_2} = \frac{R_2 \cdot R_1}{R_2 \cdot R_1} = \frac{X_{B1}}{X_{B2}} \]

\[ \frac{R_2}{R_1} = \frac{1}{2} = 0.5 \]
\[ \frac{X_{B1}}{X_{B2}} = \frac{0.578}{0.875} = 0.66 \]

\[ \therefore \frac{R_2}{R_1} \neq \frac{X_{B1}}{X_{B2}} \text{......} \]

----------so film diffusion does not control the rate.

(B) For Ash diffusion controlling we have:

\[ \frac{t}{\tau} = 1 - 3(1 - X_B)^{\frac{3}{2}} + 2(1 - X_B) \]

And \( \tau \propto R^2 \)
\[ \frac{t}{\tau_1} = 1 - 2(1 - X_B)^{\frac{2}{3}} + 2(1 - X_{B_1}) \ldots \ldots \text{4mm particle} \]

\[ \tau_1 \propto R_1^2 \quad \therefore \tau_1 = cR_1^2 \]

\[ \frac{t}{\tau_2} = 1 - 3(1 - X_{B_2})^{\frac{2}{3}} + 2(1 - X_{B_2}) \ldots \ldots \text{2 mm particle} \]

\[ \tau_2 \propto R_2^2 \quad \therefore \tau_2 = cR_2^2 \]

\[ \frac{t}{\tau_1} = \frac{cR_1^2}{R_1^2} = \frac{R_2^2}{R_1^2} = \frac{1 - 3(1 - X_{B_1})^{\frac{2}{3}} + 2(1 - X_{B_1})}{1 - 3(1 - X_{B_2})^{\frac{2}{3}} + 2(1 - X_{B_2})} \]

\[ \frac{R_2^2}{R_1^2} = \left( \frac{1}{2} \right)^2 = \frac{1}{4} = 0.25 \]

\[ \frac{1 - 3(1 - X_{B_1})^{\frac{2}{3}} + 2(1 - X_{B_1})}{1 - 3(1 - X_{B_2})^{\frac{2}{3}} + 2(1 - X_{B_2})} = \frac{1 - 3(1 - 0.578)^{\frac{2}{3}} + 2(1 - 0.578)}{1 - 3(1 - 0.875)^{\frac{2}{3}} + 2(1 - 0.875)} = 0.312 \]

\[ 0.25 \neq 0.312 \]

\[ \therefore \quad \frac{t}{\tau_2} = \frac{R_2^2}{R_1^2} \neq \frac{1 - 3(1 - X_{B_1})^{\frac{2}{3}} + (1 - X_{B_1})}{1 - 3(1 - X_{B_2})^{\frac{2}{3}} + 2(1 - X_{B_2})} \]

\[ \ldots \ldots \text{so ash diffusion does not control rate:} \]

(C) For chemical reaction controlling we have:

\[ \frac{t}{t} = 1 - (1 - X_B)^{\frac{1}{3}} \]

And \[ \tau \propto R \]

\[ \frac{t}{\tau_1} = 1 - (1 - X_{B_1})^{\frac{1}{3}} \ldots \ldots \text{(1) \ldots 4mm particles} \]

\[ \tau_1 \propto R_1 \quad \therefore \tau_1 = cR_1 \]

\[ \frac{t}{\tau_2} = 1 - (1 - X_{B_2})^{\frac{1}{3}} \ldots \ldots \text{(2) \ldots 2 mm particles} \]

\[ \tau_2 \propto R_2 \quad \therefore \tau_2 = cR_2 \]
From equations (1) and (2) we get:

\[ t = \tau_1 \left[ 1 - \left( X_{B1} \right)^{1/3} \right] = \tau_2 \left[ 1 - \left( X_{B2} \right)^{1/3} \right] \]

\[ cR_1 \left[ 1 - (1 - X_{B1})^{1/3} \right] = cR_2 \left[ 1 - (1 - X_{B2})^{1/3} \right] \]

\[ R_1 \left[ 1 - (1 - X_{B1})^{1/3} \right] = R_2 \left[ 1 - (1 - X_{B2})^{1/3} \right] \]

LHS: \[ R_1 \left[ 1 - (1 - X_{B1})^{1/3} \right] = 2 \left[ 1 - (1 - 0.578)^{1/3} \right] = 0.50 \]

RHS: \[ R_2 \left[ 1 - (1 - X_{B2})^{1/3} \right] = 1 \left[ 1 - (1 - 0.875)^{1/3} \right] = 0.50 \]

\[ \therefore \text{LHS} = \text{RHS} \]

As LHS = RHS ..... Chemical reaction controls the rate

Rate of controlling mechanism: Chemical reaction

Or

\[ \frac{t}{\tau_1} = \frac{t}{\tau_2} = \frac{R_2}{R_1} = \frac{1 - (1 - X_{B1})^{1/3}}{1 - (1 - X_{B2})^{1/3}} \]

LHS: \[ \frac{R_2}{R_1} = \frac{1}{2} = 0.50 \]

RHS: \[ \frac{1 - (1 - X_{B1})^{1/3}}{1 - (1 - X_{B2})^{1/3}} = \frac{1 - (1 - 0.578)^{1/3}}{1 - (1 - 0.875)^{1/3}} = \frac{0.25}{0.5} = 0.50 \]

\[ \therefore \text{LHS} = \text{RHS} \]

So chemical reaction controls the rate

We have for 2 mm particle:

\[ t = 1h, \ X_B = 0.875 \]

For chemical reaction controlling, we have,
\[ \frac{t}{\tau} = 1 - (1 - X_b)^{1/3} \]
\[ \frac{1}{\tau} = 1 - (1 - 0.875)^{1/3} \]
\[ \therefore \tau = 2h \]

Time required for 2 mm particle (R = 1 mm) for complete conversion is 2 h.

Now we have to find out the time required for complete conversion of 1 mm particle.

For chemical reaction controlling we have

\[ \tau \propto R \]

Let \[ \tau_2 \text{......for 2 mm particle (R}_1 = 1\text{mm)} \]
\[ \tau_2 \text{......for 1 mm particle (R}_2 = 0.5\text{mm)} \]
\[ \tau_2 \propto R_1 \]
\[ \tau_2 \propto R_2 \]
\[ \therefore \frac{\tau_1}{\tau_2} = \frac{R_1}{R_2} \]
\[ \tau_2 = \tau_1 \left( \frac{R_2}{R_1} \right) = 2 \times \frac{0.5}{1} = 1h \]

\[ \therefore \text{Time required for complete conversion for 1 mm particle = 1h} \]

12. Spherical particles of Zns (R = 1 mm) are reated in 8% oxygen stream at 900°C and 1 atm. The reaction that proceeds as per SCM is as follows.

\[ 2\text{ZnS + 2O}_2 \rightarrow 2\text{ZnO+2SO}_2 \]

Using the following data calculate:

(i) time required for complete conversion of a particle
(ii) Relative resistance of ash layer diffusion

Data:
\[ \rho_B = 4.13 \text{ g/cm}^3 = 0.0425 \text{ mol/cm}^3 \]
\[ k'' = 2.2 \text{ cm}^2 / \text{s} \]
\[ D_e = 0.08 \text{ cm}^2 / \text{s} \]
Film resistance can safely be neglected as long as growing ash layer is present.

**Solution:**
\[ 2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2 \]

Specific:
\[ \frac{2}{3}\text{ZnS} + \frac{1}{3}\text{O}_2 \rightarrow \frac{2}{3}\text{ZnO} + \frac{2}{3}\text{SO}_2 \]

**General:** \( A \) (fluid) + \( b \) \( B \) (Solid) \( \rightarrow \) Fluid and solid products

Comparing the above two reactions,
\[ b = \frac{2}{3} \]
\[ R = 1\text{mm} = 0.10\text{cm} \]
\[ \rho_B = 4.13\text{g/cm}^3 \]
\[ T = 900^\circ \text{C} = 1173\text{K}, \ P = 1 \text{ atm} \]
\[ k'' = 2.2 \text{ cm/s}, \ D_e = 0.08 \text{ cm}^2 / \text{s} \]

In our case: \( A = \text{O}_2 \)
Volume \% of \( \text{O}_2 \) in gas stream = 8
Mole \% \( \text{O}_2 \) = Volume \% \( \text{O}_2 \) (for ideal gas mixture)
Mole \% \( \text{O}_2 \) = 8
Mole \% \( \text{O}_2 \) = 8
Mole fraction \( \text{O}_2 \) = \( \frac{8}{100} \) = 0.08

\( P = 1 \text{ atm} \)

\[ \therefore \quad p_{A_8} = 0.08 \times 1 = 0.08 \text{ atm} \]

\( C_{A_8} = \text{concentration of A in bulk gas phase} \)
\[ C_{A_8} = \frac{p_{A_8}}{RT} \]
\[ R = 82.06 (\text{cm}^2\text{atm.}) / \text{mol.K} \]
\[ C_{A_8} = \frac{0.08}{82.06 \times 1173} = 8.31 \times 10^{-7} \text{ mol/cm}^3 \]
Given:

Neglect gas film resistance i.e. film diffusion is not to be considered. We have to find out time required for complete conversion of a particle. Here we have to consider following resistances:

i  resistance offered by ash layer.
ii  Resistance offered by chemical reaction (chemical step)

Time required for complete conversion is given by

\[ \tau_{\text{total}} = \tau_{\text{ash alone}} + \tau_{\text{reaction alone}} \]

Now calculate \( \tau_{\text{ash alone}} \) and \( \tau_{\text{reaction alone}} \)

1. For ash diffusion alone:

For constant size spherical particle \( \tau_{\text{ash}} \) is given by

\[ \tau_{\text{ash}} = \frac{\rho_b R^2}{6bD_e C_{Ag}} = \frac{0.0425 \times (0.1)^2}{6 \left( \frac{2}{3} \right)(0.08)(8.31 \times 10^{-7})} = 1598 \text{ s} \]

2. For chemical reaction alone:

Time for complete conversion is given by

\[ \tau_{\text{reaction}} = \frac{\rho_b R}{bk'' C_{Ag}} \]

\[ \rho_b = 0.0425 \text{ mol/m}^3 \]

\[ \tau_{\text{reaction}} = \frac{0.0425 \times 0.10}{2 \times 2 \times 8.31 \times 10^{-7}} = 3836 \text{ s} \]

\[ \tau_{\text{total}} = 1598 + 3836 = 5434 \text{ s} \]

Time required for complete conversion of the particle = 5434 s
Resistance of ash layer = \( \frac{1598}{5434} \times 100 = 29.4\% \)

Resistance of ash layer = 29.4%

13. Solid particles of uniform size are 80% converted, according to the shrinking core model (SCM) with ash diffusion step as rate as rate controlling, on passing through a reactor with uniform gas environment. What would be the conversion of solids if the reactor is made twice as large – all else remaining unchanged?

(1) Case – I: The solids are in plug flow.
(2) Case – II: The solids are in mixed flow.

Solution:

Case – I: The solids are in plug flow.

Given: Ash diffusion step is rate controlling.

For ash diffusion controlling, particles of single unchanging (uniform) size and plug flow of solids, the conversion-time expression is

\[
\frac{t_p}{\tau} = 1 - 3(1 - X_b)^{2/3} + 2(1 - X_b)
\]

\[
\frac{t}{\tau} = 1 - 3(1 - X_b)^{2/3} + 2(1 - X_b) \quad \text{....ash diffusion controls}
\]

Given: \( X_b = \frac{80}{100} = 0.80 \)

\[
\frac{t_p}{\tau} = 1 - 3(1 - 0.80)^{2/3} + 2(1 - 0.80)
\]

\[
\frac{t_p}{\tau} = 0.374 \quad \text{....for original reactor}
\]

We have to determine the conversion of solids in the new reactor.

The size of the new reactor is twice that of the original reactor. This is the only difference between these reactors.
\[ \left( \frac{t_p}{\tau} \right)_{\text{new}} = 2 \left( \frac{t_p}{\tau} \right)_{\text{original}} = 2 \times 0.374 = 0.748 \]

Conversion in the new reactor:

\[ \frac{t_p}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \]
\[ 0.748 = 1 - 3(1 - X_B)^{2/3} + 2(-X_B) \]

Find \( X_B \) by a trial and error procedure.

LHS = 0.748

RHS = \( 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \)

For \( X_B = 0.94 \), RHS = 0.66, \( X_B = 0.96 \), RHS = 0.729

For \( X_B = 0.965 \), RHS = 0.749

For \( X_B = 0.9648 \), RHS = 0.7482 = LHS

\[ \therefore X_B = 0.9648 \text{ as for this value LHS = RHS} \]

Conversion of solids in the new reactor of size twice as large for the solids in plug flow = 0.9648 or 96.48% 

Case – II: The solids are in mixed flow:

For original reactor: \( \bar{X}_B = 0.80 \)

Given: ash diffusion step is rate controlling. For mixed flow of particles of single unchanging size, uniform gas composition and ash resistance controlling we have:
\[1 - \bar{X}_B = \frac{1}{5} \frac{\tau}{t} - \frac{19}{420} \left( \frac{\tau}{t} \right)^2 + \frac{41}{4620} \left( \frac{\tau}{t} \right)^3 - \ldots\]

\[1 - 0.2 = \frac{1}{5} \frac{\tau}{t} - \frac{19}{420} \left( \frac{\tau}{t} \right)^2 + \frac{41}{4620} \left( \frac{\tau}{t} \right)^3\]

LHS = 0.20

RHS = \[\frac{1}{5} \frac{\tau}{t} - \frac{19}{420} \left( \frac{\tau}{t} \right)^2 + \frac{41}{4620} \left( \frac{\tau}{t} \right)^3\]

Let \(\frac{\tau}{t} = x\)

RHS = \[0.2x - 0.04524x^2 + 8.87 \times 10^{-3} x^3\]

For

\begin{align*}
\text{x} = 1 & \quad \text{RHS} = 0.1636, \quad \text{x} = 1.3 & \quad \text{RHS} = 0.203 \\
\text{x} = 1.5 & \quad \text{RHS} = 0.228, \quad \text{x} = 1.29 & \quad \text{RHS} = 0.2017 \\
\text{x} = 1.4 & \quad \text{RHS} = 0.2157, \quad \text{x} = 1.28 & \quad \text{RHS} = 0.20 = \text{LHS}
\end{align*}

LHS = RHS for \(x = \frac{\tau}{t} = 1.28\)

\[x = \frac{\tau}{t} = 1.28\ldots\text{for original reactor}\]

\[\therefore \frac{t}{\tau} = \frac{1}{1.28} = 0.78125\ldots\text{for original reactor.}\]

For the new reactor of size twice as large

\[W_{\text{new}} = 2W_{\text{original}}\]

And \(\tilde{t} = \frac{W}{F}\), \(F\) is same in both cases

\[\therefore \left( \frac{\tilde{t}}{\tau} \right)_{\text{new}} = 2 \left( \frac{\tilde{t}}{\tau} \right)_{\text{original}}\]

\[= 2 \times 0.78125 = 1.5625\]
\[ \frac{\tau}{t} \text{ for the new reactor} = \frac{1}{1.5625} = 0.64 \]

Conversion in the new reactor (for ash resistance controlling):

\[
1 - \overline{X}_B = \frac{1}{5} \tau - \frac{19}{420} \left( \frac{\tau}{t} \right)^2 + \frac{41}{4620} \left( \frac{\tau}{t} \right)^3
\]

\[
1 - \overline{X}_B = \frac{1}{5} (0.64) - \frac{19}{420} (0.64)^2 + \frac{41}{4620} (0.64)^3
\]

\[ \overline{X}_B = 0.9362 \]

Mean conversion of solids in the reactor of size twice as large, for mixed flow of solids = 0.9362 or 93.62%

14. In a fluidized bed reactor, particles of iron sulphide of uniform size are to be roasted. The time required for complete conversion is 20 min. The mean residence time of particles in the fluidized bed is 60 min. The particles remained as hard solids during reaction. \( \tau \) and \( R \) relationship found to be \( \tau \propto R^{1.5} \).

Calculate the fraction of original iron sulphide remaining unreacted.

Solution:

As hard material is formed during reaction we can rule out safely the possibility of film diffusion to be the controlling resistance.

With this we are diffusion, and

(1) ash layer diffusion, and
(2) chemical reaction – as the controlling resistance.

Given: \( \tau \) and \( R \) are related by \( \tau \propto R^{1.5} \)

1. For chemical reaction controlling, \( \tau \) and \( R \) are related by \( \tau \propto R \).
2. For ash layer diffusion controlling, \( \tau \) and \( R \) are related by \( \tau \propto R^2 \).

As the given relationship between \( \tau \) and \( R \) lies between 1 and 2, both these mechanisms offer resistance to conversion.

So we will first calculate the conversion by considering:

(1) Chemical reaction as the controlling resistance.
(2) Ash layer diffusion as the controlling resistance and then we will find the average of the conversion values obtained for (i) and (ii) to get the result.

**Given:** time required for complete conversion = $\tau = 20$ min.

Mean residence time of particles in the bed = $\bar{t} = 60$ min.

\[
\frac{\tau}{t} = \frac{20}{60} = 0.333 \quad \text{and} \quad \frac{\bar{t}}{\tau} = \frac{60}{20} = 3 \quad (\text{large value})
\]

(i) Chemical reaction controlling:

\[
1 - \bar{X}_B = \frac{1}{4} \left( \frac{\tau}{t} \right) - \frac{1}{20} \left( \frac{\tau}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau}{t} \right)^3 - \ldots
\]

\[
= \frac{1}{4} (0.333) - \frac{1}{20} (0.333)^2 + \frac{1}{120} (0.333)^3
\]

\[
= 0.078 \, (\text{i.e. 7.8%})
\]

(ii) Ashy layer diffusion controlling:

\[
1 - \bar{X}_B = \frac{1}{5} \left( \frac{\tau}{t} \right) - \frac{19}{420} \left( \frac{\tau}{t} \right)^2 + \frac{41}{4620} \left( \frac{\tau}{t} \right)^3 - \ldots
\]

\[
= \frac{1}{5} (0.333) - \frac{19}{420} (0.333)^2 + \frac{41}{4620} (0.333)^3
\]

\[
= 0.0619 = 0.062 \, (\text{i.e. 6.2%})
\]

Fraction of sulphide remaining unconverted:

(1) Chemical reaction controlling: $1 - \bar{X}_B = 0.078$

(2) Ash layer diffusion controlling: $1 - \bar{X}_B = 0.062$

Lower limit to expect conversion is given by (i) and

Upper limit to expect conversion is given by (ii)

The fraction remaining unconverted is between $0.062$ (i.e. $6.2\%$) and $0.078$ (i.e. $07.8\%$)

Average of fraction remaining unconverted = \[
\frac{0.062 + 0.078}{2} = 0.07
\]

\[\therefore \] Fraction of the original sulphide remaining unreacted $= 1 - \bar{X}_B = 0.07$ (i.e. 7%)
15. A fluidized bed reactor of size 20 cm ID x 2 - m long operates at steady state with a solid fed consisting of

- 30% of 50 μm radius particles
- 40% of 100 μm radius particles
- 30% of 200 μm radius particles

The fluidizing gas is in the gas phase reactant and has uniform composition. The time required for complete conversion is 5, 10 and 20 minutes for three sizes of feed under planned operating conditions. The feed rate to the reactor is 1 kg solid/min and fluidised bed contains 10 kg of solids.

The solids are hard and remain unchanged in size and weight during reaction. The change in gas phase composition in the bed is negligible.

Calculate the conversion of solids.

**Solution:**

Here we have mixed flow of a size mixture of unchanging size and uniform gas composition.

For mixed flow of solids, the mean residence time $\bar{t}(R_i)$ of material of any size $R_i$ is equal to the mean residence time of all solids in the bed.

**Given:**

- $W = $ weight of all solids in the reactor = 10 kg
- $F = $ feed rate of all solids to the reactor = 1 kg/min

$$\bar{t} = \frac{W}{F} = \frac{10}{1} = 10 \text{ min}$$

$$F(R_i) = \text{Wt. fraction of particles of size } R_i = \frac{\text{Wt.} \%}{100} \times F$$

$\tau(R_i)$ is the time required for complete conversion of particles of size $R_i$

- $F(50 \mu m) = 0.30 \times 1 = 0.3 \text{ kg/min, } \tau(50 \mu m) = 5 \text{ min}$

[A solid feed consisting of 30% of 50 μm – radius particles]
- $F(100 \mu m) = 0.4 \times 1 = 0.4 \text{ kg/min, } \tau(100 \mu m) = 10 \text{ min}$
- $F(200 \mu m) = 0.3 \times 1 = 0.3 \text{ kg/min, } \tau(200 \mu m) = 20 \text{ min}$
For 50μm radius particles…. \( \tau = 5 \text{ min} \)
For 100 μm radius particles…. \( \tau = 10 \text{ min} \)
For 200 μm radius particles…. \( \tau = 20 \text{ min} \)

We see from above data that
\[
\frac{\tau_1}{\tau_2} = \frac{R_1}{R_2} = \frac{5}{10} = \frac{50}{100} = \frac{0.50}{100} = 0.50
\]

As \( \tau \propto R \), chemical reaction step is rate controlling.

So for chemical reaction controlling in a fluidized bed reactor with no elutriation of fine particles, the mean value for value for fraction of B unconverted is given by

\[
1 - \bar{X}_B = \sum R \left[ \frac{1}{4} \frac{\tau(R_i)}{t} - \frac{1}{20} \left( \frac{\tau(R_i)}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau(R_i)}{t} \right)^3 \right] \frac{F(R_i)}{F}
\]

\[
= \left[ \frac{1}{4} \frac{\tau(50)}{t} - \frac{1}{20} \left( \frac{\tau(50)}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau(50)}{t} \right)^3 \right] \frac{F(50)}{F}
\]

\[
+ \left[ \frac{1}{4} \frac{\tau(100)}{t} - \frac{1}{20} \left( \frac{\tau(100)}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau(100)}{t} \right)^3 \right] \frac{F(100)}{F}
\]

\[
+ \left[ \frac{1}{4} \frac{\tau(200)}{t} - \frac{1}{20} \left( \frac{\tau(200)}{t} \right)^2 + \frac{1}{120} \left( \frac{\tau(200)}{t} \right)^3 \right] \frac{F(200)}{F}
\]

1 - \bar{X}_B = 0.03406 + 0.0833 + 0.11 = 0.22736 = 0.2274

\( \bar{X}_B = 0.7726 \)

Mean conversion of solids = 0.7726 x 100 = 77.26%

\[ \text{Mean conversion of solids in the fluidised bed reactor} = 77.26\% \]
1. When the heterogeneous fluid-fluid reactions take place?
   Heterogeneous fluid-fluid reactions are made to take place for one of the three reasons;
   ➢ The product of reaction may be a desired material.
   ➢ To facilitate the removal of an unwanted component from a fluid.
   ➢ To obtain a vastly improved product distribution.

2. Give the importance of equilibrium solubility in gas-liquid operations.
   The solubility of the reacting components will limit their movement from one phase to other. This factor will certainly influence the form of the rate equation since it will determine whether the reaction takes place in one or both phases.

3. Define Enhancement factor. (NOV/DEC 2014)
   The liquid enhancement factor (E) is defined as the ratio of rate of take up of gaseous „A” when reaction occurs to the rate of take up of gaseous „A” for straight mass transfer, at same \( C_{Ai}, C_A, C_{Bi}, C_B \) in the two cases. Or Enhancement factor E is defined as the ratio between the Sherwood number with chemical reaction and that without reaction.

4. ‘Enhancement factor is always greater than or equal to one’. Justify this statement.
   Since the rate of take up of „A” when reaction occurs is greater than or equal to the rate of take up of „A” for straight mass transfer, the enhancement factor is always greater than or equal to one.

5. Define Hatta number. (NOV/DEC 2013)
   Hatta number (\( M_H \)) is defined as the square root of the ratio of maximum possible conversion in the liquid film to maximum diffusion transport through the liquid film.

6. Explain the significance of Hatta number.
   The significance of Hatta number (\( M_H \)) is;
   If \( M_H > 2 \), reaction occurs in the liquid film and are fast enough.
   If \( 0.02 < M_H < 2 \), reaction is influenced by all the resistances.
   If \( M_H < 0.02 \), reactions are infinitely slow.

7. Does the enhancement factor decrease or increase with Hatta number? Explain.
   Yes, Enhancement factor (E) decrease or increases with Hatta number (\( M_H \)). Because the evaluation of „E” depends on two quantities;
   ✓ The enhancement factor for an infinitely fast reaction (\( E_i \))
   ✓ Maximum possible conversion in the film compared with maximum transport through the film (\( M_{HI} \)).

8. How do you classify the kinetic regimes in gas-liquid reactions?
   The classification of kinetic regimes in a Gas-Liquid reaction based on the relative rates of reaction and mass transfer. According to two-film theory, the reaction may occur in liquid film or in both liquid film and main body of liquid or in main body of liquid. Based on the above three factors of reactions, we have eight special cases from infinitely fast to slow reaction as;
   - Instantaneous reaction - with low \( C_{\text{liquid}} \) & high \( C_{\text{liquid}} \)
   - Fast reaction - with low \( C_{\text{liquid}} \) & high \( C_{\text{liquid}} \)
   - Intermediate rate with reaction in the film and in the main body of the liquid.
9. What do you mean by instantaneous reactions in the gas-liquid operations?
In instantaneous reactions, the absorbing component of the gas and the liquid phase reactant cannot co-exist in the same region. In such reactions, the concentration of the liquid phase reactant at the gas-liquid interface is zero.

10. What do you mean by slow reactions in the gas-liquid operations?
In slow reactions, occurs in the main body of the liquid, mass transfer resistance is negligible and the composition of liquid phase and gas phase reactants are uniform. Thus, the rate is determined by chemical kinetics alone.

12. In a gas-liquid reaction, it was observed that the reaction occurs on a plane with in the liquid film. Is the reaction slow, fast or instantaneous? Explain.
The reaction is either instantaneous of fast, with low concentration of liquid.
- For instantaneous reaction, the reaction plane exists where the two reactants interact in the liquid film.
- For fast reactions, the reaction zone exists where the two reactants completely reacted in the liquid film.

13. What are the advantages of surface renewal theory?
The biggest advantage arises from the square root dependence on the diffusion coefficient. This allows one to better predict the behavior of various solutes with different diffusion coefficients based on measured behavior of one particular solute. The square root dependence gives more accurate prediction than the linear dependence found with the two-film model. Recognize however that surface renewal is really most accurate when surface renewal rates are high.

This approach tries to apply the mathematics of the penetration theory to be more plausible physical picture. The liquid is pictured as two regions, a large well mixed bulk and an interfacial region that is renewed so fast that it behaves as a thick film. The surface renewal theory is caused by liquid flow.

15. What are the various resistances involved in developing rate equations for gas-liquid reactions?
The various resistances involved in developing rate equations for gas-liquid reactions are:
- Mass transfer resistances, to bring the reactants together.
- The resistance of the chemical reaction step.

16. Sketch the concentration profile for an instantaneous gas-liquid non-catalytic reaction
17. Write short notes on slurry reactors.

- A slurry reactor is a multiphase flow reactor in which reactant gas is bubbled through a solution containing solid catalyst particles. The solution may be either a reactant or a product or an inert.
- Slurry reactors may be operated in a batch or continuous mode. One of the main advantages of slurry reactors is that temperature control and heat recovery are easily achieved. In addition, constant overall catalytic activity can be maintained by the addition of small amounts of catalyst with each reuse during batch operation or with constant feeding during continuous operation.
- These reactors are widely used in hydrogenation of fatty acids over a supported nickel catalyst, hydroformation of CO with high-molecular-weight olefins on either a cobalt or ruthenium complex bound to polymers, etc.

18. What are the advantages of slurry reactors over fixed beds?
The advantages of slurry reactors over fixed beds are

   a. It usually has a higher rate
   b. It holds good for fast reactions on porous catalyst

Note: Slurry reactors can use very fine particles, and this lead to problems of separating catalyst from liquid. (Only disadvantage of slurry reactor)

19. Explain Film penetration theory. (May 2015), [Dec 2012] (May/June 2014)
The penetration theory for mass transfer. Here the interfacial region is imagined to be very thick continuously generated by flow. Mass transfer now involves diffusion in to this film. In this and other theories the interfacial concentration in the liquid is assumed to be in equilibrium with that in the gas

20. Write short notes on trickle bed reactors.

- A trickle bed reactor is a three-phase version in which gas and liquid reactants are brought into contact with solid catalyst particles.
- In this gas and liquid flow counter-currently downward over a fixed-bed of catalyst particles contained in a tubular reactor.
- These reactors are widely used for hydro-desulphurization of liquid petroleum fractions and hydro-treating of lubricating oils.

21. List the types of flow regime that are possible in trickle bed reactors.

- In trickle bed reactor, four types of flow regimes are possible:
  - Trickle flow regime: In this regime, gas flow is continuous.
  - Dispersed bubble regime: In this regime, liquid phase is continuous and the gas moves into the bubbles.
  - Spray regime: In this regime, gas flow rate is high while liquid rate is low. Liquid falls in droplets through the gas phase.
  - Pulsed flow regime: In this regime, flow rates of both gas and liquid are high
Total resistance to mass transfer = \( R = R_g + R_l \)
\[ \begin{align*}
= 1.25 + 120 \\
= 121.25 \text{(Pa.m}^3\text{.h)mol}
\end{align*} \]

Resistance in the gas film = \( \frac{1.25}{121.25} \times 100 = 1.03\% \)

Resistance in the gas film = \( \frac{1.25}{121.25} \times 100 = 98.97\% \)

So 1.03\% of the resistance is offered by the gas film and 98.97\% of the resistance is offered by the liquid film.
... Ans. (i)

Relative resistance:

Resistance of the liquid film relative to that of gas film = \( \frac{120}{1.25} = 96 \)
... Ans. (i)

Here the gas film resistance is very very small (1.03\%) in comparison with that of the liquid film (98.97\%). As the main resistance is in the liquid film (and with little error ignoring the gas film resistance-being very very small), we can safely say that the absorption is liquid film controlling with rate equation:

\[-r_A^* = k_{Al}(C_{Ai} - C_A)\]
... Ans. (ii)

\[-r_A^* = k_{Al}\left(\frac{P_A}{H_A} - C_A\right)\]
... Ans. (ii)

[With negligible gas phase resistance with little error, \( P_{Ai} = P_A \text{ and } C_{Ai} = P_{Ai}/H_A \).]

Since the major resistance resides in the liquid film, the rate of transfer of A is liquid film resistance controlled. So anything which lowers this resistance would be helpful. The reaction in the liquid phase lowers this resistance and hence can speed up the absorption of A.
2. \( \text{CO}_2 \) is to be removed from air. We plan to use NaOH solution to hasten (speed up) the removal of \( \text{CO}_2 \) from air at 25\(^\circ\)C (instead of pure water).

The reaction between \( \text{CO}_2 \) and NaOH is instantaneous.

\[
\text{CO}_2 + 2\text{NaOH} = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

(i) Suggest and form of rate equation that we would use when \( P_{\text{CO}_2} = 1000\text{Pa} \) and the solution is 2N.

(ii) How much can absorption be speeded compared to physical absorption using water /

Data: \( k_a = 0.80 \text{ mol/(h.m}^3\text{.Pa)} \)  
\( k_{l a} = 25 \text{ h}^{-1} \)  
\( H = 3000 \text{ (Pa.m}^3\text{)}/\text{mol} \)

Solution: The reaction is

\[
\text{CO}_2 + 2\text{NaOH} = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

\[
A + bB = \text{products, } b = 2
\]

We have to use 2N NaOH solution to speed up the absorption operation i.e., removal of \( \text{CO}_2 \) from air.

We have,
Concentration is g/l = Normality \times \text{Equivalent weight}
For NaOH, valence = 1
So equivalent weight = molecular weight = 40
Concentration = 2\times40 = 80 \text{ g/l}

Concentration of NaOH

Solution (in molar units) = \frac{\text{Concentration in g/l}}{\text{Molecular weight of NaOH}}

\[
C_B = \frac{80}{40} = 2 \text{ mol/} = 2000 \text{ mol/m}^3
\]
\( P_{\text{CO}_2} = PA=1000 \text{ Pa} \)

It is a case of instantaneous reaction with respect to mass transfer.
Now, let us have a check for instantaneous reaction with low \( C_B \) or high \( C_B \). For this, we have to estimate \( k_A \) a PA and \( k_B \) a \( C_B /b \).
\( k_s a = k_{Ag} a = 0.80 \text{ mol/(h.m}^3\text{.Pa)} \)
\( kl a = k_{Al} a = 25 \text{ h}^{-1} \)

Assuming \( D_{Al} = D_{Bl} \), we have
\( k_{Bl} a = k_{Al} a 25 \text{ h}^{-1} \)
\( b = 2, \quad PA = 1000 \text{ Pa} \)
\( k_{Ag} a \ PA = 0.80 \times 1000 = 800 \text{ mol/(h.m}^3\text{)} \)
\( \frac{k_{Bl} a \ C_{B}}{b} = \frac{25 \times 2000}{2} = 25000 \text{ mol/(h.m}^3\text{)} \)
\[ \therefore \text{ It is clear that } k_{Ag} a \ PA < k_{Bl} a \ C_{B} / b \]
As \( k_{Ag} a \ PA < k_{Bl} a \ C_{B} / b \), it is a case of instantaneous reaction with high \( C_{B} \).

The form of rate equation for this case is:

\[ -r_A = -\frac{1}{S} \frac{dN_A}{dt} = k_{Ag} PA \]

(i)

\[ -r_A'' = -r_A a = \text{Rate with reaction} = k_{Ag} a \ PA \]

For removal of \( CO_2 \) (A) using pure water for a case of straight mass transfer of A, the rate of transfer of A across the gas and liquid films is given by,

Rate for straight mass transfer \( = (-r_A^*) = \frac{p_A - H_A C_A}{1 + \frac{H_A}{k_{Ag} a \ + \ k_{Al} a}} \)

Maximum rate for straight mass transfer \( = \frac{p_A}{1 + \frac{H_A}{k_{Ag} a \ + \ k_{Al} a}} \)

\[ \frac{\text{Rate with reaction}}{\text{Rate for straight mass transfer}} = \frac{k_{Ag} a \ p_A}{\frac{p_A}{1 + \frac{H_A}{k_{Ag} a \ + \ k_{Al} a}}} \]
\[ \frac{k_A g a}{1} + \frac{H_A}{k_A g a} + \frac{H_A}{k_A l a} = k_A g a \left[ \frac{1}{k_A g a} + \frac{H_A}{k_A l a} \right] = 0.80 \left[ \frac{1}{0.8} + \frac{3000}{25} \right] = 97 \]

\[ \therefore \] By using 2N NaOH solution, the rate increases by 97 times than it for pure water. By using 2N NaOH solution, the absorption is speeded 97 times compared to physical absorption using pure water. ... Ans. (ii)

3. For highly water soluble gas such as ammonia at 10 °C

\[ H = 1.0 \text{ (Pa.m}^3\text{/s)} \]

For sparingly soluble gases such as \( O_2, N_2, NO, CH_4, H_2 \) etc., at 10°C

\[ H = 10^5 \text{ (Pa.m}^3\text{/s)} \]

For straight absorption of these gases in water, assuming no chemical reaction, determine:

(i) The relative resistances of the gas and liquid films.
(ii) The resistance that controls the absorption process.
(iii) The form of rate expression to be used for design in these two cases.
(iv) How does the solubility of the slightly soluble gas affect its rate of absorption?
(v) In which case would chemical reaction be more helpful in speeding the process?

Give justification

\[ \text{ata: } k_i = 10^{-5} \text{m/s, } k_SRT = 0.10 \text{m/s} \]
Solution:

(a) **Highly soluble gas**: \( H = 1 \text{ (Pa.m}^3 \text{)/mol} \)

(b) **Sparingly soluble gas**: \( H = 10^5 \text{ (Pa.m}^3 \text{)/mol} \)

\[
k_g = 10^{-5} \text{ m/s}
\]

\[
k_g \frac{RT}{8.314 \times 283} = \frac{0.10}{8.314 \times 283} = 4.25 \times 10^{-5} \text{ (Pa.m}^2 \text{.s)/mol}
\]

It is a straight mass transfer (absorption) of A across the gas and liquid films. So there are two resistance (of gas film and liquid film) for mass transfer of A.

The rate expression for straight mass transfer of A across the gas and liquid films is:

\[
-r_A = \frac{1}{S} \frac{dN_A}{dt} = \frac{1}{k_{Ag} + k_{Al}} \frac{H}{k_{Ag}} \Delta P_A
\]

Gas film resistance \( = \frac{1}{k_{Ag}} = \frac{1}{k_g} \)

Liquid film resistance \( = \frac{1}{k_{Al}} = \frac{H}{k_i} \)

(a) **Highly soluble gas**:

Gas film resistance \( = \frac{1}{k_g} \)

\[
\frac{1}{4.25 \times 10^{-5}} = 23529.4 \text{(Pa.m}^2 \text{s)/mol}
\]

Liquid film resistance \( = \frac{H}{k_i} \)

\[
\frac{1}{10^5} = 10^5 \text{(Pa.m}^2 \text{s)/mol}
\]
Relative resistance:

Liquid film resistance relative to the gas film resistance for highly soluble gas

\[
\frac{H}{k_i} = \frac{1}{k_g} \cdot \frac{1}{10^5} = \frac{10^5}{23529.4} = 4.25
\]

(b) Sparingly (slightly) soluble gas:

Gas film resistance

\[
H = 10^5 (\text{Pa.m}^3) / \text{mol}
\]

\[
\frac{1}{k_g} = \frac{1}{4.25 \times 10^{-5}} = 23529.4 (\text{Pa.m}^2/\text{s}) / \text{mol}
\]

Liquid film resistance

\[
\frac{H}{k_i} = \frac{10^5}{10^{-5}} = 10^{10} (\text{Pa.m}^2.\text{s}) / \text{mol}
\]

Relative Resistance:

Liquid film resistance relative to the gas film resistance for sparingly soluble gas

\[
\frac{H}{k_i} = \frac{1}{k_g} \cdot \frac{1}{10^5} = \frac{10^5}{23529.4} = 4.25 \times 10^5
\]

...Ans. (i)

(a) Highly soluble gas:

Gas film resistance = 23529.4 (Pa.m^2.s) / mol  ... (19%)

Liquid film resistance = 10^5 (Pa.m^2.s) / mol  ... (81%)
Referring to the above values (cited in %), it is clear that we have to take into account both the resistances to find the rate of absorption. None of the resistances can be ignored. Thus we have to consider both the phases. None of the resistances separately control the absorption process.

(b) Sparingly soluble gas:

Gas phase resistance = 23529.4(Pa.m\(^2\).s)/mol \(\cdots\) \((2.35\times10^4\%)\)

Liquid phase resistance = \(10^{10}\)(Pa.m\(^2\).s)/mol \(\cdots\) \((99.9997\%)\)

Referring to the above values (cited in %), it is clear that the gas film resistance is almost zero i.e. it does not offer resistance to mass transfer. The liquid film resistance is almost 100%. Hence, the entire resistance to mass transfer is offered by the liquid film. So for this case, liquid phase resistance controls the absorption process, it is a liquid film controlling process.

(a) Highly soluble gas:

As here we have to take into account both the resistances, the form of rate expression for straight mass transfer for this case is:

\[
-r^*_A = \frac{1}{\frac{1}{k_{Ag}} + \frac{H}{k_{Al}}} \Delta P_A
\]

\(\cdots\) (Ans. (iii))

\[k_g = k_{Ag} \quad \text{and} \quad k_l = k_{Al}\]

Or

\[
-r^*_A = \frac{1}{\frac{1}{Hk_{Ag}} + \frac{1}{k_{Al}}} \Delta C_{A,\text{overall}}
\]

\(\Delta P_A\) or \(\Delta C_A\) \(\cdots\) Across the gas and liquid films.

(b) Sparingly soluble gas:

Here the entire resistance is the resistance offered by the liquid film. No gas phase resistance. So the form or rate expression to be used is:
\[-r''_A = k_{Al} \left( C_{Ai} - C_A \right) = \left[ \frac{P_{Ai}}{H_A} - C_A \right] \]

... Ans. (iii)
No gas phase resistance - \( P_{Ai} = P_A \)

\[-r''_A = k_{Al} \left( \frac{P_A}{H_A} - C_A \right) \]

... Ans. (iii)

or

\[-r''_A = r' = kl \left( \frac{P}{H} - C_i \right) \]

For sparingly soluble gas (slightly soluble gas) absorbed by water we have

\[-r''_A = k_{Al} \left( \frac{P_A}{H_A} - C_A \right) \]

\[-r'_A = \frac{k_{Al} P_A}{H_A}, \quad C_A \text{ very low.} \]

\[-r'A = \alpha \frac{1}{H_A} \]

Thus the absorption is inversely proportional to \( H_A \). i.e. absorption is proportional to the solubility of gas. ...Ans. (iv)

In case of sparingly soluble gas/slightly soluble gas (i.e. gas difficult to absorb) since almost all resistance to mass transfer is in the liquid phase and reaction in liquid phase lowers this resistance we can definitely say that in this case the reaction in the liquid phase would be more helpful (i.e. this system would benefit greatly by a reaction in the liquid phase). Ans. (v)

4. Hydrogen sulfide (0.10% by volume) in a carrier gas at 2 MPa is to be absorbed at 20 °C by a solution containing 250 mol/m³ methanolamine (MEA). \( \text{H}_2\text{S} \) reacts with MEA as follows:

\[ \text{H}_2\text{S} + \text{RNH}_2 \rightarrow \text{HS}^- + \text{RNH}_3^- \]
This acid-base neutralization reaction can be regarded as irreversible and instantaneous.

(i) Determine the form of rate equation which is applicable to our case.
(ii) Find the rate of absorption of $\text{H}_2\text{S}$ in MEA solution.
(iii) Determine how much faster is absorption with MEA solution compared to physical absorption in pure water (required to find whether it is worthwhile using MEA absorbent).

Data:

\[
\begin{align*}
   k_{\text{Al}} & = 0.03 \text{ s}^{-1} \\
   k_{\text{Ag}} & = 6 \times 10^{-4} \text{ mol/(s.m}^3.\text{Pa}) \\
   H_A & = 10 \text{ (Pa.m}^3)/\text{mol}
\end{align*}
\]

$H_A$ is Henry’s law constant for $\text{H}_2\text{S}$ in water. The diffusivity of MEA in solution is 0.64 times that of $\text{H}_2\text{S}$.

Solution:

\[
\text{H}_2\text{S} + \text{RNH}_2 \rightarrow \text{HS}^- + \text{RNH}_3^+
\]

$A + bB \rightarrow $ products, $b = 1$

Given: It is an instantaneous reaction.

For instantaneous reaction we have two cases.

Cases:

(i) Instantaneous reaction with low $C_B$
(ii) Instantaneous reaction with high $C_B$

In order to suggest an appropriate form equation for give situation we have to find out whether this instantaneous reaction is with low $C_B$ or with high $C_B/b$

For deciding this we have to evaluate: $k_{\text{Ag}} a p_A$ and $k_{\text{Bi}} a C_B / b$

For high $C_B$:

\[
k_{\text{Ag}} a p_A \leq k_{\text{Bi}} a C_B / b
\]

For low $C_B$:

\[
k_{\text{Ag}} a p_A \geq k_{\text{Bi}} a C_B / b
\]

\[
k_{\text{Al}} a = 0.03 \text{ s}^{-1}, \quad k_{\text{Ag}} a = 6 \times 10^{-4} \text{ mol/(pa.m}^3.\text{S})
\]
Diffusivity of MEA (B) in solution is 0.64 times that of H₂S (A)

\[ D_{Bl} = 0.64 D_{Al} \]
\[ D_{Bl}/D_{Al} = 0.64 \]

As per two-film theory:

\[ \frac{k_{Al} a}{k_{Bl} a} = \frac{D_{Al}}{D_{Bl}} \]
\[ k_{Bl} a = k_{Al} a \left( \frac{D_{Bl}}{D_{Al}} \right) \]
\[ = 0.03(0.64) = 0.0192 \text{s}^{-1} \]
\[ k_{Ag} a \text{ Pa} = 6 \times 10^{-4} \times 2000 = 1.2 \text{ mol/(m}^3\text{s)} \]
\[ \frac{k_{Bl} a C_{Bl}}{b} = \frac{0.0192 \times 250}{1} = 4.8 \text{ mol/(m}^3\text{s)} \]

Referring to above two calculated values:

\[ k_{Ag} a \text{ Pa} < \frac{k_{Bl} a C_{Bl}}{b} \]

As \( k_{Ag} a \text{ Pa} < k_{Bl} a C_{Bl}/b \), it is an instantaneous reaction with high \( C_{Bl} \).

For instantaneous reaction with high \( C_{Bl} \), the form of rate equation is

\[ -r_A = -\frac{1}{s} \frac{dN_A}{dt} = k_{Ag} a P_A \]

...Ans. (i)

\[ -r_A'' = (-r_A) a = k_{Ag} a P_A \]
\[ \frac{p_A - H_A C_A}{k_{Ag} a + k_{Al} a} \]

with \( C_A = 0 \)

Rate for straight mass transfer

\[ -r_A = \frac{p_A - H_A C_A}{k_{Ag} a + k_{Al} a} \]

\[ = \frac{2000}{\frac{1}{6 \times 10^{-4}} + 10} \]

\[ = \frac{1}{6 \times 10^{-4} + 0.03} \]

\[ = 1 \text{ mol/(m}^3\text{s)} \]

\[ \frac{\text{Rate with reaction}}{\text{Rate for straight mass transfer}} = \frac{1.2}{1} = 1.2 \]

So with MEA solution absorption of \( \text{H}_2\text{S} \) is 20% faster than it with pure water.

... Ans. (iii)

\[ = k_{Ag} a \left[ \frac{1}{k_{Ag} a + k_{Al} a} \right] \]

\[ = 0.80 \left[ \frac{1}{0.8} + \frac{3000}{25} \right] \]

\[ = 97 \]
5. Gaseous A absorbs and reacts with B in liquid according to
\[ A(g \rightarrow l) + B(l) \rightarrow R(l), r_{Al} = k_{CA}C_B \text{ in packed bed.} \]

(i) Calculate the rate of reaction.
(ii) Determine the location of the major resistance (gas film, liquid film and bulk liquid) and behavior in the liquid film (pseudo first order reaction, instantaneous etc.) at a point in the reactor where \( p_A = 100 \text{ Pa} \) and \( C_B = 100 \text{ mol/m}^3 \text{ liquid.} \)

Data:
\[
\begin{align*}
    k &= 10^8 \text{ m liquid }/(\text{mol.h}) \\
    H_A &= 1.0 \ (\text{pa.m}^3 \text{ liquid })/\text{mol} \\
    k_{Ag} &= 0.10 \text{ mol/h.m}^3 \text{ of reactor pa} \\
    k_{Al} &= 100 \text{ m}^3 \text{ liquid}/(\text{m}^3 \text{ reactor.h}) \\
    f_i &= 0.01 \text{ m}^3 \text{ liquid }/ \text{m}^3 \text{ reactor} \\
    a &= 100 \text{ m}^2 / \text{m}^3 \text{ reactor} \\
    D_{Al} &= D_{Bl} = 10^{-6} \text{ m}^2 / \text{h} \\
\end{align*}
\]

Hint : for \( E_i < M_H / 5 \), we have instantaneous reaction and \( E = E_i \)

Solution : \( A + bB \rightarrow \text{product, } b = 1 \)
\[
K_{AI} = 100 \text{ m}^3/(\text{m}^3 \text{.h}) \\
a = \text{m}^2/\text{m}^3
\]

\[
\therefore \quad k_{AI} = \frac{k_{AI} a}{a} = \frac{100}{100} = 1.0 \text{m.h}
\]

\[
D_{AI} = D_{Bl} = 10^{-6} \text{ m}^2 / \text{h} \\
P_A = P_{AI} = 100 \text{ Pa} \\
C_B = 100 \text{ mol/m}^3
\]

Evaluate \( E_i \) and \( M_H \)
\[ M_H = \sqrt{\frac{D_{AI} k C_B}{k_{Al}}} \]
\[ = \sqrt{\frac{10^{-6} \times 10^8 \times 100}{1}} = 100 \]

\[ E_i = 1 + \frac{D_{BI} C_B H_A}{b D_{AI} P_{Al}} \]
\[ = 1 + \frac{10^{-6} \times 100 \times 1}{1 \times 10^{-6} \times 100} = 2 \]

From above calculated values we have:

\[ E_i < M_H / 5 \quad \therefore E = E_i \text{ (Given)} \]

Behaviour in liquid film:

So we have instantaneous second order reaction in the liquid film.

... Ans. (ii)

\[ k_{Ag} a P_A = 0.1 \times 100 = 10 \text{ mol/(h.m$^3$)} \]
\[ k_{Al} a = k_{bi} a = 100 \text{m$^3$(m$^3$.h)} \quad \text{as } D_{AI} = D_{Bl} \]
\[ \frac{k_{BI} a C_B}{b} = \frac{100 \times 100}{1} = 10^4 \]
\[ \therefore k_{Ag} a P_A < \frac{k_{BI} a C_B}{b} \]

\[ \therefore \text{ It is the case of instantaneous reaction with high } C_B \text{ for which the suggested rate form is} \]

\[ -r_A = \frac{1}{S} \frac{dN_A}{dt} = k_{Ag} P_A \]
\[ -r_A = a (-r_A) \]
\[ -r_A = k_{Ag} a P_A \]
\[ = 0.1 \times 100 = 10 \text{ mol/(h.m$^3$ reactor)} \]

The general rate expression is
\[ -r_A = \frac{P_A}{1 + \frac{H_A}{k_{Ag} a} + \frac{H_A}{k_{Al} a E} + \frac{1}{k_{Bf} C_i}} \]

\[ = \frac{100}{0.10 + 100 \times 2 + 10^8 \times 100 \times 0.01} \]

\[ = \frac{100}{10 + 5 \times 10^{-3} + 1 \times 10^8} \]

\[ = \frac{100}{10.005} = 9.995 = 10 \text{ mol/(h.m}^3\text{ reactor}) \]

The rate of reaction = 10 mol/(h.m$^3$ reactor)

...Ans. (i)

Total resistance = \(10 + 5 \times 10^{-3} = 10.005\), (considering \(1 \times 10^8 = 0\))

Gas film resistance = \(\frac{10}{10.005} \times 100 = 99.95\%\)

Liquid film resistance = \(\frac{5 \times 10^{-3}}{10.005} \times 100 = 0.0499 \approx 0.05\%\)

Gas film resistance = 99.95\%

... Ans. (ii)

Major resistance is in the gas film.

... Ans. (iii)

6. Gaseous A absorbs and reacts with liquid B in liquid according to

\[ \text{A(g} \to \text{l)} + \text{B(l)} \to \text{R(l)}, \quad -r_A = k C_A C_B \quad \text{in a packed bed.} \]

At a point in the reactor where \(P_A = 100\) Pa and \(C_B = 1\) mol/m$^3$ liquid.

(i) Calculate the rate of reaction in mol/(h.m$^3$ of reactor)

(ii) Resistance offered by the main body of liquid.

Data: \(k_{Ag} a = 0.10\) mol/h.m$^3$ reactor . Pa)

\(f_i = 0.01\) m$^3$ liquid/m$^3$ reactor

\(k_{Al} a = 100\) m$^3$ liquid/(m$^3$ reactor.h)
Hint: For $M_H < 0.02$, we have infinitely slow reaction.

Solution:

$$A + bB \rightarrow R, \quad -r_A = k C_A C_B, \quad b = 1$$

$a = 100 \text{ m}^2 / \text{m}^3 \text{ reator}$

$D_{Al} = D_{Bl} = 10^{-6} \text{ m}^2 / \text{h}$

$H_A = 10^5 (\text{Pa} \cdot \text{m}^3 \text{ liquid}) / \text{mol}$

First we have to determine whether it is very fast, fast, slow or very slow reaction. For this we have to evaluate $H_M$ and $E_i$

$$M_H = (D_{Al} k C_B)^{1/2}$$

$$D_{Al} = 10^{-6} \text{ m}^2 / \text{h}, \quad k = 10 \text{ m}^3 / (\text{mol} \cdot \text{h}), \quad C_B = 1 \text{ mol}/\text{m}^3$$

$$k_{Al} = \frac{k_{Al}}{a} = \frac{100}{100} = 1.0 \text{m/h}$$

$$M_H = \frac{(10^{-6} \times 10 \times 1)^{0.5}}{1} = 0.00316$$

$$E_i = 1 + \frac{D_{Bl} C_B H_A}{b D_{Al} p_{Ai}}$$

$$p_{Ai} = p_A = 100 \text{ Pa}, \quad D_{Bl} = D_{Al} = 10^{-6} \text{ m}^2 / \text{h}, \quad H_A = 10^5 (\text{Pa} \cdot \text{m}) / \text{mol}$$

$$E_i = 1 + \frac{10^{-6} \times 1 \times 10^3}{1 \times 10^{-6} \times 100} = 1 + \frac{10^3}{10^3}$$

As $M_H < 0.02$, $(M_H \text{ calculated} = 0.00316)$, we have infinitely slow reaction (without mass transfer resistance) occurring in the bulk of liquid.

...Ans.

For infinitely slow reaction, the rate is determined by kinetics alone. The form of rate expression for this case is
\[-r^*_A = \frac{k_f}{H_A} p_A C_B = k f_i C_A C_B\]

...Ans.

We have, \(f_i = 0.01 \text{ m}^3\text{liquid} / \text{m}^3 \text{ reactor}\)

\(k = 10 \text{ m}^3\text{liquid} / (\text{mol.h})\)

\[-r^*_A = k f_i C_A C_B\]

\[= \frac{k f_i}{H_A} p_A C_B\]

\[= \frac{10 \times 0.01}{10^5} \times 100 \times 1 = 1 \times 10^{-4} \text{ mol(m}^3\text{ reactor.h)}\]

Rate of reaction = \(1 \times 10^{-4} \text{mol/(m}^3\text{reactor.h)}\)

...Ans. (i)

The general rate expression is

\[-r^*_A = \frac{1}{k_{A_B} a + \frac{H_A}{k_{A_I} a E} + \frac{H_A}{k_{C_B} f_i}} p_A\]

... (1)

In our case for infinitely slow reaction,

\[-r^*_A = \frac{k f_i}{H_A} p_A C_B = k f_i C_A C_B\]

\[= \frac{1}{\left(\frac{H_A}{k f_i C_B}\right)} p_A\]

...(2)

Comparing Equation (2) and with Equation (1), there is no mass transfer resistance.

Liquid bulk resistance = \(\frac{H_A}{k f_i C_B}\)

\[= \frac{10^5}{10 \times 0.01 \times 1}\]

Liquid bulk resistance = \(1 \times 10^5 (\text{Pa.m}^3\text{h})\text{mol}\)

...Ans. (ii)
7. Derive the equation of enhancement factor for 1st order reaction.

\[ N_A = -D_{AB} \frac{dc_A}{dz} \]
\[ \frac{d}{dz} (N_A) - r_A = 0 \]

\[ \therefore \ - \frac{d}{dz} (D_{AB} \frac{dc_A}{dz} + kc_A) = 0 \]
\[ -D_{AB} \frac{d^2c_A}{dz^2} + kc_A = 0 \]

\[ C_A = C_1 \text{Cosh} \left( \frac{k}{D_{AB}} z \right) + c_2 \sinh \left( \frac{k}{D_{AB}} z \right) \]

At \ z = 0, \ C_A = C_{AO}, z = s \ C_A = 0

\[ C_1 = C_{AO} \text{ and } C_2 = \frac{-C_{AO}}{\tanh \left( \frac{k}{D_{AB}} z \right)} \]

\[ \therefore \ C_A = C_{AO} \text{Cos} \left( \frac{k}{D_{AB}} z \right) - C_{AO} \frac{\sinh \left( \frac{k}{D_{AB}} z \right)}{\tanh \left( \frac{k}{D_{AB}} z \right)} \]

\[ \frac{d}{dz} \frac{C_A}{z = 0} \Rightarrow \]
\[ N_A/z = 0 \quad \frac{D_{AB} C_{AO}}{\delta} \frac{\sqrt{D_{AB}}} {\tanh \left( \frac{k}{D_{AB}} \delta \right)} \]

\[ N_A = \frac{D_{AB} C_{AO}}{\delta} \]

\[ \therefore E = \frac{\sqrt{D_{AB}}} {\tanh \left( \frac{k}{D_{AB}} \delta \right)} \]
8. The concentration of an underscrable impurety a in air \((\text{atn} = 10^5 \text{pa})\) is to be reduced from 0.1% (100pa) to (0.02%) 20pa by absorptum in pure water. Estimate the height of tower needed for counter current operation.

Data:

For packing used:

\[ k_{A_b} a = 0.32 \text{ mol/(h.m}^3\text{.Pa)} \]
\[ k_{A_t} a = 0.10 \text{ h}^{-1} \]

The solubility of A in water is given by Henry’s law constant: \( H_A = 12.5 \text{ (Pa.m}^3\text{)/mol} \)

The flow rates of gas and liquid per m\(^2\) of tower cross-section are:

\[ F_g / A_{ca} = 1 \times 10^5 \text{ mol/(h.m}^2\text{)} \]
\[ F_l / A_{ca} = 7 \times 10^5 \text{ mol/(h.m}^2\text{)} \]

The molarity of liquid under all conditions is:

\[ C_t = 56000 \text{ mol/m}^3 \]

Solution:

![Diagram](image)

**Figure: Countercurrent tower for straight mass transfer**

As impurity A is to be removed by using pure water, it is a case of:

Straight mass transfer (absorption) of A
A (gas) → (liquid)
Also we are provided with dilute systems.

We will write first material balance for dilute solutions to find $C_{A2}$ in the exit water stream and then we will determine tower height.

For any point in the tower $p_A$ and $C_A$ are related by

$$p_A - p_{A1} = \left(\frac{F_1}{A_{cs}}\right) \pi (C_A - C_{A1})$$

$$p_{A1} = 20\text{Pa}, \quad C_{A1} = 0, \quad \pi = 10^5\text{Pa}$$

$$C_T = 56000 \text{ mol/m}^3$$

$$F_1 / A_{cs} = 7 \times 10^5 \text{ mol/}(\text{h.m}^2)$$

$$F_g / A_{cs} = 7 \times 10^5 \text{ mol/}(\text{h.m}^2)$$

$$p_A - 20 = \frac{7 \times 10^5 \times 10^5}{1 \times 10^5 \times 56000} (C_A - 0)$$

$$p_A - 20 = 12.5C_A$$

Or

$$C_A = 0.08p_A - 1.6$$

In the inlet air stream to the tower we have:

$$p_{A2} = 100\text{Pa}$$

The concentration of A in the water leaving the tower is

$$C_{A2} = 0.08p_{A2} - 1.6$$

$$= 0.08 \times 100 - 1.6$$

$$= 6.4\text{mol/m}^3$$

The concentration of A in air entering the tower is 0.10% and $\pi = 10^5\text{Pa}$

$$\therefore p_{A2} = \frac{0.10}{100} \times 10^5 = 100\text{Pa}$$
The concentration of A in air leaving the tower is 0.02%.

\[ p_{A1} = \frac{0.02}{100} \times 10^5 = 20 \text{Pa} \]

This procedure is to be used when concentration of A is given in %.

The height of tower is given by

\[ V_r = hA_{cs} = \frac{F_g}{\pi K_{Ag}^3} \int_{p_{A1}}^{p_A} \frac{dp_A}{p_A - p_A^*} \]

\[ h = \frac{F_g}{A_{cs}} \int_{p_{A1}}^{p_A} \frac{dp_A}{p_A - p_A^*} \]

Now we will evaluate \( p_A - p_A^* \) (overall gas phase driving force)

Select a few values of \( p_A \) in the tower, usually \( p_{A1}, p_{A2} \) and one or two intermediate values are sufficient.

Evaluate: \( C_A \) corresponding to \( p_A \rightarrow p_A \rightarrow (p_A - p_A^*) \).

\( C_A \) – concentration of A in the liquid corresponding to \( p_A \).

\( p_A^* \) – equilibrium partial pressure of A corresponding to liquid phase concentration \( C_A \).

Evaluate \( C_A \) from \( p_A \) by using

\[ C_A = 0.08 p_A - 1.6 \]

For \( p_A = 200 \text{Pa}, \quad C_A = 0 \text{ mol/m}^3 \)
For \( p_A = 100 \text{Pa}, \quad C_A = 6.4 \text{ mol/m}^3 \)
For \( p_A = 60 \text{Pa}, \quad C_A = 3.2 \text{ mol/m}^3 \)
For \( p_A = 80 \text{Pa}, \quad C_A = 4.8 \text{ mol/m}^3 \)

Calculate \( p_A^* \) using Henry’s law:

\[ p_{A_C_A}^* = H_A C_A = 12.5 C_A \] and tabulate.
Here we have constant \( \Delta p_A \) so graphical procedure is not required.

Now evaluate \( K_{Ag}a \)

\[
\frac{1}{K_{Ag}a} = \frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a} = \frac{1}{0.32} + \frac{12.5}{0.10} = 3.125 + 125 = 128.125
\]

\( \therefore \) Gas film resistance = \( \frac{3.125}{128.125} \times 100 = 2.5\% \)

\( \therefore \) Liquid film resistance = \( \frac{125}{128.125} \times 100 = 97.5\% \)

\[ 1/K_{Ag}a = 128.125 \]

\[ K_{Ag}a = \frac{1}{128.125} = 0.0078 \text{mol (h.m \cdot Pa)} \]

\[
h = \frac{F_r/A_{cs}}{\pi K_{Ag}a \Delta p_A} \int_{P_{A1}}^{P_{A2}} dp_A, \quad P_{A1} = 20P_{A2} = 100\text{Pa}
\]

\[
= \frac{F_r/A_{cs}}{\pi K_{Ag}a \Delta p_A} \int_{20}^{100} dp_A
\]

\[
= \frac{1 \times 10^5}{10^5 \times 0.0078 \times 20} \int_{20}^{100} dp_A
\]

\[
= \frac{1 \times 10^5}{10 \times 0.0078 \times 20} \left( 100 - 20 \right)
\]

\[ = 512.82 = 513 \text{m} \]

**Height of tower needed = 513 m**

**Comment:** Tower is unacceptably high. Here most of the resistance (97.5\%) resides in the liquid film so we can with little error consider this to be a liquid-film controlling process.
9. We plan to remove 90% of the reactant present in a gas stream by absorption in water?

Find the volume of tower required for countercurrent operation.

Data:
For gas stream:
\( F_g = 90000 \text{ mol/h} \) at \( \pi = 10^5 \text{ Pa} \)
\( p_{A_{in}} = 100 \text{ Pa}, \; p_{A_{out}} = 100 \text{ Pa} \)

For the packed bed:
\( F_l = 900000 \text{ mol/h}, \; k_{A_g} a = 0.36 \text{ mol(h.m}^3.\text{Pa}) \)
\( k_{A_l} a = 72 \text{ h}^{-1} \)

Molar density of liquid under all conditions is
\( C_T = 55556 \text{ mol/m}^3 \)

And \( H_A = 18(\text{pa.m}^3)\text{mol}, \; k = 0 \text{ m}^3(\text{mol.h}) \)

Solution:
Here we are concerned with – straight mass transfer/physical absorption of A and dilute system.

For a dilute solution for any point in the tower

\[ p_A \text{ and } C_A \text{ are related by} \]
\[ p_A - p_{A_1} = \frac{F_l \pi}{F_g C_T} (C_A - C_{A_1}) \]

\( p_{A_1} = 100 \text{ Pa}, \; C_{A_1} = 0, \pi = 10^5 \text{ Pa} \)
\( C_T = 55556 \text{ mol/m}^3 \)
\( F_i = 900000 \text{ mol/h}, \ F_g = 90000 \text{ mol/h} \)

\[
p_A - 100 = \frac{900000 \times 10^5}{90000 \times 55556} (C_A - 0)
\]
\[
p_A - 100 = 18C_A
\]

or
\[
C_A = 0.05556 \ p_A - 5.5556
\]

The concentration of A in water leaving the tower is given by
\[
C_{A2} = 0.05556 \ p_{A2} - 5.5556
\]
For \( p_{A2} = 1000 \text{ pa} \)
\[
C_{A2} = 0.05556(1000) - 5.5556
\]
\[
= 50 \text{ mol/m}^3
\]

Now select a few values of \( p_A \) in addition to \( p_{A1} \) and \( p_{A2} \) in the tower and determine
\[
\rightarrow C_A \rightarrow p_A^* \rightarrow (p_A - p_A^*)
\]

Take : \( p_A = 550 \text{ Pa} \) to \( p_A = 800 \text{ Pa} \)
For \( p_A = 550 \text{ Pa} \)
Take :
\[
C_A = 0.05556 \ p_A - 5.5556
\]
\[
C_A = 0.05556(550) - 5.5556 = 25\text{mol} / \text{m}^3
\]

\[p_A^* = H_A C_A, \ H_A = 18(\text{pa.m}^3)/\text{mol}\]
\[
p_A^* = 18 \times 25 = 450\text{Pa}
\]
\[
\therefore \quad p_A^* = p_A - p_A^* = 550 - 450 = 100 \text{ Pa}
\]

<table>
<thead>
<tr>
<th>( p_A )</th>
<th>( C_A )</th>
<th>( p_A^* = H_A C_A )</th>
<th>( \Delta p_A = p_A - p_A^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>550</td>
<td>25</td>
<td>450</td>
<td>100</td>
</tr>
<tr>
<td>800</td>
<td>38.89</td>
<td>700</td>
<td>100</td>
</tr>
<tr>
<td>1000</td>
<td>50</td>
<td>900</td>
<td>100</td>
</tr>
</tbody>
</table>

Here we have constant \( \Delta p_A \) so graphical procedure is not required (as is constant it can be taken out of the integral sign).
Next evaluate $K_{Ag}a$:

$$
\frac{1}{K_{Ag}a} = \frac{1}{k_{Ag}a} + \frac{1}{k_{Al}a} \quad k_{Ag}a = 0.36 \text{mol} / 0 \quad k_{Al}a = 72 \text{ h}^{-1}
$$

$$
= \frac{1}{0.36} + \frac{18}{72}
= 2.78 + 0.25
= 3.03
$$

\[ \therefore K_{Ag}a = 1/3.03 = 0.33 \text{ mol/(h.m Pa)} \]

The volume of tower is given by

$$
V_t = \frac{F_g}{\pi K_{Ag}a} \int_{p_{a1}}^{p_{a2}} dp_A \Delta P_A, \Delta P_A = P_A - P_A^*
$$

$$
= \frac{F_g}{\pi K_{Ag}a} \int_{100}^{1000} dp_A
$$

$$
= \frac{90000}{10^5 \times 0.33 \times 100} (1000 - 100)
$$

$$
= \frac{90000}{10^5 \times 0.33 \times 100} (1000 - 100)
$$

$$
= 24.54 \text{ m}^3
$$

10. Repeat the above problem for $H_A 1.8 \text{ Pa m}^3 / \text{mol}$

Solution:

From the solution of previous example.

For any point in the tower, $P_A$ and $C_A$ are related by

$$
C_A = 0.05556 p_A - 5.5556
$$

and

$$
C_{A2} = 50 \text{ mol/m}^3
$$

Now select few values of $p_A$ in addition to $p_{A1}$ and $p_{A2}$ and determine

$\rightarrow C_A \rightarrow P_A^* \rightarrow (p_A - p_A^*)$

Now

$$
H_A = 1.8(P.\text{am}^3) / \text{mol}
$$
For \( p_A = 550 \text{ Pa} \)

\[
C_A = 0.05556 \times 550 = 25 \text{ mol/m}^3
\]

\[
p_A^* = H_A C_A = 1.8 \times 25 = 45 \text{ Pa}
\]

\[
\Delta p_A = p_A - p_A^* = 550 - 45 = 505 \text{ Pa}
\]

For \( p_A = 275 \text{ Pa} \)

\[
C_A = 0.05556 \times 275 = 9.723 \text{ mol/m}^3
\]

\[
p_A^* = 1.8 \times 9.723 = 17.5 \text{ Pa}
\]

For \( p_A = 800 \text{ Pa} \)

\[
C_A = 0.5556 \times 800 = 38.89 \text{ mol/m}^3
\]

\[
p_A^* = 1.8 \times 38.89 = 70 \text{ Pa}
\]

For \( p_A = 1000 \text{ Pa}, C_A = 50 \text{ mol/m}^3 \) and \( p_A^*, 90 \text{ Pa}. \)

<table>
<thead>
<tr>
<th>( p_A )</th>
<th>( C_A )</th>
<th>( p_A^* = H_A C_A )</th>
<th>( \Delta p_A = p_A - p_A^* )</th>
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<tr>
<td>100</td>
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<td>0</td>
<td>100</td>
</tr>
<tr>
<td>275</td>
<td>9.7234</td>
<td>17.5</td>
<td>257.5</td>
</tr>
<tr>
<td>550</td>
<td>25</td>
<td>45</td>
<td>505</td>
</tr>
<tr>
<td>800</td>
<td>38.89</td>
<td>70</td>
<td>730</td>
</tr>
<tr>
<td>1000</td>
<td>50</td>
<td>90</td>
<td>910</td>
</tr>
</tbody>
</table>

Here \( \Delta p_A \) is not constant.

The volume of tower is given by

\[
V_r = \frac{F}{\pi} \int_{r_{A1}}^{r_A} \frac{dp_A}{-r_A}
\]

\[
-r_A = K_{Ag} a (p_A - p_A^*)
\]

From Ex. 3.2 : \( K_{Ag} = 0.33 \text{ mol/(h.m}^3\text{.Pa)} \)
\[ \frac{\pi V_r}{F_s} = \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A} \]

Evaluate the integral on RHS graphically.

\[ \frac{1}{(-r_A)} \frac{v}{s} p_A \]  The area under the curve between \( p_{A1} \) and \( p_{A2} \) integral and is equal to \( \frac{\pi V_r}{F_s} \).

\[ \frac{\pi V_r}{F_s} = \text{area under curve } \times \text{scale x-axis } \times \text{scale y-axis}. \]

Now evaluate \(-r_A\) for each \( p_A \) and tabulate.

For \( p_A = 100 \) Pa, \( p_A' = 0 \) and \( \Delta p_A = 100 \) Pa

\[ -r_A = K_{Aa} \ a \ (p_A - p_A') = K_{Aa} \ a \ \Delta p_A \]

\[ = 0.33 \times 100 = 33 \text{ mol/(h.m^3)} \]

\[ \frac{1}{(-r_A)} = \frac{1}{33} = 0.0303 \text{ (h.m^3)/mol} \]

<table>
<thead>
<tr>
<th>( p_A )</th>
<th>( p_A' )</th>
<th>( \Delta p_A = p_A - p_A' )</th>
<th>(-r_A)</th>
</tr>
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<tbody>
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<td>100</td>
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<td>100</td>
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</tr>
<tr>
<td>275</td>
<td>17.5</td>
<td>257.5</td>
<td>84.975</td>
</tr>
<tr>
<td>550</td>
<td>45</td>
<td>505</td>
<td>166.65</td>
</tr>
<tr>
<td>1000</td>
<td>90</td>
<td>910</td>
<td>300.3</td>
</tr>
</tbody>
</table>

Plot \( \frac{1}{(-r_A)} \) v/s \( p_A \)

We have : \( p_{A1} = 100 \) Pa and \( p_{A2} = 1000 \) Pa

Measure the area under the curve between \( p_A = p_{A1} = 100 \) Pa and \( p_A = \ldots \ldots \)

Refer Figure. 3.3.
\[ \frac{\pi V_r}{F_g} = \text{Area} \times \text{scale y-axis} \times \text{scale x-axis} \]

\[ = 29.5 \times \frac{0.005}{2} \times 100 = 7.375 \]

\[ V_r = \frac{7.375 F_g}{\pi} = \frac{7.375 \times 90000}{10^5} = 6.64 \text{ m}^3 \]

Volume of tower = 6.64 m$^3$

...Ans.

11. An undesired impurity is to be removed from air in a counter current tower.

Impurity in inlet air = 0.5% (500 Pa)
Impurity in outlet air = 0.1% (100 Pa)
Flow rates of gas and liquid are:

\[ \frac{F_g}{A_{cs}} = 1 \times 10^5 \text{ mol/(h.m}^2) \]

\[ \frac{F_l}{A_{cs}} = 10.6 \times 10^5 \text{ mol/(h.m}^2) \]

\[ k_{Ag} \ a = 0.60 \text{ mol/(h.m}^3 \text{.Pa}) \]

\[ k_{Al} \ a = n0.5 \text{ h}^{-1} \]
Molar density of liquid, assumed constant, is

\[ C_T = 56000 \text{ mol/m}^3 \]

And \( H_A = 15(\text{Pa.m}^3)/\text{mol} \)

Calculate the height of tower required.

**Solution:**
Here we are concerned with – straight mass transfer of A

![Figure: E 3.4 (a)](image)

For any point in the tower \( P_A \) and \( C_A \) are related by

\[
(P_A - P_{A1}) = \left( \frac{F_l}{A_{cs}} \right) \pi (C_A - C_{A1})
\]

\[ P_{A1} = 100 \text{ Pa}, \quad C_{A1} = 0, \quad \pi \times 10^5 \text{ Pa} \]

\[ C_T = 56000 \text{ mol/m}^3 \]

\[ F_l / A_{cs} = 10.6 \times 10^5 \text{ mol/l} \]

---

\[ P_A - 100 = 18.928 C_A \]

or \[ C_A = 0.05283 P_A - 5.283 \]

... (1)

The concentration of impurity (A) in the water entering the tower \([C_A,2]\) is obtained by using above relation.

\[ C_{A2} = 0.05283 P_{A2} - 5.583 \]
We have $P_{A_2} = 500 \text{ Pa}$

\[
\therefore \quad C_{A_2} = 0.05283(500) - 5.283 = 21.132 \text{ mol/m}^3
\]

$H_A = 15 \text{ (Pa.m}^3)/\text{mol}$

Now select few values of $p_A$, determine the corresponding concentration of $A$ ($C_A$) in liquid using Equation (1), calculate the equilibrium partial pressure of $A$, $p_A^*$, corresponding to $C_A$ and then calculate $\Delta p_A = p_A - p_A^*$, overall gas phase driving force.

\[
p_A = 300 \text{ Pa} \\
C_A = 0.05283 p_A - 5.283
\]

Take $C_A = 0.05283(300) - 5.283 = 10.566 \text{ mol/m}^3$

\[
p_A^* = H_A C_A \\
= 15 \times 10.566 = 158.49 \quad 158.5 \text{ Pa}
\]

$\Delta p_A = p_A - p_A^* = 300 - 158.5 = 141.5 \text{ Pa}$

<table>
<thead>
<tr>
<th>$p_A$</th>
<th>$C_A$</th>
<th>$p_A^* = H_A C_A$</th>
<th>$\Delta p_A = p_A - p_A^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>5.283</td>
<td>79.24</td>
<td>120.76</td>
</tr>
<tr>
<td>300</td>
<td>10.566</td>
<td>158.5</td>
<td>141.5</td>
</tr>
<tr>
<td>400</td>
<td>15.849</td>
<td>237.7</td>
<td>162.3</td>
</tr>
<tr>
<td>500</td>
<td>21.132</td>
<td>317</td>
<td>183</td>
</tr>
</tbody>
</table>

Here $\Delta p_A$ is not constant so we will adopt a graphical procedure for the determination of height of the tower.

We have:

\[
V_h A_{cs} = \frac{F_g}{\pi} \int_{r_{A_1}}^{r_A} dp_A \\
\frac{\pi h}{(F_g = A_{cs})} = \int_{r_{A_1}}^{r_A} dp_A \\
k_{A_g}E_a = 0.60 \text{ mol/(h.m}^3\text{Pa)}
\]

$k_{A_{al}} a = 0.5h^{-1}$

$H_A = 15(\text{Pa.m}^3)/\text{mol}$
\[
\frac{1}{K_{Ag}} a = \frac{1}{k_{Ag}} a + \frac{H_A}{K_{Al}} a \\
= \frac{1}{0.6} + \frac{15}{0.5} = 1.667 + 30 = 31.667 \\
\therefore K_{Ag} a = \frac{1}{31.667} = 0.0316 \text{ mol/(h.m}^3\text{Pa)}
\]

Gas film resistance = \(\frac{1.667}{31.667}\) 100 = 5.26%

Liquid film resistance = \(\frac{30}{31.667}\) 100 = 94.74%

So it is a liquid film controlling process (as major resistance film).

\[-r_{A}'' = K_{Ag} a(p_A - p_{A1})\]

Now evaluate \(-r_{A}''\) for each value of \(p_A\) and tabulate.

<table>
<thead>
<tr>
<th>(p_A)</th>
<th>(p_A - p_{A1})</th>
<th>(-r_{A}'')</th>
<th>(1/(-r_{A}'')</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100</td>
<td>3.16</td>
<td>0.316</td>
</tr>
<tr>
<td>200</td>
<td>120.76</td>
<td>3.82</td>
<td>0.262</td>
</tr>
<tr>
<td>300</td>
<td>141.5</td>
<td>4.47</td>
<td>0.224</td>
</tr>
<tr>
<td>400</td>
<td>162.3</td>
<td>5.13</td>
<td>1.195</td>
</tr>
<tr>
<td>500</td>
<td>183</td>
<td>5.78</td>
<td>0.173</td>
</tr>
</tbody>
</table>

\[
\frac{\pi h}{(F_g = A_{cs})} = \int_{r_{A1}}^{r_{A2}} dp_A' \\
= \int_{p_{A1}}^{p_{A2}} dp_A \\
= \text{Area under the curve} \times \text{scale y-axis} \times \text{scale x-axis}
\]

Plot \(\frac{1}{(-r_{A})}\) v/s \(p_A\) and measure area under curve between \(p_{A1} = 100\) Pa and \(p_{A2} = 500\) Pa.

Refer Figure. E 3.4 (b):

Area under the curve = 1829 mm\(^2\) = 18.29 cm\(^2\)
\[
\frac{\pi h}{(F_g/A_{cs})} = \text{Area Scaley - axis} \times \epsilon \times \text{Scale x-axis}
\]

\[
\frac{\pi h}{(F_g/A_{cs})} = 18.29 \times \frac{0.1}{2} \times \frac{100}{1}
\]

\[
= 91.45
\]

\[
h = \frac{91.45(F_g/A_{cs})}{\pi}
\]

\[
= 91.45
\]

Height of tower = 91.45 m

... Ans.

**Figure E 3.4 (b)**

12. We plan to remove about 80% of the A present in a gas stream by absorption in water containing reactant B. Material B reacts with A as per the following reaction:

\[
A(g \rightarrow l) + B(l) \rightarrow R(l)
\]

The reaction is extremely rapid so \(k = \infty\).

Determine the height of tower for countercurrent operation using following data.

**Data:**

The gas and liquid flow rates are:
\( F_g / A_{cs} = 1 \times 10^5 \text{ mol(h.m}^2\text{)} \text{ at } 10^5 \text{ Pa} \)

\( F_l / A_{cs} = 7 \times 10^5 \text{ mol(h.m}^2\text{)} \)

\( H_A = 12.5(\text{Pa.m}^3)\text{mol} \)

\( C_T \) (molar density of liquid) = 56000 mol/m\(^3\)

\( p_A \) in = 100 Pa

\( k_{A_b} a = 0.32 \text{ mol/(h.m}^3\text{.Pa)} \)

\( k_{A_l} a = 0.10 \text{ h}^{-1} \)

\( C_B = \) concentration of reactant B in water entering the tower = 800 mol/ m\(^3\). = 800 mol/m\(^3\).

Assume that the diffusivities of A and B in water are the same.

**Solution:**

\( A(g \rightarrow l) + B(l) \rightarrow R(l), \ k = \infty. \)

It is extremely rapid reaction (instantaneous reaction)

Here \( b = 1 \) (Stoichiometric coefficient of B)

\( P_{A_{in}} p_{A_2} = 100 \text{Pa} \)

0% of QA is removed from air

\[ P_{A_{out}} = P_{A_l} = 100(1 - 0.80) = 20 \text{Pa} \]

![Figure: E 3.6](image-url)
First find \( C_{b2} \) with the help of material balance.

\( C_{b2} \) is the concentration of B in exit stream from the tower.

For dilute solutions the simplified material balance yields:

\[
(P_A - P_{Al}) = \frac{(F_i / A_{cs})\pi}{(F_s / A_{cs})b} C_T (C_{bl} - C_b)
\]

\( P_{Al} = 20 \) Pa, \( \pi=10^5 \) Pa, \( b=1 \), \( C_T = 56000 \text{ mol/m}^3 \)

\( C_{bl} = 800 \text{ mol/m}^3 \)

\[
\frac{F_i}{A_{cs}} = 7 \times 10^5 \text{ mol/(h.m)}^2
\]

\[
\frac{F_s}{A_{cs}} = 1 \times 10^5 \text{ mol/(h.m)}^2
\]

\[
P_A - 20 = 10020 - 12.5 C_B
\]

or \( C_B = 801.6 - 0.08 P_A \)

The above equation relates \( C_B \) to \( p_A \) at any point in the tower.

At the bottom of the tower:

\( C_T \) (molar density of liquid) = 56000 mol/m\(^3\)

\( P_A = 100 \) Pa

\( C_{b2} = 801.6 - 0.08 P_{A2} \)

\( C_{b2} = 801.6 - 0.08 \times 100 = 793.6 \text{ mol/m}^3 \)

It is given that the reaction is extremely rapid (instantaneous).

To find the appropriate form of rate equation we have to determine whether it is instantaneous reaction with low or high \( C_B \) and for this estimate \( k_{Ag} \) a \( P_A \) and \( k_{bi} \) a \( C_B / b \) at both ends of the tower.

As \( D_{bi} = D_{Al} \) (same diffusivities in water)

\( k_{Bi} \) a \( k_{bi} \) a

We have

\( k_{Al} \) a \( k_{bi} \) a = 0.10 h\(^{-1}\)
\(k_{Ag} = 0.32 \text{ mol/(h.m}^3\text{.Pa)}\)

At top of the tower:

\[p_A = p_{Al} = 20 \text{ Pa}, \quad C_B = C_{Bl} = 800 \text{ mol/m}^3\]

\[k_{Ag} \cdot p_A = 0.32 \times 20 = 6.4 \text{ mol/(h.m}^3\text{)}\]

\[\frac{k_{Bl} \cdot a \cdot C_B}{b} = \frac{0.1 \times 800}{1} = 80 \text{ mol/(h.m}^3\text{)}\]

\[\therefore \quad k_{Ag} \cdot p_A < k_{Bl} \cdot a \cdot C_B / b\]

At bottom of the tower:

\[p_A = p_{A2} = 100 \text{ Pa}, \quad C_B = C_{B2} = 793.6 \text{ mol/m}^3\]

\[k_{Ag} \cdot p_A = 0.32 \times 100 = 32 \text{ mol/(h.m}^3\text{)}\]

\[\frac{k_{Bl} \cdot a \cdot C_B}{b} = \frac{0.1 \times 793.16}{1} = 79.32 \text{ mol/(h.m}^3\text{)}\]

At both ends of tower \(k_{Ag} \cdot p_A < k_{Bl} \cdot a \cdot C_B / b\)

As \(k_{Ag} \cdot p_A < k_{Bl} \cdot a\) we have:

Instantaneous reaction with high \(C_B\). Gas phase resistance controls. Reaction zone is at the interface and so the form of rate equation is

\[-r^*_A = (-r^*_A) \cdot k_{Ag} \cdot a \cdot p_A\]

\[-r^*_A = 0.32 \cdot p_A\]

The height of tower is given by

\[h = \frac{\left(\frac{F_s}{A_{cs}}\right)}{\pi} = \int_{p_A}^{p_{A1}} \frac{dP_A}{-r^*_A}\]

\[= \frac{\left(\frac{F_s}{A_{cs}}\right)}{\pi \cdot 0.32} = \int_{20}^{100} \frac{dP_A}{p_A}\]

\[= \frac{1 \times 10^5}{1 \times 10^5 \times 0.32} \ln \left(\frac{100}{20}\right)\]

\[= 5.03 \text{ m}\]

Height of tower for counter current operation = 5.03 m

....(Ans).
13. Derive the rate expression for instantaneous Reaction (...with low Cₖ): 

For low Cₖ we have the situation as shown in Fig. 2.4. Here an element of liquid contains either A or B not both. Consequently, reaction will occur at a plane between A-containing and B-containing liquid (in the liquid film). As reactants A and B must diffuse to this reaction plane for reaction to occur, the general rate will be decided by the rate of diffusion A and B to this reaction plane.

Figure: Concentration profiles of reactants for an infinitely fast irreversible reaction for case A-low Cₖ - (two-film theory)

At steady state, the flow rate of B toward the reaction zone will be b times that of A. Thus the rate of disappearance of A and B based on the unit interfacial surface are given by

\[ -r_A = -r_B = \frac{k_{Ag}}{b}(p_A - p_{Ai}) = k_{Al}(C_{Ai} - 0) \frac{Xo}{X} = (C_{B-0}) \frac{Xo}{Xo-x} \cdots(2.17) \]

A through gas film   A through liquid film   B through liquid film

Where, \( k_{Ag} \) – gas film mass transfer coefficient for A, mol/(m².Pa.s) 
\( k_{Al} \) – liquid film mass transfer coefficient for A, m³ liqid/(m² surface.s) 
\( k_{Bl} \) - liquid film mass transfer coefficient for B.

The liquid side coefficients are based of flow through the whole will of thickness X₀. The equilibrium relationship between \( p_A \) and \( C_A \) at the interface is given by Henry’s law
According to the two-film theory the liquid phase mass transfer coefficients for A and B are given by

\[ k_{Al} = \frac{D_{Al}}{x_0} \quad \text{and} \quad k_{Bl} = \frac{D_{Bl}}{x_0} \]

\[ \frac{k_{Al}}{k_{Bl}} = \frac{D_{Al}x_0}{D_{Bl}x_0} = \frac{D_{Al}}{D_{Bl}} \quad \text{...(2.19)} \]

Now we will eliminate the unknowns \( x, x_0, C_{Ai}, \) and \( p_{Ai} \) from the above equations to obtain desired rate equation in terms of known quantities.

From Equation (2.17) we have

\[ -r_{A}^\rightarrow = k_{Ag} (P_A - P_{Ai}) \]
\[ -r_{x}^\rightarrow = \frac{P_A - P_{Ai}}{k_{Ag}} \]

Dividing the above equations by \( H_A \) gives

\[ \frac{-r_{A}^\rightarrow}{H_A k_{Ag}} = \frac{P_A - P_{Ai}}{H_A} \quad \text{...(2.20)} \]
\[ -r_{A}^\rightarrow = k_{Al} (C_{Ai} - 0) \frac{x_0}{x} \]

\[ \frac{-r_{x}^\rightarrow}{k_{Al}} = C_{Ai} \frac{x_0}{x} \quad \text{...(2.12)} \]

Also,
\[ k_{Al} (C_{Ai} - 0) \frac{x_0}{x} = \frac{k_{Bl} (C_B - 0)}{b} \frac{x_0}{x_0 - x} \]

\[ \therefore \quad \frac{C_{Al}}{x} = \frac{k_{Bl} C_B}{b k_{Al} (x_0 - x)} \]
\[ C_{Ai} x_0 - C_{Ai} x = \frac{k_{Bl} C_B}{b k_{Al}} \]
\[ C_{Ai} x_0 = \left[ \frac{k_{Bl} C_B}{b k_{Al}} + C_{Ai} \right] x \]
\[
\frac{x_o}{x} = \frac{k_{Bl} C_B + C_{Ai}}{b k_{Al} C_{Ai}} \quad \ldots(2.22)
\]

Using Equation (2.22) to substitute for \(x_o/x\), Equation (2.21) becomes

\[
\frac{-r_A}{k_{Al}} = C_{Ai} \left[ \frac{k_{Bl} C_B + C_{Ai}}{b k_{Al} C_{Ai}} \right]
\]

\[
\frac{-r_A}{k_{Al}} = \frac{k_{Bl}}{b k_{Al}} C_B + C_{Ai} \quad \ldots(2.23)
\]

Henry’s law is

\[
P_{Ai} = H_A C_{Ai}
\]

\[
C_{Ai} = \frac{P_{Ai}}{H_A} \quad \ldots(2.24)
\]

Substituting \(C_{Ai}\) from Equation (2.24) into Equation (2.23) yields

\[
\frac{-r_A}{k_{Al}} = \frac{k_{Bl}}{b k_{Al}} C_B + \frac{P_{Ai}}{H_A}
\]

\ldots(2.25)

Adding Equations (2.20) and (2.25) gives

\[
\frac{-r_A}{H k_{Ag}} + \frac{-r_A}{k_{Al}} = \frac{P_A}{H_A} - \frac{P_{Ai}}{H_A} + \frac{k_{Bl}}{b k_{Al}} C_B + \frac{P_{Ai}}{H_A}
\]

\[
\frac{-r_A}{H k_{Ag}} + \left[ \frac{1}{H k_{Ag}} + \frac{1}{k_{Al}} \right] = \frac{P_A}{H_A} + \frac{k_{Bl}}{b k_{Al}} C_B
\]

\ldots(2.26)

We have,

\[
\frac{k_{Al}}{D_{Al}} = \frac{D_{Ai}/x_o}{D_{Al} / x_o}
\]

\[
\frac{k_{Bl}}{D_{Bl}} = \frac{D_{Ai} / x_o}{D_{Bl} / x_o}
\]

\[
\frac{k_{Bl}}{k_{Al}} = \frac{D_{Bl}}{D_{Al}}
\]
Replacing \( \frac{k_{Bl}}{k_{Al}} \) by \( \frac{D_{Bl}}{D_{Al}} \) in Equation (2.26) gives

\[
-r_A = \frac{1}{H_A k_{Ag} + 1/k_{Al}} = \frac{P_A + \frac{D_{Bl}}{D_{Al}} \frac{C_B}{b}}{H_A k_{Ag} + 1/k_{Al}}
\]

Thus

\[
-r_A = -\frac{1}{S} \frac{dN_A}{dt} = \frac{D_{Bl} C_B + \frac{P_A}{H_A}}{D_{Al} b + \frac{1}{H_A k_{Ag} + 1/k_{Al}}} \quad \text{....(2.27)}
\]

......for \( k_{Ag} p_A > \frac{k_{Bl} C_B}{b} \)

.....Reaction takes place within the liquid film ........liquid film controls.

14. Derive the rate expression for slow reaction with respect to mass transfer?

Here all reaction occurs in the main body of the liquid with the liquid film still offering a resistance to transfer of \( A \) into the main body of liquid. So the gas film, the liquid film and the main body of he liquid act as resistance in series and all the resistances will enter into the overall rate expression.

For these three steps we can write:

(a) Gas film:

\[
-r_A = k_{Ag} a(p_A - p_{Ai})
\]

(b) Liquid film:

\[
-r_A = k_{Al} a(C_{Ai} - C_A)
\]

(c) Main body of liquid:

\[
r_A = -\frac{1}{V_t} \frac{dN_A}{dt} = kC_A C_B
\]

but

\[
(-r_A) V_t = (-r_{Ai}) V_t
\]

\[
(-r_A) = (-r_{Ai}) \frac{V_t}{V_t}
\]

\[
\therefore (-r_A) = kC_A C_B f_t, \quad f_t = V_t / V_t
\]

\[
\frac{-r_A}{k_{Ao} a} = p_A - p_{Ai} \quad \text{....step (a) ........ dividing by } H_A \text{ we get}
\]
\[
\frac{-r_A}{H k_{Ag} a} = \frac{P_A}{H_A} - \frac{P_{Al}}{H_A} = \frac{P_A}{H_A} - C_{Ai}, \quad \text{as} \quad P_{Al} = H_A C_{Ai}
\]

\[
\frac{-r_A}{k_{Ai} a} = C_{Ai} - C_A \quad \ldots \ldots \text{step (b)}
\]

\[
\frac{-r_A}{k C_{B_i}} = C_A \quad \ldots \ldots \text{step (c)}
\]

Adding Equations gives

\[
(-r_A) \left[ \frac{1}{H_A k_{Ag} a} + \frac{1}{k_{Ai} a} + \frac{1}{k C_{B_i}} \right] = \frac{P_A}{H_A} - C_{Al} + C_{Ai} - C_{Al} = \frac{P_A}{H_A}
\]

\[
(-r_A) = \frac{1}{H_A k_{Ag} a} + \frac{1}{k_{Ai} a} + \frac{1}{k C_{B_i}} \cdot \frac{P_A}{H_A}
\]

\[
(-r_A) = \frac{1}{H_A k_{Ag} a} + \frac{1}{k_{Ai} a} + \frac{1}{k C_{B_i}} \cdot \frac{P_A}{H_A}
\]

Figure: Slow reaction (Case G) – showing liquid-film resistance.

15. Derive the equation for volume of tower required for mass transfer with reaction?

Mass Transfer + Reaction in a Countercurrent Tower – Plug flow G + Plug flow L:
The material balance for a differential element of tower (absorber – reactor) volume \( dV \) is

\[
\text{\textquote{A} lost by gas} = \frac{1}{b} \left( \text{\textquote{B} lost by liquid} \right)
\]

\[
F_g \, dY_A = -\frac{F_l}{b} (X_{B_1} - X_{B_2})
\]

Composition at any point in the tower from point 1 is given by

\[
F_g (Y_A - Y_{A1}) = \frac{F_l}{b} (X_{B_1} - X_B)
\]

For dilute systems (for the case where all participants in the reaction are dilute) \( p_U \approx \pi \) and \( C_U \approx C_T \),

\[
dY_A = d(\frac{p_A}{p_U}) \frac{d\pi}{\pi} \frac{dp_A}{p_a}
\]

and \( C_U \approx C_T \). \therefore \quad dX_A = dC_A/C_T

\therefore \quad \text{Equation for dilute systems simplifies to}

\[
\frac{F_g}{\pi} dp_A = -\frac{F_l}{bC_T} dC_A
\]

Integrating for the whole tower gives

\[
\frac{F_g}{\pi} (p_{A2} - p_{A1}) = -\frac{F_l}{bC_T} (C_{B1} - C_{B2})
\]

Integrating equation from point 1 to any point in the tower gives

\[
\frac{F_g}{\pi} (p_A - p_{A1}) = -\frac{F_l}{bC_T} (C_{B1} - C_B)
\]
The volume of tower or the height of tower is found by combining the material balance and the rate equation for a differential element of tower volume \( dV_r \).

\[
\begin{align*}
\left( \text{A reacted in element -} \right) & = \left( \text{A reacted in element -} \right) \\
\left( \text{from material balance} \right) & = \left( \text{from rate expression} \right) \\
\left( \text{`A’ lost by gas} \right) & = \left( \frac{1}{b} \text{B lost by liquid} \right) = \left( \text{disappearance of A} \right) \\
\left( \text{by reaction} \right)
\end{align*}
\]

\[
F_g dY_A = -\left( \frac{F_0 dX_B}{b} \right) = (-r_A^\text{a}) dV_r
\]

But,

\[-r_A^\text{a} = (-r_A^\text{a}) a\]

\((-r_A^\text{a})\) is the rate based on unit interfacial area.

With \((-r_A^\text{a}) = (-r_A^\text{a}) a\), Equation becomes

\[
F_g dY_A = -\left( \frac{F_0 dX_B}{b} \right) = (-r_A^\text{a}) a \, dV_r
\]

This on integration gives,

\[
V_r = hA_{cs} = F_g \int_{\gamma_{A_2}}^{\gamma_{A_1}} \frac{dY_A}{(-r_A^\text{a}) a} = F_1 \int_{X_{A_2}}^{X_{A_1}} \frac{dX_B}{(-r_A^\text{a}) a}
\]

For dilute systems,

\[
\frac{F_g}{\pi} dp_A = \frac{F_1}{bC_T} dC_B = (-r_A^\text{a}) dV_r = (-r_A^\text{a}) a \, dV_r
\]

Integrating equation, we get

\[
V_r = hA_{cs} = \frac{F_g}{\pi} \int_{p_{A_1}}^{p_{A_2}} \frac{dp_A}{(-r_A^\text{a}) a} = \frac{F_1}{bC_T} \int_{C_{B_2}}^{C_{B_1}} \frac{dC_B}{(-r_A^\text{a}) a}
\]

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