University of Basrah College of Engineering Chemical Engineering Department Fourth Year Second Semester

Catalytic Reactor Design

Part One:

Heterogeneous processes; Catalysis and adsorption; Classification and preparation of catalysts; Promoters and inhibitors, Rate equations of fluidsolid catalytic reactions; Hougen-Watson and power law models; Procurement and analysis of kinetic data;

Part Two:

Reaction and diffusion in porous catalysts; Isothermal and non-isothermal effectiveness factors; Effect of intra-phase transport, effect of external mass transfer,; Global reaction rate.

Part Three:

Design of catalytic reactors: Isothermal and adiabatic fixed bed reactors.

Part Four:

Kinetics of catalyst Poisoning, Kinetics of catalyst deactivation and regeneration.

Part One:

- Heterogeneous processes; Catalysis and adsorption.
- Classification and preparation of catalysts; Promoters and inhibitors.
- Rate equations of fluid-solid catalytic reactions.
- The Langmuir-Hinshelwood-Hougen-Watson (LHHW) and power law models.
- Analyzing Data from Laboratory Reactors, analysis of kinetic data.

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1- Catalysts and Catalysis:

A **Catalyst** is a substance that affects the rate of chemical reaction but emerges from the process unchanged. Normally when we talk about a catalyst, we mean one that speed up a reaction, although strictly speaking, a catalyst can either accelerate or slow the formation of a particular product species. *A catalyst changes only the rate of a reaction; it does not affect the equilibrium*. A number of catalysts both homogeneous and heterogeneous are employed in the industry. Sulfuric acid, hydrofluoric acid, vanadium pentaoxide, platinum over alumina, and zeolites with and without loading of metals or oxides are common examples

Catalysis is the occurrence, study, and use of catalysts and catalytic processes. Reactions are not catalyzed over the entire surface but only at certain **active sites** or centers that result from unsaturated atoms in the surface.

Figure 1 shows some of commercial catalyst .



Figure 1: some of commercial catalyst .

An *Active Site* is a point on the surface that can form strong chemical bonds with an adsorbed atom or molecule.

To make a catalytic process commercially viable, the number of sites per unit reactor volume should be such that the rate of product formation is on the order of 1 mol/L·hour .

A solid catalyst consists of mainly three components :

- 1. Catalytic agent
- 2. Support /carrier

3. Promoters and Inhibitors

1.1- 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.

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,MgO 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.

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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

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.

1.2-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.

1.3-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

Negative promoters or inhibitors:

Inhibitors act opposite to promoters. When added in small amounts, these can reduce catalyst activity, selectivity or stability. Inhibitor is particularly useful for reducing the activity of a catalyst for undesirable side reactions. In oxidation of ethylene, ethylene dichloride is added to inhibit CO_2 formation thus acting as an inhibitor.

• In the case of metal catalysts, the metal is generally dispersed onto a high area oxide such as alumina.

- Metal oxides also can be dispersed on a second carrier oxide such as vanadium supported on titanium, or it can be made into a high-area oxide.
- These carrier oxides can have surface areas ranging from $0.05m^2/g$ to greater than $100 m^2/g$.

• The carrier oxides generally are pressed into shapes or extruded into pellets.

• The following shapes are frequently used in applications: Table 1 lists some of the important commercial catalysts and their uses.

- -20-100 μ m diameter spheres for fluidized-bed reactors
- -0.3-0.7 cm diameter spheres for fixed-bed reactors
- -0.3-1.3 cm diameter cylinders with a length-to-diameter ratio of 3–4
- Up to 2.5 cm diameter hollow cylinders or rings.

Table1: Industrial reactions over heterogeneous catalysts.

Largest processes

Reaction	Catalyst
Catalytic cracking of crude oil	zeolites
Hydrotreating of crude oil	Co-Mo, Ni-Mo, Ni-W sulfides
Reforming of naphtha to gasoline	Supported Pt, Pt-Re, Pt-Ir
Alkylation	H ₂ SO ₄ , HF, solid acids
Polymerization of ethylene, propylene, a.o.	Supported Cr, TiCl _x /MgCl ₂
Etylene epoxidation to ethylene oxide	Suppoted Ag
Vinyl chloride (ethylene + Cl ₂)	Cu as chloride
Steam reforming of methane to CO + H ₂	Supported Ni
Water-gas shift reaction	Fe oxide, Cu-ZnO
Methanation	Supported Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO ₃	Pt-Rh gauzes
Acrylonitrile form propylene and ammonia	Bi-Mo, Fe-Sb, MoVSbNb oxides
Hydrogenation of vegetable oils	Supported Ni
Sulfuric acid	Supported V oxide
Oxidation of CO and hydrocarbons	Supported Pt, Pd
Reduction of NO _x	Rh, supported V oxide

A catalytic reaction involves physical-chemical phenomena of adsorption and desorption besides chemical reaction. As shown in Figure 2, the energy barrier or activation energy of a catalytic reaction is lower than the activation energy of a non-catalytic reaction due to the adsorption and desorption phenomena.

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The adsorption in a catalytic reaction is an exothermic phenomenon. However, either the adsorption of molecules at the surface or desorption from the surface occurs under different strengths, decreasing the degree of freedom that facilitates the reaction.

The energy of activation of a catalytic reaction is, therefore, lower than the energy barrier. Thus, it is necessary to determine the adsorption and desorption rates in a catalytic process. Thermodynamically, we do explain the adsorption phenomenon of a fluid at the surface from the Gibbs free energy. It should be spontaneous and, thus, $\Delta G_{ads} < 0$.

Energy



Reaction path

Fig.2: Comparison of a catalytic and a noncatalytic reaction potential energy changes during the reaction path.

1.2- Catalytical Reaction Steps:

As shown in figure 3, Molecules enter the reactor with uniform concentrations C_{Ao} and leave with mixing- concentrations C_{Aout} . In between, they undergo the following steps:

1. Mass transfer across a film resistance from the bulk gas phase to the external surface of the porous catalyst.

- 2. Transport of the reactants into the catalyst particle by diffusion through the pores.
- 3. Adsorption of reactant molecules onto the internal surface of the catalyst.
- 4. Reaction between adsorbed components on the catalytic surface.
- 5. Desorption of product molecules from the surface to the pores.
- 6. Diffusion of product molecules out of the pores to the external surface of the pellet.
- 7. Mass transfer of the products across a film resistance into the bulk gas phase.



Fig.4 Different size scales in a packed bed catalytic reactor.



Fig.5: Mass transfer and reaction steps for a catalyst pellet.

In a heterogeneous reaction sequence, mass transfer of reactants first takes place from the bulk fluid to the external surface of the pellet. The reactants then diffuse from the external surface into and through the pores within the pellet, with reaction taking place only on the catalytic surface of the pores. A schematic representation of this process is shown in Figures 4 and 5.

1.3-Catalytic Reactions Mechanism and Rate Equations:

For irreversible gas phase reaction, $A(g) \rightleftharpoons B(g)$ global rate for catalyst particles is expressed in terms of temperature and concentration of A in bulk gas stream which can be measured or specified directly. Global rates of catalytic reactions are usually expressed per unit mass of catalyst.

1.3.1-Langmuir-Hinshelwood –Hougen-Watson(LHHW) model :

The Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach accounts for the surface concentrations of the species taking part in the reaction.

Relating surface species to the observed species partial pressures in the gas phase provides equations that can be fitted to the kinetic data.

Based on the Langmuir adsorption isotherm, the approach was first developed by Hinshelwood and therefore sometimes termed as Langmuir-Hinshelwood kinetics. Hougen and Watson [1943] developed a similar approach and popularize the Langmuir-Hinshelwood kinetics.

• The LHHW approach assumes that all active sites are energetically uniform and, upon adsorption, adsorbed species do not interact with species already adsorbed.

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- Active sites have similar kinetic and thermodynamic characteristics and the entropy and enthalpy of adsorption are constant and not functions of the adsorbed amount.
- The species adsorption restricts itself to only monolayer coverage and the rate of adsorption is proportional to the concentration of the active sites not occupied (empty) and the partial pressure of the component in the gas phase.
- Rate derived by this method takes into account the adsorption-desorption process occurring over the surface along with the surface reaction.
- Rate equation derived can be extrapolated more accurately to concentrations lying beyond the experimentally measured values.

The rate equation derived from mechanistic model that simulates the actual surface phenomenon during the process is preferred for reactions involving solid catalysts. The Langmuir-Hinshelwood–Hougen-Watson(LHHW) approach is one of the most commonly used way of deriving rate expressions for fluid solid catalytic reactions. The advantages of this method are that :

During this method of derivation of rate expression, all the physical transport steps like mass transfer from bulk phase to catalyst surface or diffusion of reactants from pore mouth to interior pore (intraparticle diffusion) are excluded. Thus, it is assumed that the external and internal mass transport processes are very rapid relative to the chemical rate process occurring on or within the catalyst particle.

The chemical rate depends on as shown in figure 6:

- (1) chemisorption steps
- (2) surface reaction steps
- (3) desorption steps

This simple kinetic model assumes isothermal condition about and within catalyst that is temperature gradient is zero.



Fig. 6: The Langmuir-Hinshelwood-Hougen-Watson (LHHW)

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In LHHW model development, the rate equation is first derived in terms of surface concentration of adsorbed species and vacant sites. Then, these surface concentrations are related to the fluid or bulk concentration that is directly measurable.



Langmuir





Hougen

<u>1.3.1.1-Adsorption Step:</u> Types of adsorption:

- 1-Physical adsorption (Physisorption)
- 2-Chemical adsorption (Chemisorption)

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Comparison of physical and chemical adsorptions

Physical adsorption	Chemical adsorption
Binding forces are weak where	Binding forces are strong where
binding occurs through van der	binding occurs through chemical
Waals' forces.	bonding and electron transfer
	takes place.
Reversible with the adsorbed	Mostly irreversible with the
species unchanged when	adsorbed species may be
desorbed.	different when desorbed.
Occurs through multilayer	Occurs through monolayer
coverage.	coverage (only active sites are
	covered).
Applied in the determination of	Applied in the determination of
surface area, pore volume, and	catalytic surface area.
pore size of materials.	
Low heat of adsorption is	Heat of adsorption is many times
involved such as that of	greater and comparable to that of
liquefaction.	heat of reaction.
Usually occurs at low	Usually requires high
temperatures.	temperatures.
Rate of adsorption is fast.	Rate of adsorption may be fast.
	Any value between low and fast.
Non-specific to the surface	Specific to the surface
(adsorbent).	(adsorbent).
Low activation energies are	Usually high activation energies
involved.	are involved.

Because chemisorption is usually a necessary part of a catalytic process, we shall discuss it before treating catalytic reaction rates. The Jetter S will represent an active site; alone, it will denote a vacant site, with no atom, molecule, or complex adsorbed on it. The combination of S with another letter (e.g., A· S) will mean that one unit of species A will be adsorbed on the site S. Species A can be an atom, molecule, or some other atomic combination, depending on the circumstances. Consequently, the adsorption of A on a site S is represented by $A(g) + S \rightleftharpoons A \cdot S$

The total molar concentration of active sites per unit mass of catalyst is equal to the number of active sites per unit mass divided by Avogadro's number and will be labeled C_t (mol/gcat). The molar concentration of vacant sites, C_V , is the number of vacant sites per unit mass of catalyst divided by Avogadro's number. In the absence of catalyst deactivation, we assume that the total concentration of active sites remains constant. Some further definitions include, as shown in figure 7.

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 P_i = partial pressure of species i in the gas phase, (atm or kPa)

 $C_{is} =$ surface concentration of sites occupied by species i, (mol\g cat)

- Ct: Total number of active sites per unit mass of catalyst divided by Avogadro's # (mol/g cat)
- C_v: Number of vacant sites per unit mass of catalyst divided by Avogadro's #



 C_{ν} is not measurable, but the total number of sites C_t can be measured

In the absence of catalyst deactivation, assume the total number of active sites remains constant:

Site balance:

$$\mathbf{C}_{t} = \mathbf{C}_{\nu} + \mathbf{C}_{\mathsf{A} \cdot \mathsf{S}} + \mathbf{C}_{\mathsf{B} \cdot \mathsf{S}}$$

We will use the site balance equation to put C_{ν} in terms of measurable species

Fig.7: schematic representation of adsorption phenomena.

Rate of adsorption = rate of attachment – rate of detachment

rate of attachment of a molecules to the surface is directly proportional to the product of the partial pressure of *A* and the concentration of a vacant sites.

The rate of detachment of molecules from the surface can be a first-order process; that is, the detachment from the surface is usually directly proportional to the concentradon of sites occupied by the adsorbed molecules

 $r_{AD} = k_A P_A C_V - k'_A C_{AS}$ (1) In terms of the adsorption equilibrium constant K_A where



<u>1.3.1.2-Surface Reaction Step:</u>

After the molecule is adsorbed onto the surface, it can react by a few different mechanisms:

1. **Singe site mechanism**: Only the site to which the reactant is absorbed is involved in the reaction

 $\begin{array}{ccc} A & B \\ I & \rightleftharpoons & I \\ -S- & -S- \end{array} & A \cdot S \rightleftharpoons B \cdot S & r_{S} = k_{S} \left[C_{A \cdot S} - \frac{C_{B \cdot S}}{K_{S}} \right] & \dots (3)$

Where

$$K_S = \frac{k_S}{k'_S}$$

2. Dual site mechanism: Adsorbed reactant interacts with another vacant site to form the product

$$A \cdot S + S \rightleftharpoons S + B \cdot S$$

$$A \cdot S \leftrightarrow S \leftrightarrow B$$

$$A \cdot S \leftrightarrow S$$

$$A \cdot S \leftarrow S$$

$$A \cdot S$$

$$A \cdot S \leftarrow S$$

$$A \cdot$$

3. Eley-Rideal mechanism: reaction between adsorbed reactant and a molecule in the gas phase

 $A \cdot S + B(g) \rightleftharpoons C \cdot S$

1.3.1.3-Desorption Step:

Products are desorbed into the bulk gas phase

Desorption:
$$B \cdot S \rightleftharpoons B + S$$
 $r_D = k_D C_{B \cdot S}$

$$-\frac{\mathsf{P}_{\mathsf{B}}\mathsf{C}_{\mathsf{V}}}{\mathsf{K}_{\mathsf{D}}} = \dots \dots (6)$$

Where :

$$K_D = \frac{k_D}{k'_D}$$

1.4-Derive a Rate Law for Catalytic Rractions:

• Postulate catalytic mechanism, and then derive the rate law for that mechanism

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- Assume pseudo-steady state hypothesis (rate of adsorption = rate of surface reaction = rate of desorption)
- No accumulation of species on the surface or near interface
- Each species adsorbed on the surface is a reactive intermediate
- Net rate of formation of species i adsorbed on the surface is 0, $r_{i \cdot S}=0$
- One step is usually rate-limiting
- If the rate-limiting step could be sped up, the entire rxn would be faster
- Although reactions involve all 7 steps, only adsorption, surface reaction, or desorption will be rate limiting
- The surface reaction step is rate limiting ~70% of the time!

Steps to derive the rate law

- \checkmark Select among types of adsorption, surface reaction, and desorption
- ✓ Write rate laws for each individual step, assuming all are reversible
- ✓ Postulate which step is rate limiting
- ✓ Use non-rate-limiting steps to eliminate the surface concentration terms that cannot be measured

The reaction equation have the general form:

$-r_A = \frac{(Kinetic Term) * (Potential Term)}{(Adsorption Term)^n}$

We need to select one of these 3 reactions as the rate limiting step, then derive the corresponding rate equation, and see if this rate equation matches experimental data. Which step is the most logical to start with?

- a) Adsorption
- b) Surface reaction
- c) Desorption
- d) None of the above
- e) Any of these would be "logical" they all have equal probability of being the rate limiting step

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1. Adsorption:	A(g) + S ≓ /	A∙S	$r_{AD} = k_A \left(F_{AD}\right)$	$P_A C_V - \frac{C_{A.S}}{K_A}$)
2. Surface reaction:	A·S + S ≓ S	S + B∙S	$r_{S} = k_{S} \begin{bmatrix} C \end{bmatrix}$	$A \cdot S C_v - \frac{C_{B \cdot S}}{K_S}$	$\left[\frac{C_v}{s}\right]$
3. Desorption:	B·S ≓ B + \$	6	$\mathbf{r}_{\mathrm{D}} = \mathbf{k}_{\mathrm{D}} \mathbf{c}$	$\frac{P_{B}C_{V}}{K_{D}}$	
Adsorption on Surfac	ce	A + c	$S \Leftrightarrow A \bullet S$	S	
Surface Reaction					
Si	ingle Site	A∙S	$\Leftrightarrow B \bullet S$		
D	ual Site	A∙S	$+S \Leftrightarrow B$	\bullet S+S	
Desorption from Sur	face	B∙S	\Leftrightarrow B + S		

Derive the rate equation for when the surface reaction is rate limiting

(true ~70% of the time) For Dual site mechanism:

$$-r'_{A} = r_{S} = k_{S} \left[\frac{C_{A.S}C_{V} - \frac{C_{B.S}C_{V}}{K_{S}}}{K_{S}} \right]$$

Or Singe site mechanism:

$$r_{\rm S} = k_{\rm S} \left[C_{\rm A.S} - \frac{C_{\rm B.S}}{K_{\rm S}} \right]$$

 $C_{A \cdot S}$, C_{ν} , and $C_{B \cdot S}$ need to be expressed in terms of measurable quantities.

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- For surface reaction-limited mechanisms, k_{S} is small and k_{A} and k_{D} are relatively large
- Therefore r_{AD}/k_A and r_D/k_D are very small, and can be approximated as equal to zero .

Use this relationship to eliminate $C_{A \cdot S}$ and $C_{B \cdot S}$ from their respective rate equations and the site balance to eliminate C_V

$$\mathbf{r}_{\mathsf{AD}} = \mathbf{k}_{\mathsf{A}} \left[\mathbf{P}_{\mathsf{A}} \mathbf{C}_{\mathsf{V}} - \frac{\mathbf{C}_{\mathsf{A} \cdot \mathsf{S}}}{\mathsf{K}_{\mathsf{D}}} \right] \qquad \rightarrow \frac{\mathbf{r}_{\mathsf{AD}}}{\mathsf{k}_{\mathsf{A}}} = \mathbf{0} = \mathbf{P}_{\mathsf{A}} \mathbf{C}_{\mathsf{V}} - \frac{\mathbf{C}_{\mathsf{A} \cdot \mathsf{S}}}{\mathsf{K}_{\mathsf{A}}}$$

$$\rightarrow \frac{C_{A.S}}{K_A} = P_A C_V$$

 $\rightarrow C_{A\cdot S} = K_A P_A C_v$

Use $r_D/k_D = 0$ & r_D equation to solve for $C_{B \cdot S}$

$$\begin{split} r_{D} &= k_{D} \left[C_{B \cdot S} - \frac{P_{B}C_{V}}{K_{D}} \right] \qquad \rightarrow \frac{r_{D}}{k_{D}} = 0 = C_{B \cdot S} - \frac{P_{B}C_{V}}{K_{D}} \\ &\rightarrow \frac{P_{B}C_{V}}{K_{D}} = C_{B \cdot S} \end{split}$$

Use site balance to solve for C_V :

$$C_{t} = C_{v} + C_{A.S} + C_{B.S}$$

Make substitutions for $C_{A \cdot S}$ & $C_{B \cdot S}$, solve for C_{ν}

$$\rightarrow C_{v} = C_{t} - K_{A}P_{A}C_{v} - \frac{P_{B}C_{v}}{K_{D}}$$

$$\rightarrow C_{v} + K_{A}P_{A}C_{v} + \frac{P_{B}C_{v}}{K_{D}} = C_{t}$$

$$\rightarrow C_{v} \left(1 + K_{A}P_{A} + \frac{P_{B}}{K_{D}}\right) = C_{t}$$

$$C_{v} = \frac{C_{t}}{1 + K_{D}} + \frac{P_{D}}{K_{D}} = C_{t}$$

 $1 + K_A P_A + P_B / K_D$ Substitute $C_{A \cdot S}$, $C_{B \cdot S}$, & C_v in one of the following equations:

$$\begin{split} r_{S} &= k_{S} \left[C_{A:S} - \frac{C_{B:S}}{K_{S}} \right] \\ &- r'_{A} = r_{S} = k_{S} \left[C_{A:S} C_{V} - \frac{C_{B:S} C_{V}}{K_{S}} \right] \\ &\rightarrow - r'_{A} = r_{S} = k_{S} \left[K_{A} P_{A} \left(\frac{C_{t}}{1 + K_{A} P_{A} + P_{B}/K_{D}} \right)^{2} - \frac{P_{B}}{K_{S} K_{D}} \left(\frac{C_{t}}{1 + K_{A} P_{A} + P_{B}/K_{D}} \right)^{2} \right] \end{split}$$

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This is the rate equation in terms of measurable species and rate constants for the surface reaction control .

Now derive the rate equation for when adsorption is rate limiting

$$-\mathbf{r'}_{A} = \mathbf{r}_{AD} = \mathbf{k}_{A} \left(\mathbf{P}_{A} \mathbf{C}_{v} - \frac{\mathbf{C}_{A \cdot S}}{\mathbf{K}_{A}} \right)$$

Concentration of vacant and occupied sites must be eliminated from the rate equation If adsorption is rate limiting, $k_s >> k_{AD}$, so r_s/k_s can be approximated as 0. Then

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$$r_{S} = k_{S} \left[C_{A.S}C_{V} - \frac{C_{B.S}C_{V}}{K_{S}} \right]$$

$$\rightarrow \frac{r_{S}}{k_{S}} = 0 = C_{A.S}C_{V} - \frac{C_{B.S}C_{V}}{K_{S}}$$

$$\rightarrow \frac{C_{B.S}C_{V}}{K_{S}} = C_{A.S}C_{V}$$

$$\rightarrow \frac{C_{B.S}}{K_{S}} = C_{A.S} \qquad (8)$$

Need to put $C_{B \cdot S}$ in measureable terms

If adsorption is rate limiting, $k_D >> k_{AD}$, so in the desorption equation , r_D/k_D can be approximated as 0. Then:

$$r_{D} = k_{D} \left[C_{B \cdot S} - \frac{P_{B}C_{v}}{K_{D}} \right] \longrightarrow \frac{r_{D}}{k_{D}} = 0 = C_{B \cdot S} - \frac{P_{B}C_{v}}{K_{D}}$$
$$\rightarrow \frac{P_{B}C_{v}}{K_{D}} = C_{B \cdot S} \qquad (9)$$

Subsitute equations(7 and 8)in equation (9) and solve for C_{ν} using the site balance equation

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$C_t = C_v + C_{A \cdot S} + C_B$	s	(10)
$\rightarrow C_{t} = C_{v} + \frac{C_{B \cdot S}}{K_{S}} + \frac{C_{B \cdot S}}{K_{S}}$	R _B C _v K _D	
$\rightarrow C_{t} = C_{v} + \frac{P_{B}C_{v}}{K_{S}K_{D}} +$	- P _B C _v K _D	
$\rightarrow C_{t} = C_{v} \left(1 + \frac{P_{B}}{K_{S}K_{C}} \right)$	$-+\frac{P_B}{K_D}$	
$\rightarrow \frac{C_{t}}{1 + \frac{P_{B}}{K_{S}K_{D}} + \frac{P_{B}}{K_{D}}} = 0$	CVIS	
Substitute C_v into the expression	n for C _{B·S:}	
$C_{B.S} = \frac{P_B C_t}{K_D \left(1 + \frac{P_B}{K_S K_D}\right)}$	$+\frac{P_B}{K_D}$	(11)
Substitute C_{B-S} into C_{A-S} :		
$C_{A \cdot S} = \frac{P_B C}{K_S K_D \left(1 + \frac{F_B C}{K_B C}\right)}$	$\frac{P_B}{K_P} + \frac{P_B}{K_P}$	
Use these eas (11 and 12) to repl	ace $C_{AS} & C_{\mu}$ in r_{AD}	
$\rightarrow r_{AD} = k_A \left[\frac{P_A}{1 + \frac{P_B}{K_S K}} \right]$	$\frac{C_{t}}{C_{D}} + \frac{P_{B}}{K_{D}} - \frac{K_{A}K_{S}K_{I}}{K_{D}}$	$\frac{P_BC_t}{D\left(1 + \frac{P_B}{K_SK_D} + \frac{P_B}{K_D}\right)}\right)$
$\rightarrow r_{AD} = k_A C_t \left(\frac{P_A}{1 + \frac{P_B}{K_S K_D}} \right)$	$\frac{P_{B}}{K_{D}} - \frac{P_{B}}{K_{A}K_{S}K_{D}\left(1 + \frac{1}{K_{S}}\right)}$	$\frac{\overline{P_{B}}}{S_{N}K_{D}} + \frac{P_{B}}{K_{D}} \right) \qquad \dots $

This is the rate equation in terms of measurable species and rate constants for the adsorption control .

For the reaction $A+B \rightleftharpoons C+D$ Let the reaction follows the mechanism given below ;Adsorption on SurfaceA + S

$$A + S \Leftrightarrow A \bullet S$$
$$B + S \Leftrightarrow B \bullet S$$

Surface Reaction Dual Site

$$A \bullet S + B \bullet S \Leftrightarrow C \bullet S + D \bullet S$$

Surface Reaction

Eley-Rideal

$$A \bullet S + B(g) \Leftrightarrow C \bullet S + D(g)$$

 $C \bullet S \Leftrightarrow C + S$

 $D \bullet S \Leftrightarrow D + S$

Desorption form Surface

Among the various steps described, the slowest step controls the overall rate of reaction and the other remaining steps are assumed to be at near equilibrium conditions. This approach greatly simplifies the overall rate expression, reducing the number of rate constants and equilibrium constants to be determined from experimental data. Further each step in this method is assumed to be elementary and the number of sites is conserved in each step.

(1) A + S ⇒ A.S ---- Adsorption of reactant A on surface vacant site S
(2) B+S ⇒ B.S ---- Adsorption reactant B on surface vacant site S
(3) A.S+B.S ⇒ C.S+D.S ---- Surface reaction between adsorbed A and B
(4) C.S ⇒ C+S ---- Desorption of product C from surface creating a vacant site site ---- Desorption of product D from surface creating a vacant site

Therefore, the controlling step can be either of the following:

- (1) Surface reaction
- (2) Adsorption
- (3) Desorption

Now total concentration of active sites on surface, C_t , will be the summation concentrations of all sites on which either ractants or products are adsorbed and the concentration of vacant sites.

 $C_t = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$

Case 1 : Rate is surface reaction controlling

The surface reaction is the slowest step and is the rate controlling. According to the mechanism, surface reaction occurs between adsorbed A and adsorbed B producing adsorbed C & adsorbed D.

The rate of surface reaction is given as

 $r_s = k_s C_{AS} C_{BS} - k_s C_{CS} C_{DS} k_s =$ rate constant for forward surface reaction

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 $\mathbf{k}_{s}^{'}$ = rate constant for reverse surface reaction

$$= k_{s} \left[C_{AS} C_{BS} - \frac{k_{s}}{k_{s}} C_{CS} C_{DS} \right]$$
$$= k_{s} \left[C_{AS} C_{BS} - \frac{1}{K_{s}} C_{CS} C_{DS} \right] \qquad \because K_{s} = \frac{k_{s}}{k_{s}'} \qquad (14)$$

Now, since all the other steps are considered to be in equilibrium, therefore concentration of adsorbed species can be obtained as follows. For adsorption steps and desorption steps :

From step (1)
$$K_A = \frac{C_{AS}}{C_A C_V}$$
 From step (4) $K_C = \frac{C_{CS}}{C_C C_V}$

From step (2)
$$K_B = \frac{C_{BS}}{C_B C_V}$$
 From step (5) $K_D = \frac{C_{DS}}{C_D C_V}$

 K_A, K_B, K_C, K_D are adsorption equilibrium constants.

Then, the adsorbed phase concentrations can be written as $C_{AS} = K_A C_A C_V$

$$C_{BS} = K_B C_B C_V \qquad C_{CS} = K_C C_C C_V \qquad C_{DS} = K_D C_D C_V$$

Substituting all these value in equation (14)

$$\boldsymbol{r}_{s} = \boldsymbol{k}_{s} \left[\boldsymbol{C}_{AS} \boldsymbol{C}_{BS} - \frac{1}{K_{s}} \boldsymbol{C}_{CS} \boldsymbol{C}_{DS} \right] = \boldsymbol{k}_{s} \left[\boldsymbol{K}_{A} \boldsymbol{C}_{A} \boldsymbol{C}_{V} \cdot \boldsymbol{K}_{B} \boldsymbol{C}_{B} \boldsymbol{C}_{V} - \frac{K_{C}}{K_{s}} \boldsymbol{C}_{C} \boldsymbol{C}_{V} \cdot \boldsymbol{K}_{D} \boldsymbol{C}_{D} \boldsymbol{C}_{V} \right]$$

or,
$$r_s = k_s \left[K_A K_B C_A C_B C_V^2 - \frac{K_C K_D}{K_s} C_C C_D C_V^2 \right]$$

or
$$r_s = k_s K_A K_B \left[C_A C_B - \frac{K_C K_D}{K_s K_A K_B} C_C C_D \right] C_V^2$$
(15)
Now.

Now,

For the reaction $A+B \rightleftharpoons C+D$, at equilibrium, the overall equilibrium constant is

$$K = \frac{C_C C_D}{C_A C_B}.$$

All concentrations correspond to the equilibrium conditions in gas phase.

$$K = \frac{\left(C_{CS} / K_{C}C_{V}\right)\left(C_{DS} / K_{D}C_{V}\right)}{\left(C_{AS} / K_{A}C_{V}\right)\left(C_{BS} / K_{B}C_{V}\right)} = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}} \cdot \frac{K_{A}K_{B}C_{V}^{2}}{K_{C}K_{D}C_{V}^{2}}$$

Or, $K = \frac{K_{A}K_{B}}{K_{C}K_{D}} \cdot K_{S}$ $\therefore K_{S} = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}}$ (17)

Substituting (16) &(17) in equation (15),

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$$r_{S} = k_{S} K_{A} K_{B} \left[C_{A} C_{B} - \frac{1}{K} C_{C} C_{D} \right] \frac{C_{O}^{2}}{\left(1 + K_{A} C_{A} + K_{B} C_{B} + K_{C} C_{C} + K_{D} C_{D} \right)^{2}}$$

$$r_{s} = k_{s} K_{A} K_{B} C_{o}^{2} \frac{C_{A} C_{B} - \frac{1}{K} C_{c} C_{D}}{\left(1 + K_{A} C_{A} + K_{B} C_{B} + K_{c} C_{c} + K_{D} C_{D}\right)^{2}}$$
....(18)

The above rate expression can also be derived in terms of bulk partial pressure.

Case 2: Rate is adsorption control

(a) Adsorption of A controlling:

Let adsorption of A be the slowest step so that adsorption of B, surface reaction and desorption of C are at equilibrium.

Adsorption of A is given as

$$A + S \rightleftharpoons AS$$

Rate of adsorption $r_a = k_a C_A C_V - k_d C_{AS}$

$$r_a = k_a \left[C_A C_V - \frac{k_d}{k_a} C_{AS} \right]$$

Or,
$$r_a = k_a \left[C_A C_V - \frac{1}{K_A} C_{AS} \right]$$
 $K_A = \frac{k_a}{k_d}$ (adsorption equilibrium constant for A)
 $r_a = k_a C_V \left[C_A - \frac{1}{K_A} \frac{C_{AS}}{C_V} \right]$ (19)

Now as other steps are in equilibrium :

$$K_{S} = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}}$$

$$K_B = \frac{C_{BS}}{C_B C_V} K_C = \frac{C_{CS}}{C_C C_V} K_D = \frac{C_{DS}}{C_D C_V}$$

$$C_{BS} = K_B C_B C_V \qquad C_{CS} = K_C C_C C_V C_{DS} = K_D C_D C_V$$

. (21)

Then,

$$C_{AS} = \frac{C_{CS}C_{DS}}{K_SC_{BS}} = \frac{K_CC_CC_V.K_DC_DC_V}{K_SK_BC_BC_V} = \frac{K_CK_D}{K_SK_B}\frac{C_CC_DC_V}{C_B} \qquad (20)$$

Substituting equation (20) in equation (19) gives

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A C_V} \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{K_C K_D}{K_S K_A K_B} \frac{C_C C_D}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K} \frac{C_C C_D}{C_B} \right]$$

 $\mathbf{K} = \frac{\mathbf{K}_{S} \mathbf{K}_{A} \mathbf{K}_{B}}{\mathbf{K}_{C} \mathbf{K}_{D}} = \text{Overall equilibrium constant.}$

Now

$$C_t = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$$

$$C_t = C_V + \frac{K_C K_D}{K_S K_B} \cdot \frac{C_C C_D C_V}{C_B} + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V$$

$$C_t = C_V \left[1 + \frac{K_C K_D}{K_S K_B} \cdot \left(\frac{C_C C_D}{C_B} \right) + K_B C_B + K_C C_C + K_D C_D \right]$$

Substituting value of C_V from equation(22) in equation (21) gives

Similarly expression when desorption of product is the rate controlling step can be derived.

For desorption of C controlling the whole reaction, the rate expression can be derived as:

Guidelines for finding Mechanisms from experimental observation:

- More than 70% of heterogeneous reaction mechanisms are surface reaction limited
- If a species appears in the numerator of the rate law, it is probably a reactant
- If a species appears in the denominator of the rate law, it is probably adsorbed in the surface

Example 1:

We now propose a mechanism for the hydrodemethylation of toluene. We assume that toluene is adsorbed on the surface and then reacts with hydrogen in the gas phase to produce benzene adsorbed on the surface and methane in the gas phase. Benzene is then desorbed from the surface. Because approximately 75% of heterogeneous reaction mechanisms are surface-reaction limited rather than adsorption or desorption-limited, we begin by mechanisms are assuming the reaction between adsorkd toluene and gaseous hydrogen to be surface-reaction-rate-limited. Symbolically, this mechanism and associated rate laws for each elementary step are.

$$C_6H_5CH_3 + H_2 \longrightarrow C_6H_6 + CH_4$$

COC CHIGW Adsorption: $T(g) + S \longrightarrow T \cdot S$

$$r_{\rm AD} = k_{\rm A} \left(C_v P_{\rm T} - \frac{C_{\rm T} \cdot {\rm s}}{K_{\rm T}} \right)$$

Surface reaction: $H_2(g) + T \cdot S \longrightarrow B \cdot S + M(g)$

$$r_{\rm S} = k_{\rm S} \left(P_{\rm H_2} C_{\rm T \cdot S} - \frac{C_{\rm B \cdot S} P_{\rm M}}{K_{\rm S}} \right)$$

Desorption: $B \cdot S \longrightarrow B(g) + S$

$$r_{\rm D} = k_{\rm D} \left(C_{\rm B \cdot S} - K_{\rm B} P_{\rm B} C_v \right)$$

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For surface-reaction-limited mechanisms,

$$r_{\rm S} = k_{\rm S} \left(P_{\rm H_2} C_{\rm T \cdot S} - \frac{C_{\rm B \cdot S} P_{\rm M}}{K_{\rm S}} \right)$$

we see that we need to replace $C_{T\cdot S}$ and $C_{B,S}$ in the above equation by quantities that we can measure.For surface-reaction-limited mechanisms, we use the adsorption rate to obtain $C_{T\cdot S}$

$$\frac{r_{\rm AD}}{k_{\rm A}} \approx 0$$

Then

$$C_{T-S} = K_T P_T C_v$$

and we use the desorptinn rate Equation to obtainC _{BS}:

 $\frac{r_{\rm D}}{k_{\rm D}} \approx 0$

Then

$$C_{B\cdot S} = K_B P_B C_v$$

The total concentration of sites is

$$C_t = C_v + C_{\mathsf{T}\cdot\mathsf{S}} + C_{\mathsf{B}\cdot\mathsf{S}}$$

Substituting Equations for $C_{T,S}$ and $C_{B,S}$ into the site balance equation and rearranging, we obtain

FNG

$$C_v = \frac{C_t}{1 + K_{\rm T}P_{\rm T} + K_{\rm B}P_{\rm B}}$$

Next, substitute for C $_{BS}$ and C_{TS} and then substitute for C_V in surface reaction equation to obtain the rate law for the case of surface-reaction control:

$$-r_{\rm T}' = \frac{\widetilde{C_t k_{\rm S} K_{\rm T}} (P_{\rm H_2} P_{\rm T} - P_{\rm B} P_{\rm M} / K_{\rm P})}{1 + K_{\rm T} P_{\rm T} + K_{\rm B} P_{\rm B}}$$

1.5-Eley Rideal Model:

Apart from power law and Langmuir-Hinshelwood models, other kinetic models are also used to fit the data. Eley Rideal model depicts the reaction mechanism in which one reactant species (say A) is adsorbed while the second reactant species (say B) is not adsorbed on the catalyst surface. The reaction then occurs when the passing gas molecules of B in gas phase directly reacts with the adsorbed species A. The schematic representation is shown in Fig. 8.



Catalyst surface

Fig. 8: Eley Rideal mechanism for reaction of adsorbed A with gas phase B producing product AB

- (1) $A + S \rightleftharpoons AS$
- (2) $AS + B(g) \rightarrow P$

1- Assuming that step 2, the reaction between adsorbed A and gas phase B is irreversible and the rate determining step, then the rate of reaction can be written as(the reaction is not irrevesibile)

C DUGW

$$r = k C_{As} C_{B}$$

.....(25)

For Adsorption Step

 $A + S \leftrightarrow A \bullet S$

$$\mathbf{r}_{AD} = \mathbf{k}_{A} \left[\mathbf{P}_{A} \mathbf{C}_{V} - \mathbf{C}_{AS} / \mathbf{k}_{A} \right]$$

(a) equilibrium : $r_{AD} = 0$ C_A

 $C_{AS} = k_A P_A C_V$

$$\mathbf{r}_{AD} / \mathbf{k}_{A} \approx \mathbf{0} \qquad \mathbf{C}_{AS} = \mathbf{k}_{A} \mathbf{P}_{A} \mathbf{C}_{V}$$

 $\mathbf{C}_{\mathrm{T}} = \mathbf{C}_{\mathrm{V}} + \mathbf{C}_{\mathrm{A}\cdot\mathrm{S}} = \mathbf{C}_{\mathrm{V}} + \mathbf{k}_{\mathrm{A}}\mathbf{P}_{\mathrm{A}}\mathbf{C}_{\mathrm{V}}$



Substituting value of C_{AS} from equation(27) in equation (25)

2-If the products are chemisorbed then the reaction may become reversible as shown below(the reaction is reversibile)

$$AS + B(g) \xrightarrow{k} PS$$
$$PS \rightarrow P + S$$

Then the rate expression can be written as

 $\mathbf{r} = \mathbf{k} \ \mathbf{C}_{\mathsf{As}} \ \mathbf{C}_{\mathsf{B}} - \mathbf{k}_{\mathsf{b}} \mathbf{C}_{\mathsf{Ps}} \tag{29}$

The concentration of adsorbed product is $C_{PS} = K_P C_P C_V$

$$C_t = C_{AS} + C_{PS} + C_V = K_A C_A C_V + K_P C_P C_V + C_V = C_V (1 + K_A C_A + K_P C_P)$$
$$C_V = \frac{C_t}{1 + K_A C_A + K_P C_P}$$

$$C_{AS} = K_A C_A C_V = \frac{K_A C_A C_t}{1 + K_A C_A + K_P C_P}$$

$$C_{AS} = K_A C_A C_L = \frac{K_A C_A C_t}{K_P C_P C_t}$$

$$C_{PS} = K_P C_P C_V = \frac{1 + K_A C_A + K_P C_P}{1 + K_A C_A + K_P C_P}$$

Substituting C_{AS} and C_{PS} in rate expression gives:

1.6-Analyzing Data from Laboratory Reactors:

The objectives of analyzing data include :

• Determining catalyst activity, selectivity and stability .

• Determining the effect of important process variables such as temperature, pressure, reactant concentrations.

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• Finding a rate equation .

1.6.1- Integral Analysis of Rate Data:

In this method a series of run are made in a packed bed at a fixed initial concentrations C_{A0} and a fixed temperature while varying the catalyst mass W and/or initial molar flow rate F_{A0} to generate a range of W/F_{A0} values at different conversions X_A . A rate equation is then selected for testing using the design equation for packed bed reactor.

$$\frac{W}{F_{A_o}} = \int_0^{x_{Af}} \frac{dX_A}{-r_A}$$

First simpler rate equations such as zero order, first order, second order irreversible are tried. Mechanistic reaction models can also be tested. The W/F_{A0} and the right hand integral in the design equation are evaluated numerically and plotted to test for linearity (Fig.10). Linearity of the plot is used as criterion for judging if the selected rate equation is a useful model for the data i.e consistent with the data. If not then another rate equation may be tried.



Fig.10. Typical plot of W/F_{A0} vs integral value for linearity test in integral analysis of rate data.

1.6.2-Initial Rate Analysis:

Initial rate analysis for a reaction may be done to understand the mechanism of a reaction. Initial rate is defined as the rate at zero conversion. It is obtained by extrapolation of the rate vs conversion data to zero conversion. For higher accuracy, the conversion data are collected at very low conversion region. In this method, the dependence of initial rate data on partial pressure or total pressure of the reactant is studied.

Consider the reaction $A+B \rightleftharpoons C+D$

The rate expression derived from Langmuir Hinshelwood model when surface reaction is controlling is.

$$\mathbf{r}_{S} = \mathbf{k}_{S} \mathbf{K}_{A} \mathbf{K}_{B} \mathbf{C}_{O}^{2} \frac{\mathbf{C}_{A} \mathbf{C}_{B} - \frac{1}{K} \mathbf{C}_{C} \mathbf{C}_{D}}{\left(1 + \mathbf{K}_{A} \mathbf{C}_{A} + \mathbf{K}_{B} \mathbf{C}_{B} + \mathbf{K}_{C} \mathbf{C}_{C} + \mathbf{K}_{D} \mathbf{C}_{D}\right)^{2}}$$

Now at zero conversion all the product concentration will tend to zero, hence putting $C_C = 0 \& C_D = 0$, the rate expression simplifies to

$$r_{i} = k_{s}K_{A}K_{B}C_{O}^{2} \frac{C_{A}C_{B}}{(1 + K_{A}C_{A} + K_{B}C_{B})^{2}}$$

Where r_i is the initial rate. Now, if a equimolal initial concentration of C_A and C_B is used then $C_A{=}C_B$.

Then assuming ideal gas mixture, $C_A=P_A\setminus RT$: where P_A is the partial pressure of A. Similarly $C_B=P_B\setminus RT$: where P_B is the partial pressure of B.

Now since it is an equimolal mixture, then at initial condition $P_A = P_B = 0.5P_t$, where Pt is the total pressure.

Or $C_A = C_B = 0.5P_t \setminus RT$

Then substituting C_A and C_B in equation [3] becomes

$$\mathbf{r}_{i} = \mathbf{k}_{s} \mathbf{K}_{A} \mathbf{K}_{B} \mathbf{C}_{0}^{2} \frac{\left(\frac{\mathbf{p}_{t}}{2RT}\right)^{2}}{\left(1 + \mathbf{K}_{A} \frac{\mathbf{p}_{t}}{2RT} + \mathbf{K}_{B} \frac{\mathbf{p}_{t}}{2RT}\right)^{2}}$$

$$\mathbf{Or} \qquad \mathbf{r}_{i} = \frac{\mathbf{p}_{t}^{2} \left(\frac{\mathbf{k}_{S} \mathbf{K}_{A} \mathbf{K}_{B} \mathbf{C}_{0}^{2}}{4R^{2}T^{2}}\right)}{\left[1 + \left(\frac{\mathbf{K}_{A} + \mathbf{K}_{B}}{2RT}\right)\mathbf{p}_{t}\right]^{2}}$$

$$\mathbf{Or} \qquad \mathbf{r}_{i} = \frac{\mathbf{A}\mathbf{p}_{t}^{2}}{\left[1 + B\mathbf{p}_{t}\right]^{2}}$$

$$(31)$$

$$\mathbf{W} \text{here } \mathbf{A} = \frac{\mathbf{k}_{s} \mathbf{K}_{A} \mathbf{K}_{B} \mathbf{C}_{0}^{2}}{4R^{2}T^{2}} \text{ and } \mathbf{B} = \frac{\mathbf{K}_{A} + \mathbf{K}_{B}}{2RT}$$

On plotting initial rate \mathbf{r}_i as a function of total pressure \mathbf{p}_t , a typical curve as shown in Fig 11 is obtained. Hence if kinetic data for a reaction give similar plot then it can be deduced that the reaction is surface reaction controlled.

When adsorption of A is controlling the dependence of initial rate on total pressure can be derived in similar way as

$$\mathbf{r}_{i} = \frac{\mathbf{A}\mathbf{p}_{t}}{1 + \mathbf{B}\mathbf{p}_{t}} \tag{32}$$

Where
$$A = \frac{k_a C_o}{2RT}$$
 and $B = \frac{K_B}{2RT}$

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For this mechanism a typical plot of initial rate ri as a function of total pressure p_t is shown in Fig 11. When reaction data satisfy this plot then the reaction is said to be adsorption A controlling. In similar way other models can be tested for fitting.

However, it should be noted that though the initial rate analysis is simple and can reduce the number of rate expressions to be tested against the experimental but cannot substitute a differential or integral analysis. It should be used as only as preliminary kinetic analysis method.



Fig. 11. Typical plot for initial rate vs total pressure for reactions $A + B \rightleftharpoons C + D$ when equimolal mixture of A and B is used. A) surface reaction controlling B) adsorption of A controlling

Figure 12 shows the general types of initial rate expressions.

- Forward rates
- Product terms negligible



Fig.12: General types of initial rate expressions

1.6.3-Linear and Nonlinear Regression of Rate Data:

For a Langmuir –Hinshelwood type rate equation:

$$-\mathbf{r}_{A} = \frac{\mathbf{k} \mathbf{p}_{A} \mathbf{p}_{B}}{\mathbf{1} + \mathbf{K}_{A} \mathbf{p}_{A} + \mathbf{K}_{B} \mathbf{p}_{B}}$$

the value of rate law parameters k, K_A , K_B cannot be analyzed as simply as in power law kinetics. The rate law parameters can be determined by linear least square or nonlinear least square method. In linear least square method, the above LH rate equation can be linearized by dividing throughout by p_A and p_B and inverting it as shown below:

$$-\frac{\mathbf{p}_{\mathbf{A}}\mathbf{p}_{\mathbf{B}}}{\mathbf{r}_{\mathbf{A}}} = \frac{1}{\mathbf{k}} + \frac{\mathbf{K}_{\mathbf{A}}}{\mathbf{k}}\mathbf{p}_{\mathbf{A}} + \frac{\mathbf{K}_{\mathbf{B}}}{\mathbf{k}}\mathbf{p}_{\mathbf{B}}$$
(33)

The parameters can be estimated by multiple regression technique using the following equation for N experimental runs. For the ith run :

$$Y_i = a_0 + a_1 X_{1i} + a_2 X_{2i}$$
 (34)

The best values of the parameters a_0 , a_1 and a_2 are found by solving following three equations

$$\begin{split} \sum_{i=1}^{N} \mathbf{Y}_{i} &= \mathbf{N}\mathbf{a}_{o} + \mathbf{a}_{1}\sum_{i=1}^{N} \mathbf{X}_{1i} + \mathbf{a}_{2}\sum_{i=1}^{N} \mathbf{X}_{2i} \\ \sum_{i=1}^{N} \mathbf{X}_{1i}\mathbf{Y}_{i} &= \mathbf{a}_{o}\sum_{i=1}^{N} \mathbf{X}_{1i} + \mathbf{a}_{1}\sum_{i=1}^{N} \mathbf{X}_{1i}^{2} + \mathbf{a}_{2}\sum_{i=1}^{N} \mathbf{X}_{1i}\mathbf{X}_{2i} \\ \sum_{i=1}^{N} \mathbf{X}_{2i}\mathbf{Y}_{i} &= \mathbf{a}_{o}\sum_{i=1}^{N} \mathbf{X}_{2i} + \mathbf{a}_{1}\sum_{i=1}^{N} \mathbf{X}_{1i}\mathbf{X}_{2i} + \mathbf{a}_{2}\sum_{i=1}^{N} \mathbf{X}_{2i}^{2} \end{split}$$

The above LH rate equation can also be solved by non-linear regression analysis. Usually linearized least square analysis is used to obtain the initial estimates of the rate parameters and used in non-linear regression. In non linear analysis the rate law parameters are first estimated to calculate the rate of reaction ' r_c '. Then the values of rate law parameters that will minimize the sum of the squares of difference of the measured reaction rate rm and the calculated reaction rate r_c , that is the sum of (r_m - r_c)² for all data points, are searched. If there are N experiments with K number of parameter values to be determined then the function to be minimized is given by:

$$\sigma^{2} = \sum_{i=1}^{N} \frac{\left(\mathbf{r}_{im} - \mathbf{r}_{ic}\right)^{2}}{\mathbf{N} - \mathbf{K}}$$
(35)

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Here r_{im} and r_{ic} are the measured and calculated reaction rate for 'i'th run respectively. The parameter values giving the minimum of the sum of squares, σ^2 , can be searched by various optimization techniques using software packages.

Example 2:

The rate law for the ydrogenation (H) of ethylene (E) to form ethane (A) $H_2 + C_2H_4 \rightarrow C_2H_6$ over a cobalt-molybdenum catalyst is:

$$-\mathbf{r}_{\mathbf{E}}' = \frac{\mathbf{k}\mathbf{P}_{\mathbf{E}}\mathbf{P}_{\mathbf{H}}}{1 + \mathbf{K}_{\mathbf{E}}\mathbf{P}_{\mathbf{E}}}$$

Suggest a mechanism and rate-limiting step consistent with the rate law and then derive the rate law.

Solution:

 $H = H_2$

E = Ethylene

A = Ethane

$$H_2 + C_2 H_4 \xrightarrow{cat} C_2 H_6$$

 $H + E \longrightarrow A$

Because neither H_2 or C_2H_6 are not in the denominator of the rate law they are either not adsorbed or weakly adsorbed. Assume H_2 in the gas phase reacts with C_2H_6 adsorbed on the surface and ethane goes directly into the gas phase. Then check to see if this mechanism agrees with the rate law

Eley Rideal Model

$E + S E \bullet S$	$\mathbf{r}_{AD} = \mathbf{k}_{AD} \left[\mathbf{P}_{E} \mathbf{C}_{V} - \frac{\mathbf{C}_{E \bullet S}}{\mathbf{K}_{E}} \right]$
$E \bullet S + H \longrightarrow A + S$	$\mathbf{r}_{\mathrm{S}} = \mathbf{k}_{\mathrm{S}} \mathbf{C}_{\mathbf{E} \bullet \mathrm{S}} \mathbf{P}_{\mathrm{H}_{2}}$

 $E \bullet S \longrightarrow A + S$

Assume surface reaction $C_{F \cdot S} = K_F P_F C_V$

$$r_{S} = k_{S} [C_{E \bullet S} P_{H}]$$

 $C_{T} = C_{V} + C_{E \bullet S}$

$$-\mathbf{r}_{A}' = \mathbf{k}_{S}\mathbf{K}_{E}\mathbf{C}_{T}\left[\frac{\mathbf{P}_{E}\mathbf{P}_{H}}{1 + \mathbf{K}_{E}\mathbf{P}_{E}}\right]$$

$$-r_A = k \left[\frac{P_E P_H}{1 + K_E P_E} \right]$$

Example 3:

t-Butyl alcohol (TBA) is an important octane enhancer that is used to replace lead additives in . TBA was produced by the liquid-phase hydration (W) of isobutene (I) over an Amberlyst-15 catalyst. The system is normally a multiphase mixture of hydrocarbon, water, and solid catalysts. However, the use of cosolvents or excess TBA can achieve reasonable miscibility.

The reaction mechanism is believed to be

Derive a rate law assuming:

- (a) The surface reaction is rate-limiting.
- (**b**) The adsorption of isobutene is limiting.
- (c) The reaction follows Eley-Rideal kinetics

 $I \cdot S + W \longrightarrow TBA \cdot S$

and the surface reaction is limiting.

(d) Isobutene (I) and water (W) are adsorbed on different sites

 $I + S_1 \rightleftharpoons I \cdot S_1$ $W + S_2 \rightleftharpoons W \cdot S_2$

TBA is *not* on the surface, and the surface reaction is rate-limiting. e) What generalization can you make by comparing the rate laws derived in parts (a) through (d)? Solution:

$$I + S \leftrightarrow I \circ S \qquad r_{ADI} = k_{AI} \left[C_{I}C_{V} - \frac{C_{I \circ S}}{K_{I}} \right]$$
$$W + S \leftrightarrow W \circ S \qquad r_{ADW} = k_{AW} \left[C_{W}C_{V} - \frac{C_{W \circ S}}{K_{W}} \right]$$
$$W \circ S + I \circ S \leftrightarrow TBA \circ S + S \qquad r_{S} = k_{S} \left[C_{W \circ S}C_{I \circ S} - \frac{C_{V}C_{TBA \circ S}}{K_{S}} \right]$$
$$TBA \circ S \leftrightarrow TBA + S \qquad r_{D} = K_{D} \left[C_{TBA \circ S} - \frac{C_{TBA}C_{V}}{K_{D}} \right]$$

(a)

Surface Rxn Limited

$$\frac{r_{ADI}}{k_A} = 0 \qquad C_{I \bullet S} = K_I C_I C_V \qquad C_{W \bullet S} = K_W P_W C_V \qquad \frac{r_{ADW}}{k_W} = 0$$

$$\frac{I}{K_D} = 0 \qquad C_{TBA \bullet S} = \frac{C_{TBA} C_V}{K_D} = K_{TBA} C_{TBA} C_V, \text{ since } \frac{1}{K_D} = K_{TBA}$$

$$r_S = K_S K_1 K_W C_V \left[C_I C_W - \frac{C_{TBA}}{K_P} \right] \qquad K_p = \frac{K_S K_1 K_W}{K_{TBA}}$$

$$C_{T} = C_{V} + C_{I \bullet S} + C_{W \bullet S} + C_{TBA \bullet S} = C_{V}(1 + K_{I}C_{I} + K_{W}C_{W} + K_{TBA}C_{TBA})$$


(b) Adsorption of isobutene limited



Eley Rideal Kinetics

$$\mathbf{r}_{S} = \mathbf{k}_{S} \left[\mathbf{C}_{W} \mathbf{C}_{I \bullet S} - \frac{\mathbf{C}_{TBA \bullet S}}{K_{S}} \right]$$

$$\begin{split} &C_{I*S} = K_{I}C_{I}C_{V} \\ &C_{TBA*S} = K_{IBA}C_{TBA}C_{V} \\ &-r_{I}' = \frac{k \left[C_{W}C_{I} - \frac{C_{TBA}}{K_{H}} \right]}{1 + K_{I}C_{I} + K_{TBA}C_{TBA}}, \text{ where } k = k_{S}K_{I}C_{T} \text{ and } K_{H} = \frac{K_{I}K_{S}}{K_{TBA}} \end{split}$$

Example(4):

The dehydration of n-butyl alcohol (butanol) over an alumina-silica catalyst. The data in Figure were obtained at 750°F in a modified differential reactor. The feed consisted of pure butanol.

(a) Suggest a mechanism and rate-controlling step that are consistent with the experimental data.

(b) Evaluate the rate law parameters.

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(c) At the point where the initial rate is a maximum, what is the fraction of vacant sites? What is the fraction of occupied sites by both A and B?

(d) What generalizations can you make from studying this problem?

(e) Write a question that requires critical thinking and then explain why your question requires critical thinking.



PA0 (atm)

Initial reaction rate as function of initial partial pressure of butanol.

Solution:

(a)

A (butanol)
$$\rightleftharpoons$$
 B (butene) + C (water)

Possible mechanism:

 $A + S \rightleftharpoons A \cdot S$ $r_{AA} = K_{AA} \left(P_A C_S - \frac{C_{AS}}{K_{AA}} \right)$

$$A \cdot S + S \rightleftharpoons B \cdot S + C \cdot S$$

$$K_{AA}$$

$$r_{S} = k_{S} (C_{A-S} C_{S} - C_{B-S} C_{C-S} / K_{S})$$

 $B \cdot S \rightleftharpoons B + S$ $r_{DB} = k_{DB} (C_{B,S} - P_B C_S/K_{DB})$

 $C \cdot S \rightleftharpoons C + S$ $r_{DC} = k_{DC} (C_{CS} - P_C C_S/K_{DC})$

Assume surface reaction controlling:

$$\frac{-r_{AA}}{k_{AA}} \equiv 0 \qquad C_{A-S} = P_A K_{AA} C_S$$

$$\frac{-r_{DB}}{k_{DB}} \equiv 0 \qquad C_{B-S} = \frac{P_B C_S}{K_{DB}} = P_B K_{AB} C_S$$

$$\frac{-r_{CC}}{k_{DC}} \equiv 0 \qquad C_{C-S} = \frac{P_C C_S}{K_{DC}} = P_C K_{AC} C_S$$

$$-r'_A = r_S = k_S \left(P_A K_{AA} C_S^2 - \frac{P_B P_C C_s^2}{K_S K_{DB} K_{DC}} \right) = k_S K_{AC} C_S^2 \left(P_A - \frac{P_B P_C}{K_{eq}} \right) \text{ where } K_{eq} = K_S K_{AA} K_{DC} K_{DB}$$
site balance: $C_T = C_S + C_{AS} + C_{BS} + C_{CS} = C_S (1 + K_{AA} P_A + K_{AB} P_B + K_{AC} P_C)$

$$\therefore -r'_A = \frac{k_S K_{AA} C_T^2 (P_A - P_B P_C / K_{eq})}{(1 + P_A K_{AA} + P_B K_{AB} + P_C K_{AC})^2}$$
If $P_{BO} = 0$ and $P_{CO} = 0$, then
$$-r'_{A0} = \frac{k_S K_{AA} C_T^2 P_{A0}}{(1 + P_{A0} K_{AA})^2} = \frac{k_1 P_{A0}}{1 + k_2 P_{A0}^2 + k_3 P_{A0}} \qquad \text{where } \begin{cases} k_1 = k_3 K_{AA} C_T^2 \\ k_2 = K_{AA}^2 \\ k_3 = 2 K_{AA} \end{cases}$$
(b)
From the figure,
Point number 1 2 3 4 5 6
$$-r'_{A0} \left(\frac{1bmoles}{1r + 1b carl} \right) \qquad 0 \quad 0.275 \quad 0.5 \quad 0.77 \quad 0.77 \quad 0.5 \\ P_{A0} (atm) \qquad 0 \quad 4.5 \quad 27 \quad 54 \quad 112 \quad 229 \\ \sqrt{\frac{P_A}{-r_{A0}}} = -r_{A05} \quad 6.45 \quad 8.14 \quad 12.06 \quad 21.4 \end{cases}$$

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At large
$$P_{A0}$$
: $-r_{A0} = \frac{k_1 P_{A0}}{k_2 P_{A0}^2} = \frac{k_1}{k_2} \left(\frac{1}{P_{A0}}\right)$; using point 6: $\frac{k_1}{k_2} = (229) (0.5) = 114$
At small P_{A0} : $-r_{A0} = k_1 P_{A0}$; using point 2: $k_1 = 0.061 \Rightarrow k_2 = 5.34 \times 10^4$
 $-r_{A0} = \frac{0.061 P_{A0}}{1 + 5.34 \times 10^4 P_{A0}^2 + k_3 P_{A0}}$; so $k_3 = \frac{0.061}{-r_{A0}} - \frac{1}{P_{A0}} - 5.34 \times 10^4 P_A$
Using point 3: $k_3 = 7.05 \times 10^{-2}$
Using point 4: $k_3 = 3.19 \times 10^{-2}$
Using point 5: $k_3 = 1.05 \times 10^{-2}$
 $M = reason for the different values of k_3 is from reading the graph)$
 $25.0 - y = 4.3103 + 0.073937x R = 0.99583$
 $20.0 - \frac{1}{0}$
 $10.0 - \frac{1}{0}$
 10.0

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(**C**)

Find the percent of vacant sites.

%vacant =
$$\frac{C_s}{C_T} = \frac{C_S}{C_S(1 + K_{AA}P_A + K_{AB}P_B + K_{AC}P_C)}$$

 P_{b} and $P_{c} = 0$ so that reduces to:

%vacant =
$$\frac{1}{1 + K_{AA}P_{A0}} = \frac{1}{1 + 0.01596 * 90} = 0.41$$

Find the percent of sites occupied by A and B. No B will have occupied any sites at X = 0. So:

$$\%A = \frac{K_{AA}P_A}{1 + K_{AA}P_A} = \frac{0.01595*90}{1 + 0.01595*90} = 0.59$$

Example 5:

The experimental data for the gas-phase, catalytic, irreversible reaction $A + B \rightarrow C$ is given in the table. Suggest a rate law & mechanism consistent with the data. Approach: Use graphs to show how $-r_A$ varies with P_i when P_j and P_k are held constant.

Run	P _A (atm)	P _B (atm)	P _c (atm)	- <mark>r'_A(mol/g·s</mark>)
1	0.1	1	2	0.073
2	1	10	2	3.42
3	10	1	2	0.54
4	1	20	2	6.80
5		20	10	2.88
6	20	1	2	0.56
7	1	1	2	0.34
8		20	5	4.5

Solution:



We need to use these graphs to determine whether A, B, & C are in the numerator, denominator, or both.





 $-\underline{r'_A} \downarrow \text{ with } \uparrow P_C \rightarrow \underline{rnx} \text{ is }$ irreversible so P_C must be in the denominator of $-\underline{r'_A}$. Therefore, C is adsorbed on surface

The rate law suggested for the experimental data given for the gas-phase, catalytic, irreversible reaction $A + B \rightarrow C$ is:

$$-r'_{A} = \frac{kP_{A}P_{B}}{1 + K_{A}P_{A} + K_{C}P_{C}}$$

Suggest a mechanism for this rate law.

 P_A and P_C are in the denominator. A (reactant) and C (product) must be adsorbed on the surface, but B is not adsorbed on the surface:

Adsorption of reactant A:

$$A + S \Box \quad A \cdot S \quad r_{AD} = k_A P_A C_V - k_{-A} C_{A \cdot S} \quad \rightarrow r_{AD} = k_A \left(P_A C_V - \frac{C_{A \cdot S}}{K_A} \right)$$

Desorption of product C:

$$\mathbf{C} \cdot \mathbf{S} \square \quad \mathbf{C} + \mathbf{S} \quad \mathbf{r}_{DC} = \mathbf{k}_{D} \mathbf{C}_{C \cdot S} - \mathbf{k}_{-D} \mathbf{P}_{C} \mathbf{C}_{V} \quad \rightarrow \mathbf{r}_{DC} = \mathbf{k}_{D} \left(\mathbf{C}_{C \cdot S} - \frac{\mathbf{P}_{C} \mathbf{C}_{V}}{\mathbf{K}_{D}} \right)$$

Surface reaction step: B is not adsorbed on the surface, so B must be in the gas phase when it reacts with A adsorbed on the surface.

The overall reaction is irreversible, so this step is likely irreversible

$A \cdot S + B \rightarrow C \cdot S \qquad \qquad r_S = k_S C_{A \cdot S} P_B$

Postulate that the surface reaction is the rate limiting step since that is true the majority of the time. Check if that is consistent with the observed kinetics

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Example 6:

Methyl ethyl ketone (MEK) is an important industrial solvent that can be produced from the dehydrogenation of butan-2-ol (Bu) over a zinc oxide catalyst $A \rightarrow B+C$ $Bu \rightarrow MEK + H_2$

The following data giving the reaction rate for MEK were obtained in a differential reactor at 490°C.

P _{Bu} (atm)	2	0.1	0.5	1	2	1
$P_{\rm MEK}$ (atm)	5	0	2	1	0	0
$P_{\rm H_2}$ (atm)	0	0	1	1	0	10
$r'_{\rm MEK}$ (mol/h·g cat.)	0.044	0.040	0.069	0.060	0.043	0.05 9

a- Suggest a reaction mechanism and rate-limiting step consistent with the rate law. *[Hint:* Some species might be weakly adsorbed.]

One possible mechanism is the following one

(1)
$$A + S \leftrightarrow A \cdot S$$

(2) $A \cdot S + S \leftrightarrow B \cdot S + C \cdot S$
(3) $B \cdot S \leftrightarrow B + S$
(4) $C \cdot S \leftrightarrow C + S$

If the limiting step is 2(irreversible surface reaction) and the others at Pseudo Steady State (steps 1,3,and 4).

$$P_A C_V = \frac{C_{A \cdot S}}{K_1}$$

$$C_{B \cdot S} = \frac{P_B C_V}{K_3}$$

$$C_{C \cdot S} = \frac{P_C C_V}{K_4}$$

A site's balance will yield

$$C_T = C_V + C_{A \cdot S} + C_{B \cdot S} + C_{C \cdot S}$$

Therefore,

$$C_{T} = C_{V} + C_{V}P_{A}K_{1} + \frac{C_{V}P_{B}}{K_{3}} + \frac{C_{V}P_{C}}{K_{4}}$$

Solving for C_V

$$C_{V} = \frac{C_{T}}{1 + P_{A}K_{1} + \frac{P_{B}}{K_{3}} + \frac{P_{C}}{K_{4}}}$$

Substituting the expressions for C_V and $C_{A^{\cdot S}}$ into the equation for $-r'_A$

$$-r'_{A} = k_{2}C_{A \cdot S}C_{V} = k_{2}K_{1}P_{A}C_{V}^{2} = \frac{k_{2}K_{1}P_{A}C_{T}^{2}}{\left(1 + P_{A}K_{1} + \frac{P_{B}}{K_{3}} + \frac{P_{C}}{K_{4}}\right)^{2}}$$

which for the case of weak adsorption of MEK and H2 reduces to

$$-r_{A}' = \frac{k_{2}K_{1}P_{A}C_{T}^{2}}{\left(1 + P_{A}K_{1}\right)^{2}}$$

b- First we need to calculate the rate constants involved in the equation for $-r_A$ in part (a). We can rearrange the equation to give the following

$$\sqrt{\frac{P_A}{r'_{MEK}}} = \frac{1}{\sqrt{k_1}} + \frac{k_2}{\sqrt{k_1}} P_A$$

which is a linear equation with slope equal to $\frac{k_{2}}{2}$

and intercept equal to $\frac{1}{\sqrt{k_1}}$.



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Thus from the slope and intercept data:

$$k_1 = 0.56 \frac{mol}{h \cdot gcat \cdot atm}$$
 and $k_2 = 2.04 \frac{1}{atm}$

Thus,

$$-r_{A}' = r_{B}' = \frac{0.56P_{A}}{(1+2.04P_{A})^{2}}$$

Homework Problems:

1-The reaction $A + B \rightarrow C$ is speculated to occur with adsorption of A and C on one type of site; independent adsorption of B on a second type of site; and the surface reaction between adsorbed A and adsorbed B is the rate limiting step.

a) Determine the fraction of vacant sites?

b) Determine the fractions of adsorbed species.?

c) Determine the reaction rate expression according to the described mechanism?

d) Qualitatively sketch the dependence of the reaction rate on P_A , P_B , P_C (i.e., One sketch for each, with other partial pressures held constant)?

2-The formation of propanol on a catalytic surface is believed to proceed by the following mechanism NASAR D

$$O_2 + 2S \rightleftharpoons 2O \cdot S$$

$$C_3H_6 + O \cdot S \rightarrow C_3H_5OH \cdot S$$

$$C_3H_5OH \cdot S(\rightleftharpoons C_3H_5OH + S)$$

Suggest a rate-limiting step and derive a rate law.

Answer:

$$-r_{B} = r_{S} = \frac{k_{3}C_{T}P_{B}\sqrt{K_{A}P_{A}}}{1 + \sqrt{K_{A}P_{A}} + K_{C}P_{C}}$$

3- The irreversible, gas-phase, solid-catalyzed reaction $A+B\rightarrow C$ is carried out in a differential reactor.

(a) Determine a mechanism	and rate-limiting step	consistent with the	he following
data:			

Run	$-r_{\rm A} \times 10^4$ (mol/g cat. · s)	P _A (atm)	P _B (atm)	P _C (atm)
1	1.0	1	1	1
2	1.5	1000	1	1
3	4.5	1	4.5	1
4	4.5	0.001	1003	0
5	4.5	0.002	503	0
6	4.5	1	504	1000
7	4.5	1	4	0
8	4.8	4	4	.4

(b) Evaluate all rate law parameters.

(c) Where would you take additional data points?

(d) Discuss what you learned from this problem.

4- Given the following reaction rate expression and the following data

$$-r_A = \frac{k_1 C_A}{l + k_2 C_A}$$

-r _A *10	³ (mole/min.g cat.)	1.52	0.825	0.69	0.465	0.25
CA	(mole/m ³)	0.85	0.62	0.45	0.25	0.15

Find the kinetic parameters?

5-The reaction $A_2 + B_2 \rightarrow C$ is speculated to occur with adsorption of A and B on the same site. If no product adsorption takes place, and both A and B dissociate upon adsorption and the surface

reaction between adsorbed A and adsorbed B is the rate limiting step.

a) Determine the fraction of vacant active sites?

- **b**) Determine the fractions of adsorbed species.?
- c) Determine the reaction rate expression according to the described mechanism?
- **d**) Qualitatively sketch the rate versus the partial pressure of A_2 , B_2 and C.

6-Given the following reaction rate expression and the following data

	$-r_A = \frac{k_A \sqrt{C_A C_B}}{1 + k_B \sqrt{C_A C_B}}$				
$-r_{A} * 10^{7} (g$	mole/.g cat sec)	1.113	1.06	0.986	0.65767
$C_{A} \times 10^{7}$	(gmole/cm ³)	1.5	2.5	3.5	4.5
$C_{\rm B} \times 10^5$	(gmole/cm ³)	0.8264	0.3226	0.1587	0.0769

Find the kinetic parameters?

7- The reaction $A_2 + B \rightarrow C$ is speculated to occur with adsorption of A and C on one type of site; independent adsorption of B on a second type of site; If A dissociates upon adsorption and the surface reaction between adsorbed A and adsorbed B is the rate limiting step.

a) Determine the fraction of vacant active sites?

b) Determine the fractions of adsorbed species.?

c) Determine the reaction rate expression according to the described mechanism?

8-Given the following reaction rate expression and the following data

$$-r_A = \frac{k_1 C_A C_B}{1 + k_2 C_A C_B}$$

-r _A *1	0 ³ (mole/min.g cat.)	3.52	2.825	1.69	0.865	0.45
C _A	(mole/m ³)	0.85	0.62	0.45	0.25	0.15
C _B	(mole/m ³)	0.45	0.32	0.25	0.10	0.05

Find the kinetic parameters?

Part Two:

- Reaction and diffusion in porous catalysts.
- Isothermal and non-isothermal effectiveness factors.

- Effect of intra-phase transport.
- Effect of external mass transfer.
- Global reaction rate.

2-Internal Diffusion Phenomena:

Catalysts contain active sites which are located inside the pores. Therefore, molecules must first diffuse into the pores. until reaching the sites before reaction.

The internal molecular diffusion inside pores can be the limiting step and therefore it is unwanted. Basically, there are three forms of diffusions occurring in the pores of the catalyst:

1. **Molecular (bulk) diffusion**: may occur in big pore diameters $(1-10\mu m)$ where the mean free path of the molecules is small compared to the pore diameter.

The calculation of binary molecular diffusion coefficients in gases has been the subject of much research. Two relationships that are widely used are the Chapman–Enskog formula and the Fuller formula. The Chapman–Enskog formula is

$$D_{AB} = 0.0018583 \frac{T^{3/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{p_t \sigma_{AB}^2 \Omega_{AB}}$$
(1)

 $\begin{aligned} D_{AB}\left(cm^{2}/s\right) &= bulk \ diffusivity \\ T(K) &= temperature \\ M_{A} \& M_{B} &= molecular \ weight \ of \ A \ and \ B, \ respectively \\ p_{t}\left(atm\right) &= total \ pressure \ of \ the \ gas \ mixture \\ \sigma_{AB}\left(A^{0}\right) &= \text{constant in Lennard-Jones potential-energy functions for the molecular pair AB} \\ \varepsilon_{AB} &= \text{constant in Lennard-Jones potential-energy functions for the molecular pair AB} \end{aligned}$

 Ω_{AB} = collision integral

2. **Knudsen diffusion**: exists in middle pore diameters (10-1.000 Å) where the mass transport happens by collision between the molecules and the wall.

However, as the pores become smaller, collisions between the molecules and the pore walls become significant for gas-phase systems. The collisions between the diffusing molecules and the wall gives rise to *Knudsen diffusion*. The Knudsen diffusion coefficient, in m^2/s , in a straight round pore can be calculated from the formula:

$$D_K = 48.5 d_p \left(\frac{T}{M}\right)^{\frac{1}{2}} m^2/s$$
(2)

Where dp is the pore diameter in m, T is the temperature in kelvin, and the molar mass of the diffusion species, M, is in kg/kmol or g/mol. The Knudsen diffusion coefficient varies with the pore diameter, which implies that a range of diffusion coefficients applies to a catalyst with a significant pore size distribution.

3. **Configuration diffusion**: exists in pores where the diameter of molecules is of the same order of the pore diameter.

For a binary system, it has been shown that the pore diffusion coefficient can be expressed as a function of the two quantities using the following relationship:

where α depends on the ratio of the molar fluxes of the two species:

$$\alpha = 1 + \frac{N_2}{N_1}$$

For equimolar counterdiffusion, $N_1 = -N_2$, $\alpha = 0$ and then

It would not be fruitful to describe diffusion within each and every one of the tortuous pathways individually; consequently, we define an Effective Diffusion (De) so as to describe the average diffusion taking place at any position r in the pellet. An equation that relates De to either the bulk or the Knudsen diffusivity is

$$D_{\rm e} = \frac{D_{\rm AB} \phi_{\rm p} \sigma_{\rm c}}{\tilde{\tau}}$$
(5)

where

 $\tilde{\tau} = \text{tortuosity}^1 = \frac{\text{Actual distance a molecule travels between two points}}{\text{Shortest distance between those two points}}$

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

 σ_c = Constriction factor

Although this value is reasonable for $\tilde{\tau}$, values for $\tilde{\tau} = 6$ to 10 are not unknown. Typical values of the constriction factor, the tortuosity, and the pellet porosity are, respectively, $\sigma_c = 0.8$, $\tilde{\tau} = 3.0$, and $\phi_p = 0.40$.

Diffusion of molecules in porous catalysts is highly dependent on the dimensions of the pore network. Figure 13 shows typical values of the gas-phase diffusivity as a function of pore size.



Figure 13:Influance of pore size on the gas-phase diffusivity.

2.1-Effectiveness Factor η:

In a porous catalyst, the internal surface area within the pores constitutes the effective surface on which the active metals are deposited. Hence, for reaction to occur, the reactants need to travel through the pores to reach the active sites. If there is any resistance in diffusion of the reactants through the pores, then both the activity and selectivity of the process is affected. In the absence of any internal mass transfer resistance within the pores the concentration of reactants can be assumed to uniform and equal to the surface concentration. Hence, the rate of reaction will also be uniform across the catalyst pellet and equal to the rate evaluated at surface

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conditions. However, in the presence of diffusional resistance, concentration of reactants gradually decreases from the surface towards the center of the catalyst pellet, resulting in a concentration gradient. When this concentration gradient is large enough, significant variation in reaction rate occurs within the pellet. The average rate within pellet will be less than the rate corresponding to the surface concentration. As pellet size decreases, the effect of intrapellet transport becomes less significant.

Rate of reaction for the whole catalyst pellets at any time is defined with respect to outer surface conditions in term of effectiveness factor η as : Actual rate of whole pellet $(r_p) = \eta \times rate$ evaluated at outer surface conditions (r_s)

or, $\eta = \frac{\text{actual rate of whole pellet}}{\text{rate evaluated at outer surface conditions}} = \frac{r_p}{r_s}$ (6)

Actual rate of whole pellet rp takes intrapellet mass transfer effects if any into account.

2.1.1-Effectiveness Factor at Isothermal Conditions :

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 $r + \Delta r$ of the pellet (Figure 14). Note that even though A is diffusing inward toward the center of the pellet, the convention of our shell balance dictates that the flux is 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 .s, indicating that the flux is actually in the direction of decreasing r



Fig.14: Shell balance on a catalyst pellet.

For an irreversible first order reaction $A \rightarrow B$, at isothermal for a spherical catalyst pellet of radius 'R_s', mass balance over a spherical shell volume of thickness ΔR at steady state will be :

(Rate of diffusion of reactant into element) - (Rate of diffusion of reactant out of element) = Rate of disappearance of reactant within element due to reaction

Rate of reaction per unit mass of catalyst $\left(\frac{mol}{kgcat.sec}\right) = \mathbf{k}_1 \mathbf{C}$ Rate of reaction per unit volume of catalyst $\left(\frac{mol}{m^3cat.sec}\right) = \mathbf{k}_1 \mathbf{C} \boldsymbol{\rho}_p$ Where $\boldsymbol{\rho}_p$ is the density of pellet $\left(\frac{kg}{m^3}\right)$.

The units of k₁ is $\left(\frac{m^3}{kg.sec}\right) = k \left(\frac{m}{sec}\right) * S_a \left(\frac{m^2}{kg}\right)$

Where $S_a\left(\frac{m^2}{kg}\right)$ is the is the total active area inside the porous pellet per gram of pellet.

Then the mass balance equation over the element of thickness ΔR can be written as :

$$\left[-4\pi R^2 D_e \frac{dC}{dR}\right]_R - \left[-4\pi R^2 D_e \frac{dC}{dR}\right]_{R+\Delta R} = \left(4\pi R^2 \Delta R\right) \rho_p k_1 C$$

If limit is taken as $\Delta R \rightarrow 0$ and assuming that effective diffusivity is independent of concentration of reactant the above equation can be written

Solving the differential equation (7) with boundary conditions (8) and (9) following relation is obtained

$$\frac{C}{C_{\rm S}} = \frac{R_{\rm s}}{R} \frac{\sinh(3\varphi_{\rm s} R / R_{\rm s})}{\sinh 3\varphi_{\rm s}}$$
(10)

Where ϕ_s is a dimensionless group defined as

$$\varphi_{\rm s} = \frac{R_{\rm s}}{3} \sqrt{\frac{k_1 \ \rho_{\rm p}}{D_{\rm e}}} \tag{11}$$

The (ϕ_s) is called **Thiele Modulus** for spherical pellet. Equation (10) gives the concentration profile of A in the pellet.

This concentration profile is used to evaluate the rate of reaction r_P for the whole pellet. Calculating the diffusion rate of reactant into pellet at position R_s per unit mass of catalyst pellet.

$$\mathbf{r}_{p} = \frac{1}{m_{p}} 4\pi R_{s}^{2} \mathbf{D}_{e} \left(\frac{d\mathbf{C}}{d\mathbf{R}}\right)_{\mathbf{R}=\mathbf{R}_{s}}$$
(12)

 $m_p = \frac{4}{3}\pi R_s^2 \rho_p = mass of pellet$

Substituting the value of m_p in equation (12)

$$\mathbf{r}_{p} = \frac{3}{\mathbf{R}_{s}\rho_{p}} \mathbf{D}_{e} \left(\frac{d\mathbf{C}}{d\mathbf{R}}\right)_{\mathbf{R}=\mathbf{R}_{s}}$$
(13)

Or

Differentiating
$$\frac{C}{C_s} = \frac{R_s}{R} \frac{\sinh(3\varphi_s R/R_s)}{\sinh 3\varphi_s}$$
 and evaluating the derivative at $R = R_s$ and

substituting in equation (14), following relation for η can be obtained for isothermal conditions.

$$\eta = \frac{1}{\varphi_{\rm s}} \left(\frac{1}{\tanh 3\varphi_{\rm s}} - \frac{1}{3\varphi_{\rm s}} \right) \tag{15}$$

Where for spherical pellets of radius \mathbf{r}_s , for a first-order reaction is given as ϕ_s

$$\varphi_{s} = \frac{R_{s}}{3} \sqrt{\frac{k_{1}\rho_{p}}{D_{e}}}.$$
(16)

 k_1 is rate constant, ρ_p is pellet density; *De* is effective diffusivity

Hence, to calculate Thiele modulus, both effective diffusivity De and rate constant k_1 need to be known. Fig 15 shows the typical plot of η vs ϕ_s . The Concentration profile in a spherical catalyst pellet in is shown in fig 16.



Fig. 15. Typical plot effectiveness factor η as function of Thiele modulus φ s



Fig. 16: Concentration profile in a spherical catalyst pellet.

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

$$R_{Ap} = \eta R_{As}$$

- $r_{A,obs} \left(\frac{mol}{kg s} \right) = \eta k \left(\frac{m}{s} \right) S_a \left(\frac{m^2}{kg} \right) C_{A,es} \left(\frac{mol}{m^3} \right)$

The resulting expression for the effectiveness factor for first order reaction is:

$$\eta = \frac{1}{\phi_s} \left(\frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right)$$

1- When $\varphi_s \leq \frac{1}{3}$, $\eta \rightarrow 1$ (17)

As the figure shows, for small values of $\varphi s \eta \rightarrow 1$. Equation (16) shows that small values of φs are obtained when the :

- 1. Pellets are small
- 2. Diffusivity is large
- 3. Reaction is intrinsically slow (catalysts of low activity).

2- When
$$\phi \geq 5$$
), $\eta = \frac{1}{\varphi s}$ (18)

as For such large φ_s , intra-particle diffusion has a large effect on the rate. At this condition, diffusion into the pellet is relatively slow and reaction occurs before the reactant has diffused far into the pellet.

When $\eta \rightarrow 1$, rate for the whole pellet is the same as the rate at surface concentration Cs and the entire catalyst surface is fully active.

When $\eta \ll 1$, the concentration within pellets drops from C_s to nearly zero in a narrow region near \mathbf{r}_s . At this condition, only the surface near the outer periphery of the pellet is effective and the catalyst surface in the central portion of the pellet is not utilized. This situation can be caused by large particles, low De or high k_1 ; that is very active catalysts.

Hence, low effectiveness factors are more likely with very active catalysts. More active the catalyst, the more is the possibility that intrapellet diffusion resistance will reduce global rate.

As noted in Equation 16, the Thiele modulus for spherical pellet is defined as:

$$\phi = \frac{R}{3} \sqrt{\frac{k_V}{D_{\text{eff}}}}$$
Where $k_V \left(\frac{1}{sec}\right) = k_1 \rho_P = k(\frac{m}{sec}) * S_a(\frac{m^2}{kg}) * \rho_P \left(\frac{kg}{m^3}\right)$

In the analysis of other shapes using an approximate one-dimensional analysis, a generalized Thiele modulus has been proposed. The characteristic length (Lc) for the catalyst particle is defined as the total particle volume divided by the external surface area through which diffusion occurs. Thus, we can define a generalized Thiele modulus as

With this new definition of the Thiele modulus, the solution must also change, and the three new equations for the effectiveness factor are:

$$\phi = L \sqrt{\frac{k_V}{D_{\text{eff}}}},$$

$$\eta = \frac{\tanh(\phi)}{\phi} \text{ (plane wall)}$$

For each of the three geometries (plane wall, infinite cylinder, and sphere) considered thus far, the generalized Thiele modulus becomes, respectively

als .

For $\ \eta=1$, entire volume of pellet is reacting at the same high rate

For $\ \eta pprox 0$, pellet reacts at low rate; reactant unable to penetrate into pellet

• Effectiveness Factors for Non-First-Order Reactions:

The results presented thus far pertain to first-order reactions. As noted earlier, an interesting result for the first-order case is that the effectiveness factor does not depend on the value of the surface concentration, but only on the temperature. Effectiveness factors can also be derived for other types of kinetics, and we start by considering a reaction of order n; thus, let us consider a rate equation of the form

$$\left(-R_{\rm A}\right) = k_V C_{\rm A}^n$$

The general equation for irreversible reactions second order or higher can be estimated from the formula:

The value of the Thiele modulus includes the surface concentration, which in turn means that the effectiveness factor depends on the surface concentration of reactant. In this case, the mole balance equation becomes a nonlinear differential equation and requires a numerical solution. For first order reversible reaction $A \leftrightarrow B$ the Thiel modulus is given by

It can be seen that \emptyset_s for reversible reactions is greater than for irreversible reactions, so the effectiveness factor (η) for reversible reactions is less than η for irreversible reactions.

The rate of reaction for for reversible reactions is given by

The fact of reaction for for the reactions is given by

$$r_p = k_R (C_A - C_{A.equ})$$
Where:

$$k_R = \frac{k_1 (K+1)}{K}$$

$$K = \frac{k_1}{k_2} = \left(\frac{C_{B,eq}}{C_{A,eq}}\right) = \frac{C_{Ao} * x_e}{C_{Ao}(1-x_e)} = \frac{x_e}{1-x_e}$$

2.3-Estimation of Diffusion- and Reaction-Limited Regimes:

It is instructive to compare this actual pellet production rate to the rate in the absence of diffusional resistance. If the diffusion were arbitrarily fast, the concentration everywhere in the pellet would be equal to the surface concentration, corresponding to the limit $\phi=0$ then $\eta \rightarrow 1$.

The pellet rate for this limiting case is simply

$$R_{As} = -kc_{As} \tag{23}$$

For η near unity, the entire volume of the pellet is reacting at the same high rate because the reactant is able to diffuse quickly through the pellet.

For η near zero, the pellet reacts at a low rate. The reactant is unable to penetrate significantly into the interior of the pellet and the reaction rate is small in a large portion of the pellet volume. The pellet's diffusional resistance is large and this resistance lowers the overall reaction rate.

As the particle diameter becomes very small, the Thiele modulus decreases, so that the effectiveness factor approaches 1 and the reaction is surface-reaction-limited. On the other hand, when the Thiele modulus is large, the internal effectiveness factor is small and the reaction is diffusion-limited within the pellet (see figure 17).



Fig.17: Effectiveness factor for different reaction orders and catalyst shapes.

As particle diameter \downarrow , $\phi_n \downarrow$, $\eta \rightarrow 1$, rxn is surface rxn limited As particle diameter \uparrow , $\phi_n \uparrow$, $\eta \rightarrow 0$, rxn is diffusion limited

2.3.1-Significance of Intrapellet Diffusion:

The Weisz–Prater criterion uses measured values of the rate of reaction, (r_{Aobs}), to determine if internal diffusion is limiting the reaction.

The basic assumption is that if $\varphi_s \leq \frac{1}{3}$, then $\eta \to 1$.

When $\varphi_s \leq \frac{1}{3}$

Or
$$\frac{R_s}{3}\sqrt{\frac{k_1\rho_p}{D_e}} \le \frac{1}{3}$$
 $\therefore \varphi_s = \frac{R_s}{3}\sqrt{\frac{k_1\rho_p}{D_e}}$

Simplifying and squaring , $\frac{R_s^2 k}{I}$

$$\operatorname{ng}, \frac{R_s^2 k_1 \rho_p}{D_e} \leq 1$$

Now
$$k_1 = \frac{r_p}{\eta C_s} = \frac{r_p}{C_s}$$
, where r_p is the measured rate and $\eta \to 1$.

Substituting k₁, $\frac{R_s^2 \rho_p r_p}{D_e C_s} \le 1$. This is known as the Weisz Criteria.(24)

This criterion can be approximately used for most catalytic kinetics though it is derived for a 1st order reaction. There are no diffusion limitations(the internal diffusion may be neglected) and consequently no concentration gradient exists within the pellet.

However, there is a diffusion limitations (the internal diffusion is very strong) and consequently there is a concentration gradient within the pellet

.....(26)

The summary of the **Weisz–Prater criterion** dictates that

If $C_{\rm WP} \ll 1$	no internal diffusion limitations present
If $C_{\rm WP} \ge 1$	internal diffusion limitations present

Example 1:

 $C_{WP} \gg 1$

Dehydrogenation of hydrocarbon (mol.wt = 58) at atmospheric pressure was carried out over chromia-alumina catalysts at 530 0 C. The reaction follows a first order kinetics with rate constant of 0.94 cm³/s. g cat. The spherical catalysts are of 30 mm diameter and average pore radius is 11 nm. Pellets have porosity of 0.35 and density of 1 gm/cm³. Assume Knudsen diffusivity to be dominant. Predict an effectiveness factor for the catalysts. Use parallel pore model with a tortuosity factor of 3.0 **Solution:**

Density of catalysts pellets = 1 gm/cm³ , T= 530 $^{\circ}$ C; D_p= 0.3 cm ; R_s= 0.3/2 = 0.15 cm

 $k_1 = 0.94 \text{ cm}^3 \text{ /s. g cat}$; a=pore radius = 11 nm = 11 × 10⁻⁷ cm

 $\delta = 3$; $\epsilon = 0.35$

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$$(D_k)_A = 9.7 \times 10^3 a \left(\frac{T}{M_A}\right)^{1/2}$$

 $M_A=58$; a = 11 nm = 11 × 10⁻⁷ cm; T= 530 $^{0}C = 530 + 273 = 803$ K

$$(D_k)_A = 9.7 \times 10^3 \times 11 \times 10^{-7} \left(\frac{803}{58}\right)^{1/2} = 0.0397 \text{ cm}^2/\text{s}$$

 $D_e = \frac{\varepsilon D}{\delta}$

 $D{=}D_K{=}\;0.0397\;cm^2{/}s$; $\;\delta=3$, $\epsilon=0.35$

$$D_e = \frac{\varepsilon D}{\delta} = \frac{0.35 \times 0.0397}{3} = 4.63 \times 10^{-3} \text{ cm}^2/\text{s}$$

$$\varphi_{s} = \frac{R_{s}}{3} \sqrt{\frac{k_{1}\rho_{p}}{D_{e}}} = \frac{0.15}{3} \sqrt{\frac{0.94 \times 1}{4.63 \times 10^{-3}}} = 0.712$$
$$\eta = \frac{1}{\varphi_{s}} \left[\frac{1}{\tanh 3\varphi_{s}} - \frac{1}{3\varphi_{s}} \right] = \frac{1}{0.712} \left[\frac{1}{\tanh(3 \times 0.712)} - \frac{1}{3 \times 0.712} \right] = 0.786$$

Example 2:

The first-order, irreversible reaction (A \rightarrow B) takes place in a 0.3 cm radius spherical catalyst pellet at *T* = 450 K.At 0.7 atm partial pressure of A, the pellet's production rate is 2.5×10^{-5} mol/(gm. sec).

Determine the production rate at the same temperature in a 0.15 cm radius spherical pellet. The pellet density is $\rho_p = 0.85 \text{ g/cm}^3$. The effective diffusivity of A in the pellet is $De = 0.007 \text{ cm}^2/\text{sec}$.

Solution:

 $\begin{aligned} r_{Ap} &= \eta \ r_{As} \\ r_A &= \eta \ k \ C_{As} \\ \eta &= \frac{1}{\emptyset_s} \left(\frac{1}{\tanh(3\emptyset_s)} - \frac{1}{3\emptyset_s} \right) \end{aligned}$

The surface concentration and pellet production rates are given by

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$$C_{AS} = \frac{P_A}{RT} = \frac{0.7 \ atm}{0.082 \frac{m^3 atm}{kmol. K} * 450 \ K} = 1.9 * 10^{-5} \ \frac{kmol}{m^3} = 1.9 * 10^{-5} \frac{mol}{cm^3}$$

 $r_{A} = \ 2.5 \times 10^{-5} \ mol/(gm. \ sec) * \ 0.85 \ g/cm^{3} = 2.125 \ mol \ cm^{3}.sec$

$$\begin{split} \varphi &= \frac{R}{3} \sqrt{\frac{k_V}{D_{\text{eff}}}} \\ r_A &= \frac{1}{\phi_s} \left(\frac{1}{tanh(3\phi_s)} - \frac{1}{3\phi_s} \right) * k \ C_{A_s} \\ 2.125 \ \frac{mol}{cm^3 \cdot sec} &= \frac{1}{\phi_s} \left(\frac{1}{tanh(3\phi_s)} - \frac{1}{3\phi_s} \right) * k * 1.9 * 10^{-5} \frac{mol}{cm^3} \\ k &= 2.61 \frac{1}{sec} \\ \phi_s &= \frac{0.3 \ cm}{3} \sqrt{\frac{2.61 \frac{1}{sec}}{0.007 \ \frac{cm^2}{sec}}} = 1.93 \\ \eta &= \frac{1}{\phi_s} \left(\frac{1}{tanh(3\phi_s)} - \frac{1}{3\phi_s} \right) = \frac{1}{1.93} \left(\frac{1}{tanh(3*1.93)} - \frac{1}{3*1.93} \right) = 0.38 \end{split}$$

The smaller pellet is half the radius of the larger pellet, so the Thiele modulus is half as large or $\phi_s = 0.964$, which gives $\eta = 0.685$.

The production rate is therefore $:r_A = 0.685 * 2.6 * 1.9 * 10^{-5} = 3.38 * 10^{-5} \frac{mol}{cm^3 sec}$

We see that decreasing the pellet size increases the production rate by almost 60%. Notice that this type of increase is possible only when the pellet is in the diffusion-limitted regime.

Example 3:

The rate constant for the first-order cracking of cumene on a silica-alumina catalyst was measured to be $0.80 \text{ cm}^3 (s.g_{cat})$ in a laboratory reactor: Is the observed rate constant the true rate constant or is there influence of pore diffusion? Additional data:

$$\mathbf{R} = 0.25 \ cm: \ \rho_p = 1.2 \frac{gm}{cm^3} : \ D_e = 1.0 * 10^{-3} \ \frac{cm^2}{sec}$$

Solution:

the Thiele modulus is defined in terms of the characteristic length of a pellet:

$$\phi_0 = L_p \sqrt{\frac{k}{D_{TA}^e}} = \frac{R_p}{3} \sqrt{\frac{k}{D_{TA}^e}} = \left(\frac{(0.25)(\text{cm})}{3}\right) \sqrt{\frac{k\left(\frac{\text{cm}^3}{\text{s} \cdot \text{gcat}}\right) \cdot 1.2\left(\frac{\text{gcat}}{\text{cm}^3}\right)}{1.0 \times 10^{-3}\left(\frac{\text{cm}^2}{\text{s}}\right)}} = 2.9\sqrt{k}$$

$$\eta = \frac{1}{\phi_s} \left(\frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right)$$

$$\eta = \frac{1}{2.9\sqrt{k}} \left(\frac{1}{tanh(3*2.9\sqrt{k})} - \frac{1}{3*2.9\sqrt{k}} \right)$$

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$$k = 0.80 \frac{cm^3}{sec. gm_{cat}}$$

$$\eta = 0.15$$

Since η is small, there is a great influence of pore diffusion on the observed rate. Or we can use the Weisz–Prater criterion

Example 4:

A rate of 10^5 mole/hr m³ cat is observed for a gas concentration of Aof 20 mole/m³. The catalyst particle diameter is 2.4 mm.

Let us assume effective diffusivity is 5×10^{-5} m²/hr.Is there a strong pore diffusion resistance?

Solution:

 $r_{Ap} = \eta r_{As}$ $r_A = \eta k C_{As}$ $\eta k = \frac{r_A}{C_{As}} = \frac{10^5}{20} = 5000 \ hr^{-1}$

Since η depends on k, we used a trial and error solution. We expect η to be small. Let us assume some value, say 0.01.

$$k = \frac{5000}{\eta} = \frac{5000}{0.01} = 5 \times 10^5$$
$$\phi_s = \frac{R}{3} \sqrt{\frac{k_v}{D_e}} = \frac{2.4 \times 10^{-3}}{6} \sqrt{\frac{5 \times 10^5}{5 \times 10^{-5}}} = 40$$

$$\eta = \frac{1}{\phi_s} \left(\frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right) = 0.025$$

η assumed	k=5000/η	Thiele	η equation
0.01	5x10 ⁵	40	0.025
0.03	1.67×10^5	23	0.0433
0.063	7.93x10 ⁴	15.9	0.0627

Since $\eta = 0.0627$ and $\phi_s > 5$ the internal diffusion is very strong : Or we can use the Weisz–Prater criterion

Example 5:

The experimental data below is for first order reaction carried out in spinning basket reactor. If the internal diffusion is important, find the effectiveness factor for each spherical pellet.

Dp cm	r _A mol/gm.hr
0.6	0.09
0.3	0.162

The internal diffusion control when $\phi_s \ge 5$ and $\eta = 1/\phi_s$

$$r_{A_1} = \eta_1 \ k \ C_{A_{S1}} \qquad \text{for pellet 1}$$

$$r_{A_2} = \eta_2 \ k \ C_{A_{S2}} \qquad \text{for pellet 2}$$

$$r_{A_1} = \frac{\eta_1}{\eta_2}$$

$$\frac{0.09}{0.162} = \frac{\eta_1}{\eta_2}$$

 $\eta_1=0.556\,\eta_2$

$$\frac{\phi_{s1}}{\phi_{s2}} = \frac{R_{p1}}{R_{p2}}$$

$$\frac{\phi_{s1}}{\phi_{s2}} = \frac{\frac{0.6}{2}}{\frac{0.3}{2}} = 2$$
$$\phi_{s1} = 2\phi_{s2}$$

 $\eta = 1/\phi_s$ The internal diffusion control

 $\begin{aligned} &\frac{1}{\eta_1} = 2 \frac{1}{\eta_2} \\ &\text{Assume } \eta_2 = 0.3 \text{ then } \eta_1 = 0.1668 \text{ then } \phi_{s1} = \frac{1}{\eta_1} = 5.99 \\ &\text{From equation () } \phi_{s2} = 2.996 \text{ then } \eta_2 = 0.336 \\ &\eta_1 = 0.1858 \qquad \phi_{s1} = \frac{1}{\eta_1} = 5.39 \\ &\phi_{s2} = 2.69 \qquad \eta_2 = 0.37 \text{ then } \eta_1 = 0.205 \text{ then } \phi_{s1} = \frac{1}{\eta_1} = 4.878 \\ &\phi_{s2} = 2.439 \qquad \text{then } \eta_2 = 0.41 \rightarrow \eta_1 = 0.227 \rightarrow \phi_{s1} = \frac{1}{\eta_1} = 4.386 \rightarrow \phi_{s2} = 2.193 \rightarrow \eta_2 = 0.45 \rightarrow \eta_1 = 0.253 \rightarrow \phi_{s1} = \frac{1}{\eta_1} = 3.944 \rightarrow \phi_{s2} = 1.972 \rightarrow \eta_2 = 0.506 \rightarrow \eta_1 = 0.281 \rightarrow \phi_{s1} = 3.55 \rightarrow \phi_{s2} = 1.774 \rightarrow \eta_2 = 0.56 \\ &\text{and we continue calculation until } \eta_2 \text{ become constant .} \end{aligned}$

2.4-Significance of External Mass Transfer:

For first order reactions we can use an overall effectiveness factor to help us analyze diffusion, flow, and reaction in packed beds. We now consider a situation where external and internal resistance to mass transfer to and within the pellet are of the same order of magnitude (Figure 18). At steady state, the transport of the reactants from the bulk fluid to the external surface of the catalyst is equal to the net rate of reaction of the reactant within and the pellet.



Fig.18: Mass transfer and reaction steps.

The observed rate is also equal to the rate at which reactant "A" is transferred from the bulk fluid to the external surface ("es") of the porous catalyst pellet. The rate of mass transfer(M_A) from the bulk fluid to the external surface is.

and $a_{es}\left(\frac{m^2}{kg}\right)$ is the external "geometric" pellet area per unit mass of pellet (for a sphere, the external area = $4\pi R^2$).

$$a_{es} = \frac{6}{\rho_{cat} * d_p} \tag{28}$$

$$R_{Ap} = \eta R_{As}$$

For a first-order reaction in a spherical catalyst.

$$R_{Ap} = \frac{1}{\phi_s} \left[\frac{1}{tanh(3\phi_s)} - \frac{1}{3\phi_s} \right] k C_{As}$$

ls At equilibrium $R_{Ap} = M_A$: then(29)

$$\eta \, k \left(\frac{m}{s}\right) \, S_{a} \left(\frac{m^{2}}{kg}\right) \, C_{A,es} \left(\frac{mol}{m^{3}}\right) = k_{m} \left(\frac{m}{s}\right) \, a_{es} \left(\frac{m^{2}}{kg}\right) \left(C_{A,bulk} - C_{A,es}\right)$$

Now substitute this expression for $C_{A,es}$ into either of the above expressions for $-r_{A,obs}$ (a little quicker with the second one) and rearrange to get our final goal!

$$-r_{A,obs} = \Omega k S_a C_{A,bulk}$$
(31)

Where

$$\Omega = \left(\frac{\eta k_m a_{es}}{k_m a_{es} + k S_a \eta}\right) \qquad (32)$$

where Ω , The Overall Effectiveness Factor, is the ratio between the observed rate and the rate that would be obtained if all active sites in the pellet were exposed to A at concentration C_{A,bulk}.

You should know the following limiting behavior: Since.

$$k_1$$
 is $\left(\frac{m^3}{kg.sec}\right) = k\left(\frac{m}{sec}\right) * S_a\left(\frac{m^2}{kg}\right)$

Then

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... (35)

Or

 $\frac{1}{\eta k_1}$ Resistance due to Internal Diffusion $\frac{1}{k_m a_{es}}$ Resistance due to External Mass Transfer

Ω Overall Effectiveness Factor

$$\boldsymbol{\Omega} = \begin{bmatrix} \frac{1}{\frac{1}{\eta^+} \frac{k_1}{k_m a_{es}}} \end{bmatrix}$$

1-External mass transfer control: $k_m a_{es} \gg \eta k_1$

$$\Omega \rightarrow \frac{k_m a_{es}}{k_1}$$
$$-r_{A,obs} = k_m a_{es} C_{A,bulk}$$

$$-r_{A,obs} = k_m a_{es} \left(C_{A,bulk} - C_{A,es} \right) ; C_{A,bulk} >> C_{A,es}$$

2-Negligible external mass transfer resistance

 $k_m a_{es} \ll \eta \ k_1$ $\Omega \rightarrow \eta$ $R_{Ap} = \eta \ k_1 C_{A_b}$ $C_{A_s} = C_{A_b}$

3- With negligible external and internal mass transfer resistance, $\Omega \ge \eta \ge 1$, all active sites inside the pellet are exposed to $C_{A,b}$, and we have "kinetic control":

$$R_{Ap} = k_1 C_{Ab}$$

2.4.1-Mears' Criterion for External Mass Transfer:

The Mears criterion, like the Weisz–Prater criterion, uses the measured rate of reaction, , (kmol/kg cat.sec) to learn if mass transfer from the bulk gas phase to the catalyst surface can be neglected. Mears proposed that when

$$\frac{-r'_{\rm A}\rho_{\rm b}Rn}{k_{\rm c}C_{\rm Ab}} < 0.15 \tag{36}$$

external mass transfer effects can be neglected.

where n = reaction order R = catalyst particle radius, m $\rho_{b} =$ bulk density of catalyst bed, kg/m³ $= (1 - \phi)\rho_{c}$ ($\phi =$ porosity) $\rho_{c} =$ solid density of catalyst, kg/m³ $C_{Ab} =$ bulk reactant concentration, mol/dm³ $k_{c} =$ mass transfer coefficient, m/s

The mass transfer coefficient for single spheres is calculated from the Frössling correlation:

In this gas-phase catalytic reaction example, and for most liquids, the Schmidt number is sufficiently large that the number 2 in Equation (37) is negligible with respect to the second term when the Reynolds number is greater than 25. As a result, Equation (37) gives

1

$$k_m = 0.6 \left(\frac{D_{AB}}{d_p}\right) \left(\frac{d_p * u}{v}\right)^{\frac{1}{2}} \left(\frac{v}{D_{AB}}\right)^{\frac{1}{2}}$$
$$k_m = 0.6 \left(\frac{D_{AB}^{\frac{2}{3}}}{v^{\frac{1}{6}}}\right) * \left(\frac{u^{\frac{1}{2}}}{d_p^{\frac{1}{2}}}\right)$$

 $k_m = 0.6 * (Term 1) * (Term 2)$ (38)

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Term 1 is a function of the physical properties D_{AB} and ν , which depend on temperature and pressure only. The diffusivity always increases with increasing temperature for both gas and liquid systems. However, the kinematic viscosity ν increases with temperature ($\nu \propto T^{3/2}$) for gases and decreases exponentially with temperature for liquids. Term 2 is a function of flow conditions and particle size. Consequently, to increase k_m and thus the overall rate of reaction per unit surface area, one may either decrease the particle size or increase the velocity of the fluid flowing past the particle. For this particular case of flow past a single sphere, we see that if the velocity is doubled, the mass transfer coefficient and consequently the rate of reaction is increased by a factor of $(U_2/U_1)^{0.5} = 2^{0.5} = 1.41$ or 41%

Figure 19 shows the variation in reaction rate with Term 2 in Equation (38), the ratio of velocity to particle size. At low velocities the mass transfer boundary layer thickness is large and diffusion limits the reaction. As the velocity past the sphere is increased, the boundary layer thickness decreases, and the mass transfer across the boundary layer no longer limits the rate of reaction. One also notes that for a given velocity, reaction-limiting conditions can be achieved by using very small particles. However, the smaller the particle size, the greater the pressure drop in a packed bed.

When one is obtaining reaction rate data in the laboratory, one must operate at sufficiently high velocities or sufficiently small particle sizes to ensure that the reaction is not mass transfer-limited.

Increasing the gas-phase velocity and decreasing the particle size will increase the overall rate of reaction for reactions that are externally mass transfer–limited.



Fig. 19: Regions of mass transfer-limited and reaction-limited reactions.
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2.5-Internal and External Heat and Mass Transfer:

To quickly estimate the importance of external mass-transfer limitations, the magnitude of the change in concentration across the boundary layer can be calculated from the observed rate and the mass-transfer coefficient:

$$\boldsymbol{r}_{A} = \boldsymbol{k}_{m} \boldsymbol{a}_{es} (\boldsymbol{C}_{Ab} - \boldsymbol{C}_{As}) \tag{39}$$

The effects of heat transfer are completely analogous to those of mass transfer. The heat flux, q, across the stagnant boundary layer is related to the difference in temperature and the heat-transfer coefficient, h according to:

$$\boldsymbol{q} = \boldsymbol{h}(\boldsymbol{T}_{\boldsymbol{b}} - \boldsymbol{T}_{\boldsymbol{s}}) \tag{40}$$

Steady state requires that the heat flux is equivalent to the heat generated (or consumed) by reaction:

$$r_{A} * \Delta H_{r} = h(T_{b} - T_{s})$$

$$\frac{r_{A} * \Delta H_{r}}{h} = T_{b} - T_{s} = \Delta T$$
(41)
(42)

where ΔH_r is the heat of reaction per mole of *A* converted. To estimate the influence of heat-transfer limitations on the observed rate, the change in temperature across the film is found by evaluating the observed rate of heat generated (or consumed) and the heat-transfer coefficient (obtained from *J* factor correlations, similar to the case of mass-transfer coefficients):

Equation (42) can also be used to find the maximum temperature change across the film. Using Equation (39) to eliminate the observed rate, the resulting equation relates the concentration change across the film to the temperature change:

$$\frac{k_m a_{es} (c_{A_b} - c_{A_s}) * \Delta H_r}{h} = T_b - T_s = \Delta T \qquad (43)$$

The maximum temperature change across the film will occur when C_{AS} approaches zero, which corresponds to the maximum observable rate. Solving Equation (43) for ΔT_{max} with $C_{AS} = 0$ gives the following expression:

$$\Delta T_{max} = \frac{k_m a_{es} * \Delta H_r * C_{A_b}}{h}$$
 (44)

that can always be calculated for a reaction, independent of an experiment. If both external heat and mass transfer are expected to affect the observed reaction rate, the balances must be solved simultaneously.

The relationship between temperature and concentration is:

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$T = T_s + \left[\frac{\Delta H_r * D_e}{k_e}\right] \left(C_{A_s} - C_{A_b}\right)$	(45)

 $T_{max} - T_s = \frac{\Delta H_r * D_e}{k_e} * C_{A_s}$

Homework Problems:

1- A first order irreversible catalytic reaction $A \rightarrow P$ is carried out at isothermal conditions, *in absence of all external transport effects*, in a stirred basket reactor on two different size catalyst pellets. The pellets are spherical. The catalyst activity and pore structure of the pellets are identical. Therefore the kinetic rate constant and effective diffusivity are identical in pellets of both sizes. The temperature, pressure and bulk reactant concentration are identical in both runs. The following data are obtained.

	Pellet Diameter(cm)	Observed Rate x 10 ⁵	
		(mol/cm ³ cat.s)	
Run 1	1.0	3.0	
Run 2	0.1	15.0	

a) Estimate the Thiele modulus(θ_S) and effectiveness factor η for each particle. Are internal diffusion effects pronounced in each pellet size?

b)What pellet diameter is needed to completely eliminate internal diffusion resistance at the temperature of these experiments (i.e. $\eta \approx 1$).

2- The first-order reaction $A \rightarrow B$ was carried out over two different-sized pellets. The pellets were contained in spinning basket reactor that was operated at sufficiently high rotation speeds so the external mass transfer resistance was negligible. The

results of two experiment runs made under identical conditions are as given in Table below

(a) Estimate the Thiele modulus and effectiveness factor for each pellet.

(b) How small should the pellet be made to virtually eliminate all internal diffusion resistance?

Measured Rate (obs) (mol/g cat \cdot s) × 10 ⁵		Pellet Radius (m)	
Run 1	3.0	0.01	
Run 2	15.0	0.001	

3- The rate of isomerization of n-butane on a silica-alumna spherical catalyst measured at 5 atm and 50°C, in a laboratory reactor with high turbulence in the gas phase surrounding the catalyst pellet is given below. Turbulence ensures that the external diffusion resistances are negligible. Kinetic studies indicate that the rate is first order and irreversible. The effective diffusivity is 0.08 cm²/sec at the reaction conditions, and the density of the catalyst pellet is 1 g/cm³ regardless of the size. The measured rates when pure n-butane surrounds the catalyst are as follows:

Particle diameter (in)	1/16	1/8	1⁄4	3/8	1
Rate mol/sec/g of catalyst	4.88 x 10 ⁻⁴	4.85 x 10 ⁻⁴	4.01 x 10 ⁻⁴	3.54 x 10 ⁻⁴	1 x 10 ⁻⁵
118		an in	8		

From the above data, determine the intrinsic first order rate constant in the absence of intraparticle diffusion. Also predict the rate if the particle size is 1.5 inch. It may be assumed that effectiveness factor (η) is inverse of Thiele modulus (θ_s) (i.e. $\eta = 1/\theta_s$) when $\theta_{s} \geq 3$. OFFIC

4- The irreversible, first-order reaction of gaseous $A \rightarrow B$ occurs in spherical catalyst pellets with a radius of 2 mm. For this problem, the molecular diffusivity of A is 1.2 X 10⁻¹ cm² s⁻¹ and the Knudsen diffusivity is 9×10^{-3} cm² s⁻¹. The intrinsic first-order rate constant determined from detailed laboratory measurements was found to be 5.0 s⁻¹. The concentration of A in the surrounding gas is 0.0 I mol L⁻¹. Assume the porosity and the tortuosity of the pellets are 0.5 and 4, respectively.

(a) Determine the Thiele modulus for the catalyst pellets.

(b) Find a value for the internal effectiveness factor.

(c) For an external mass-transfer coefficient of $32s^{-1}$ (based on the external area of the pellets), determine the concentration of A at the surface of the catalyst pellets.

5-The importance of diffusion in catalyst pellets can often be determined by measuring the effect of pellet size on the observed reaction rate. In this exercise, consider an irreversible first-order reaction occurring in catalyst pellets where the surface concentration of reactant A is $C_{AS} = 0.15$ M.

Data:

Diameter of sphere (cm)	0.2	0.06	0.02	0.006
r_{obs} (mol/h/cm ³)	0.25	0.80	1.8	2.5

(a) Calculate the intrinsic rate constant and the effective diffusivity.

(b) Estimate the effectiveness factor and the anticipated rate of reaction (r_{obs}) for a finite cylindrical catalyst pellet of dimensions 0.6 cm x 0.6 cm (diameter = length).

6- Ercan et al. studied the alkylation of ethylbenzene, *EB*, with light olefins (ethylene and propylene) over a commercial zeolite Y catalyst in a fixed-bed reactor with recycle.. The solid-catalyzed liquid-phase reaction was carried out in excess ethylbenzene at 25 bar and 190°C.

Assume the reaction is pseudo-first-order with respect to olefin. The porosity of the catalyst was 0.5, the tortuosity was 5.0, and the density was 1000 kg m⁻³. The observed rate (robsJ and rate constant (k_{obs}) were measured for two different catalyst pellet sizes. Relevant results are given below:

		External surface		
R _p		area of catalyst,	r _{obs}	<i>k</i> _{obs}
(m m)	(m s ⁻¹)	$S_p (\mathrm{m}^2 \mathrm{kg}^{-1})$	(kmol (kgcat s) ⁻¹)	$(m^3 (kgcat s)^{-1})$
0.63	5.69×10^{-4}	4.62	$8.64 imes 10^{-6}$	$0.33 imes 10^{-3}$
0.17	1.07×10^{-3}	17.13	11.7×10^{-6}	1.06×10^{-3}

(a) Determine whether or not external and internal mass transfer limitations are significant for each case. Assume the diffusivity of olefins in ethylbenzene is $D_{AB} = 1.9 * 10-4 \text{ cm}^2\text{S}^{-1}$.

(b) Calculate the Thiele modulus, (θ_S) , and the internal effectiveness factor), for each case.

(c) Determine the overall effectiveness factor for each case.

7- The production rate of a heterogeneously, first-order reaction in a 0.75cm diameter spherical pellet is $R_{Ap} = 3.25*10^5 \text{ mol/cm}^3$.s when the catalyst is exposed to pure, gaseous A at a pressure of 1 atm and a temperature of 525 K. This reaction's activation energy is E=18600 cal/mol. Further, the effective diffusivity of A in the pellet is $D_A=0.009 \text{ cm}^2$ /s at 525 K and that diffusion is in the regime of Knudsen floow. The bulk fluid and the external surface concentrations can be assumed the same. Find the production rate if the catalyst is changed to a cylindrical pellet that is 0.5 cm in diameter and 1.0 cm in length, and the temperature is increased to 600 K.

8- A gas-phase hydrogenation reaction was studied using a catalyst fine enough to avoid any effect of pore diffusion. The rate equation is:

$$A + 2H_2 \rightarrow B$$

$$r = \frac{kP_A P_{H_2}}{(1+12P_B)^2}$$

a- For the following gas compositions, sketch the concentration gradients for A, H₂, and B for the case where the reaction is rapid enough to make P_{Aave} 10% less than P_A. Assume $D_A = 1 \setminus 4D_{H2}$

Case 1 Case 2

$P_A = 1$ atm	$P_A = 1$ atm
$P_B = 0$	$P_B = 0.5$ atm
$P_{H2} = 2 \text{ atm}$	$P_{H2} = 1.2 \text{ atm}$

b. Estimate the effectiveness factors for the two cases.

9-For the 1st order reaction $\mathbf{A} \rightarrow \mathbf{B}$ which takes place over a spherical catalyst particle: The maximum temperature rise over the catalyst is equal to 90 °F.

The effective diffusivity $De = 5*10^{6} \text{ ft}^{2}/\text{sec}$

The effective thermal conductivity ke =0.25 Btu/hr.ft. °F

The heat of reaction is Δ HR = -5000 Btu/mole

What is the concentration of component A on the surface of the catalyst particle?

10-For the 2nd order reaction $\mathbf{A} \to \mathbf{B}$ which takes place over a spherical catalyst particle:

The maximum temperature rise over the catalyst is equal to 100 oF.

The effective diffusivity $De = 5*10 6 \text{ ft}^2/\text{sec}$

The effective thermal conductivity ke =0.25 Btu/hr.ft °F

The heat of reaction is $\Delta HR = -5000$ Btu/mole

a) What is the concentration of component A on the surface of the catalyst particle?

b) What is the rate of mass transfer if the bulk concentration is $2*C_{As}$ and the mass transfer coefficient for the binary system is 1 cm/sec

11- Consider a porous catalyst pellet with a diameter of 6 mm. The porosity of the pellet is 0.55, the tortuosity factor is 4.0, the internal surface area is 200 m²/g, and the pellet density is 2.0 g/cm³. The following first-order reaction occurs in the pellet at a temperature of 475 K: A \rightarrow B where ($-r_A$) = kC_A

The rate constant at the reaction temperature has a value of 0.1 s⁻¹. The molecular weight of A and B is 16 g/mol. The bulk diffusion coefficient of A in the reacting mixture is $5 \times 10-5$ m²/s. Determine the value of the effectiveness factor in the pellet.

Part Three:

- Design of catalytic reactors.
- Isothermal and adiabatic fixed bed reactors.

3.1-Fixed-bed Reactors Design:

Reactions on solid catalysts are often carried out in tubes or pipes packed with spherical, cylindrical, or ring-shaped catalyst particles. For exothermic reactions, small-diameter tubes are used to permit nearly isothermal operation and prevent a temperature runaway. For small-scale operation, a cooling jacket can be placed around each pipe. But for large production, hundreds or thousands of tubes containing catalyst are mounted in a heat exchanger, with coolant circulated on the shell side. The design is more complicated than for homogeneous reactions, since there are radial as well as axial temperature gradients in the tubes, and there may also be significant concentration and temperature gradients near the surface of the individual particles.

In the chemical industry fixed-bed reactors are the standard type of reactors for heterogeneously catalyzed gas phase reactions (two phase reactors). Multiple layers of these screens constitute the catalyst bed that are used in commercial processes for the oxidation or synthesis.

Applications of fixed bed reactor can be described in table 2.

Basic Chemical Industry	Petrochemical Industry	Petroleum Refining
Steam reforming :	Ethylene oxide	Catalytic reforming
primary	Ethylene dichloride	Isomerization
secondary	Vinylacetate	Polymerization
Water-gas-shift		·
CO-methanation	Butadiene	(Hydro)desulfurization
Ammonia synthesis Sulfuric synthesis Acid synthesis	Maleic anhydride Phthalic anhydride	Hydrocracking
Methanol synthesis	Cyclohexane	
Oxo synthesis	Styrene	
	Hydrodealkylation	

 Table 2 : Main fixed-tube reactor processes.

Fixed-bed reactors can be operated under adiabatic or nonadiabatic conditions that depend of temperature change. Because of the necessity of removing or adding heat, it may not be possible to use a single large-diameter tube packed with catalyst. In this event the reactor may be built up of a number of tubes encased in a single body to prevent excessive temperatures. There are types of fixed-bed reactors as shown in figures 20and 21.

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Fig. 21 : Multitube Fixed bed reactor for exothermic and endothermic reactions.

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Consider an isothermal catalytic reaction in a PBR where there is no pressure drop and the catalyst pellets are uniformly packed & spherical. The kinetics are 1st order, and k, all physical parameters, and the inlet conditions (pure A in feed, $A \rightarrow$ products) are given. Derive an equation for X_A, taking into account the diffusion to and within each catalyst particle, but ignore diffusion down the length of the reactor.

The design equation for packed bed reactor is

Case 1: First order reaction ,both external and internal resistance are important.

 \emptyset_s is independent on conversion x , also the effectivnees factor. Then

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$$R_{Ap} = \left[\frac{1}{\frac{1}{\eta} + \frac{k_{1}}{k_{m}a_{es}}}\right]k_{1}C_{Ab}$$

$$\Omega = \left[\frac{1}{\frac{1}{\eta} + \frac{k_{1}}{k_{m}a_{es}}}\right]$$

$$\int \frac{dW}{F_{Ao}} = \int_{0}^{x} \left(\frac{dx}{\Omega k_{1}C_{Ab}}\right) = \int_{0}^{x} \frac{dx}{\Omega k_{1}C_{Ao}(1-x)}$$

$$\int \frac{dW}{F_{Ao}} = \frac{1}{\Omega k_{1}C_{Ao}} \int_{0}^{x} \frac{dx}{1-x}$$

$$\frac{W}{F_{Ao}} = \frac{-1}{\Omega k_{1}C_{Ao}} \ln(1-x)$$
The weight of Catalyst is:

$$W = \frac{-F_{Ao}}{\Omega k_{1}C_{Ao}} \ln(1-x)$$
Or to find the conversion from

$$x = 1 - e^{\frac{W * \Omega k_{1}C_{Ao}}{F_{Ao}}}$$
Since :

$$W = \rho_{cat} * V_{cat}$$

$$W = \rho_{cat} (1-e) * A_{c} * Z$$
And

$$F_{Ao} = C_{Ao} * A_{c} * u$$
 and $\rho_{bed} = \rho_{cat} (1-e)$

Where:

e = porosity of bed (void fraction). ρ_{bed} : bed density (kg/m³ bed) A_c : Cross section area of reactor or tube (m²). Z: reactor length (m). u : gas velocity (m/sec). F_{A_o} : molar flow rate (mole/sec). Then:

$$x = 1 - e^{\frac{-\rho_{cat} (1-e) * A_c * Z * \Omega k_1 C_{Ao}}{C_{Ao} * A_c * u}}$$
$$x = 1 - e^{\frac{-\rho_{bed * Z * \Omega k_1}}{u}}$$

$$\frac{Z}{u} = \frac{V(Reactor Volume)}{Q_o(Volumetric Flow rate)} = \frac{m^3}{\frac{m^3}{sec}} = \tau(Residant Time)$$
$$x = 1 - e^{-\rho_{bed}} * \Omega k_1 * \tau$$

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$$k^* =
ho_{bed} * \Omega k_1$$

$$x = 1 - e^{-k^* \tau}$$
$$C_A = C_{Ao} e^{-k^*}$$

Case 2: First order reaction, external mass transfer control.

τ

$$R_{Ap} = \left[\frac{1}{\frac{1}{\eta} + \frac{k_1}{k_m a_{es}}}\right] k_1 C_{A_b}$$

$$k_m a_{es} \gg \eta k_1$$

Then

$$R_{Ap} = k_m a_{es} C_{Ab}$$

$$\int \frac{dW}{F_{A_o}} = \int_0^x \left(\frac{dx}{k_m a_{es} C_{A_b}}\right) = \frac{1}{k_m a_{es} * C_{A_o}} \int_0^x \frac{dx}{(1-x)}$$

The weight of Catalyst is: $W = \frac{-F_{A_0}}{k_m a_{es} * C_{Ao}} \ln(1-x)$

$$W = \frac{F_{A_0}}{k_m a_{es} * C_{Ao}} \ln \frac{1}{1-x}$$

Or to find the conversion from $k_m a_{es} * C_{Ao} * W$

$$x = 1 - e^{-\frac{\kappa_m a_{es} * C_{Ao} * V}{F_{A_o}}}$$

$$x = 1 - e^{\frac{-\rho_{bed * Z * k_m a_{es}}}{u}}$$
$$x = 1 - e^{-k_m a_{es} * \tau * \rho_{bed}}$$
$$C_A = C_{Ao} e^{-k_m a_{es} * \tau * \rho_{bed}}$$

aes: external surface area of catalyst per catalyst mass.

$$a_{es} = \frac{6}{\rho_{cat} * d_p} \left(\frac{m^2}{kg}\right)$$

Case 3: First order reaction, internal diffusion control.

$$R_{Ap} = \left[\frac{1}{\frac{1}{\eta} + \frac{k_1}{k_m a_{es}}}\right] k_1 C_{Ab}$$

 $k_m a_{es} \ll \eta k_1$ $\Omega \rightarrow \eta$ $R_{Ap} = \eta k_1 C_{Ab}$

$$\int \frac{dW}{F_{A_o}} = \int_0^x \left(\frac{dx}{\eta k_1 C_{A_b}}\right) = \frac{1}{\eta k_1 C_{A_o}} \int_0^x \frac{dx}{(1-x)}$$

$$\eta \text{ and } \phi_s \text{ are not function of } x$$
$$\eta = \frac{1}{\phi_s} \left(\frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right)$$
$$\phi_s = \frac{R}{3} \sqrt{\frac{k_V}{D_e}}$$

The weight of Catalyst is:

$$W = \frac{-F_{A_0}}{\eta k_1 C_{A_0}} \ln(1-x)$$
$$W = \frac{F_{A_0}}{\eta k_1 C_{A_0}} \ln \frac{1}{1-x}$$

Or to find the conversion from

$$x = 1 - e^{-\frac{W*\eta k_1 C_{A_0}}{F_{A_0}}}$$

$$x = 1 - e^{-\rho_{bed}*\eta k_1*\tau}$$

$$C_A = C_{A_0} e^{-\rho_{bed}*\eta k_1*\tau}$$

The concentration and conversion profiles down a reactor of length Z for all cases are shown in Figure 22.



Fig. 22: Axial concentration (a) and conversion (b) profiles in a packed bed.

Example 1:

The decomposition of hydrazine over a packed bed of alumina-supported iridium catalyst is of interest . In a proposed study, a 2% hydrazine in 98% helium mixture is to be passed over a packed bed of cylindrical particles 0.25 cm in diameter and 0.5 cm in length at a gas-phase velocity of 15 m/s and a temperature of 750 K. The kinematic viscosity of helium at this temperature is $4.5 \, 10^{-4} \, m^2$ /s. The hydrazine decomposition reaction is believed to be externally mass transfer–limited under these conditions. If the packed bed is 0.05 m in length, what conversion can be expected? Assume isothermal operation.

Additional information

$$D_{AB} = 0.69 \times 10^{-4} \text{ m}^2/\text{s}$$
 at 298 K
Bed porosity: 30%
Bed fluidicity: 95.7%

Solution:

$$x = 1 - e^{-k_m a_{es} * \tau * \rho_{bed}}$$

$$C_A = C_{Ao} e^{-k_m a_{es} * \tau * \rho_{bed}}$$

Calculate the mass transfer coefficient k_m

$$\operatorname{Re} = \frac{d_p U}{\nu} = \frac{(3.61 \times 10^{-3} \text{ m})(15 \text{ m/s})}{4.5 \times 10^{-4} \text{ m}^2/\text{s}} = 120.3$$
$$D_{AB}(750 \text{ K}) = D_{AB}(298 \text{ K}) \times \left(\frac{750}{298}\right)^{1.75} = (0.69 \times 10^{-4} \text{ m}^2/\text{s})(5.03)$$

 D_{AB} (750 K) = 3.47 × 10⁻⁴ m²/s $Sc = \frac{\nu}{D_{ev}} = \frac{4.5 \times 10^{-4} \text{ m}^2/\text{s}}{3.47 \times 10^{-4} \text{ m}^2/\text{s}} = 1.30$ $\frac{k_m d_p}{D_{AB}} = 2 + 0.6 * \left(\frac{\rho * d_p * u}{u}\right)^{\frac{1}{2}} * \left(\frac{\nu}{D_{AB}}\right)^{\frac{1}{3}}$ $\frac{k_m d_p}{D_{AB}} = 2 + 0.6 * (120.3)^{\frac{1}{2}} * (1.3)^{\frac{1}{3}} = 9.23$ $k_m = \frac{9.23 * 3.47 * 10^{-4}}{3.61 * 10^{-3}} = 0.887 \frac{m}{sec}$ $\tau = \frac{Z}{u} = \frac{0.05}{15} = 0.0033 \, sec$ $a_{es} = \frac{6}{\rho_{cat} * d_n}$ $-k_m * \frac{6}{\rho_{cat} * d_p}$ $*\tau*(1-e)
ho_{cat}$ $x = 1 - e^{-k_m a_{es} * \tau * \rho_{bed}} = 1$ $x = 1 - e^{\frac{-6 \cdot k_m \cdot \tau \cdot (1-e)}{dp}}$ x = 1 - 0.17 = 0.83

3.2-Second Order Reaction in PBR:

The rate of mass transfer(M_A) from the bulk fluid to the external surface is. $M_A = k_m a_{es} (C_{Ab} - C_{As})$ The rate of reaction is given by: $r_A = \eta k_2 C_{AS}^2$

At equilibrium $M_A = r_A$ then $k_m a_{es} (C_{A_b} - C_{A_s}) = \eta k_2 C_{AS}^2$

$$C_{AS}^{2} + \left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)C_{AS} - \left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)C_{Ab} = 0$$

$$C_{AS} = \frac{-\left(\frac{k_m a_{es}}{\eta k_2}\right) + \sqrt{\left(\frac{k_m a_{es}}{\eta k_2}\right)^2 + 4\left(\frac{k_m a_{es}}{\eta k_2}\right)C_{Ab}}}{2}$$

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The general equation for irreversible reactions second order or higher can be estimated from the formula:

$$\phi_s = L_{\sqrt{\left(\frac{n+1}{2}\right)\frac{k_V * C_{AS}^{n-1}}{D_e}}$$

For second order reaction(n=2) and for spherical pellet L=R3

$$\phi_s = L \sqrt{\left(\frac{n+1}{2}\right) \frac{k_V * C_{AS}^{n-1}}{D_e}}$$
$$\phi_s = \frac{R}{3} \sqrt{\left(\frac{3}{2}\right) \frac{k_2 C_{AS}}{D_e}}$$

For second order reaction and for large values of the Thiele modulus, the effectiveness factor is calculated by two methods:

(a)
$$\eta = \frac{1}{\phi_s}$$

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

Consequently, for reaction orders greater than 1, the effectiveness factor decreases with increasing concentration at the external pellet surface (function of conversion). The preceding discussion of effectiveness factors is valid only far isothermal conditions. Note that the Thiele Modulus will be a function of position. For simple design procedure we use method (a).

Case 1: internal diffusion control. $C_{Ab} = C_{AS}$

$$r_{Ap} = \eta k_2 C_{Ab}^2$$

$$\int \frac{dW}{F_{A_{o}}} = \int_{0}^{x} \frac{dx}{r_{A_{p}}} = \int_{0}^{x} \frac{dx}{\eta \, k_{2} C_{Ab}^{2}} = \frac{1}{k_{2} C_{Ao}^{2}} \int_{0}^{x} \frac{dx}{(1-x)^{2} \eta}$$

$$\int \frac{dW}{F_{A_{o}}} = \frac{1}{k_{2} C_{Ao}^{2}} \int_{0}^{x} \frac{dx}{(1-x)^{2} \frac{1}{\varphi_{s}}}$$

$$\int \frac{dW}{F_{A_{o}}} = \frac{1}{k_{2} C_{Ao}^{2}} \int_{0}^{x} (\frac{\varphi_{s}}{(1-x)^{2}}) \, dx$$

$$\varphi_{s} = \frac{R}{3} \sqrt{\left(\frac{3}{2}\right) \frac{k_{2} C_{As}}{D_{e}}} = \frac{R}{3} \sqrt{\left(\frac{3}{2}\right) \frac{k_{2} C_{Ab}}{D_{e}}}$$

$$\int \frac{dW}{F_{A_{o}}} = \frac{1}{k_{2} C_{Ao}^{2}} \left(\int_{0}^{x} \frac{\frac{R}{3} \sqrt{\left(\frac{3}{2}\right) \frac{k_{2} C_{Ab}}{D_{e}}}}{(1-x)^{2}} \, dx \right)$$

Define

$$c = \frac{R}{3} \sqrt{\frac{3}{2} * \frac{k_2}{D_e}}$$

$$\int \frac{dW}{F_{A_0}} = \frac{c}{k_2 C_{A0}{}^2} \left(\int_0^x \frac{C_{Ab}{}^{0.5}}{(1-x)^2} dx \right)$$

$$\int \frac{dW}{F_{A_0}} = \frac{C_{A0}{}^{0.5} * c}{k_2 C_{A0}{}^2} \left(\int_0^x \frac{(1-x){}^{0.5}}{(1-x)^2} dx \right)$$

$$\int \frac{dW}{F_{A_0}} = \frac{C_{A0}{}^{0.5} * c}{k_2 C_{A0}{}^2} \left(\int_0^x \frac{1}{(1-x){}^{1.5}} dx \right)$$

The integration could be calculated numerically or analytically The integral value =3 $(1 - x^{0.5})$

$$\int \frac{dW}{F_{A_o}} = \frac{C_{A_o}^{0.5} * c}{k_2 C_{A_o}^2} * 3(1 - x^{0.5})$$

$$W = \frac{3 c * F_{A_0}}{k_2 C_{A_0}^{1.5}} (\sqrt{x} - 1)$$

Note:

The units of
$$\left(\frac{3 c * F_{A_0}}{k_2 C_{A_0}^{1.5}}\right)$$
 is kg_{cat}
 $W = \rho_{cat} (1-e) * A_c * Z$

Case 2: mass transfer control: From equation 2

$$C_{AS} = \frac{-\left(\frac{k_m a_{es}}{\eta k_2}\right) + \sqrt{\left(\frac{k_m a_{es}}{\eta k_2}\right)^2 + 4\left(\frac{k_m a_{es}}{\eta k_2}\right)C_{Ab}}}{2}$$

$$C_{AS}^{2} = \left(\frac{-\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right) + \sqrt{\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)^{2} + 4\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)C_{Ab}}}{2}\right)^{2}$$

$$C_{AS}^{2} = \frac{\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)^{2} + 2\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)C_{Ab} - \frac{k_{m}a_{es}}{\eta k_{2}}\sqrt{\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)^{2} + 4\left(\frac{k_{m}a_{es}}{\eta k_{2}}\right)C_{Ab}}}{2}$$

 $C_{As} \approx 0$ in most mass transfer-limited reactions Then

$$\left(\frac{k_m a_{es}}{\eta k_2}\right)^2 + 2\left(\frac{k_m a_{es}}{\eta k_2}\right)C_{Ab} = \frac{k_m a_{es}}{\eta k_2}\sqrt{\left(\frac{k_m a_{es}}{\eta k_2}\right)^2 + 4\left(\frac{k_m a_{es}}{\eta k_2}\right)C_{Ab}}$$

$$\frac{k_m a_{es}}{\eta k_2} + 2C_{Ab} = \sqrt{\left(\frac{k_m a_{es}}{\eta k_2}\right)^2 + 4\left(\frac{k_m a_{es}}{\eta k_2}\right)C_{Ab}}$$

$$C_{Ab} = \frac{\sqrt{\left(\frac{k_m a_{es}}{\eta k_2}\right)^2 + 4\left(\frac{k_m a_{es}}{\eta k_2}\right)C_{Ab}} - \frac{k_m a_{es}}{\eta k_2}}{2}$$

$$\varphi_s = \frac{R}{3}\sqrt{\left(\frac{3}{2}\right)\frac{k_2 C_{AS}}{D_e}} = \frac{R}{3}\sqrt{\left(\frac{3}{2}\right)\frac{k_2 C_{Ab}}{D_e}}$$

$$\eta = \frac{1}{\varphi_s}$$

$$C_{Ab} = C_{Ae}(1-x)$$

The above equations solved by trial and error to C_{Ab} , ϕ_s , and η at different x

X	Øs	η
0	of Lit	
0.1	- GP	
0.2	The second second	
X final		

Example 2:

Design a packed bed reactor in which the second order reaction $A \rightarrow B + 2C$ is being conducted under internal diffusional limiting conditions and the exit conversion is 0.8. The fluid is being pumped into the reactor at a superficial velocity of u = 4 m/sec. The reaction is being conducted at temperature $T = 260^{\circ}C = 533K$ and at inlet pressure of P = 4.94 atm.

$$D_e=2.667 * 10^{-8} \text{ m}^2 / \text{sec:} \ \rho_{cat} = 2000 \frac{kg}{m^3} : d_p = 0.4 \ cm \ \rho_{gas} = 1.9 \frac{kg}{m^3}$$

 $k = 50 \frac{m^6}{gm_{cat}.mol.sec}$: $F_{Ao} = 1 \frac{mol}{sec}$ $D_C = 1 m$ Solution: $F_A = F_{Ao}(1-x)$ $F_B = F_{Ao}x$ $\frac{F_C = 2F_{Ao}x}{F_T = F_{Ao}(1+x)}$ $\boldsymbol{C}_{A} = \frac{F_{A}}{\nu} = \frac{F_{Ao}(1-x)}{\nu_{o}(1+\epsilon x)} = \boldsymbol{C}_{Ao} \frac{1-x}{1+\epsilon x}$ $\epsilon = 3 - 1 =$ $C_A = C_{Ao} \frac{1-x}{1+2x}$ $C_{Ao} = \frac{4.94 \text{ atm. kmol. K}}{0.082m^3 \text{ atm } * 533K} = 0.13302 \frac{\text{kmol}}{m^3} = 133.02 \frac{\text{mol}}{m^3}$ $\phi_{s} = \frac{R}{3} \sqrt{\left(\frac{3}{2}\right) \frac{k_{2} C_{AS}}{D_{s}}} = \frac{R}{3} \sqrt{\left(\frac{3}{2}\right) \frac{k_{2} C_{AS}}{D_{s}}}$ $\phi_{s} = \frac{0.4 * 10^{-2} (m)}{2 * 3} \sqrt{\frac{3 * 50m^{6} \cdot sec * mol * 2000 kgcat * C_{As}}{2 * 1 * 10^{-3} kgcat \cdot mol \cdot sec * 2 \cdot 667 * 10^{-8} m^{2}m^{3} * m^{3}}}$ $\phi_s = 5.0 * 10^5 C_{As}^{0.5}$ $\eta = \frac{1}{\phi_{\rm s}} = 2.0 * 10^{-5} C_{As}^{-0.5}$

When internal diffusion control. $C_{Ab} = C_{AS}$ Then $\eta = \frac{1}{\varphi_s} = 2.0 * 10^{-5} C_{Ab}^{-0.5}$ $\eta = 2.0 * 10^{-5} C_{Ao}^{-0.5} * \left(\frac{1-x}{1+2x}\right)^{-0.5}$

$$\eta = 1.734 * 10^{-6} * \left(\frac{1-x}{1+2x}\right)^{-0.5}$$

At inlet x=0 then $\eta = 1.734 * 10^{-6}$ At outlet x=0.8 then $\eta = 6.25 * 10^{-6}$

The internal diffusion is very strong and can not be neglected

$$r_{Ap} = \eta k_2 C_{Ab}^{2}$$

$$\int \frac{dW}{F_{A_0}} = \int_{0}^{x} \frac{dx}{r_{A_p}}$$

$$\int_{0}^{x} \frac{dx}{\eta k_2 C_{Ab}^{2}} = \frac{1}{k_2 C_{A0}^{2}} \int_{0}^{x} \frac{dx}{(1-x)^2 \mathbf{1} \cdot \mathbf{734} * \mathbf{10^{-6}} * (\frac{1-x}{1+2x})^{-\mathbf{0.5}}}$$

$$\int \frac{dW}{F_{A_0}} = \frac{gm_{cat} \cdot mol. \sec * m^{6}}{50m^{6} * (\mathbf{133.02})^{2}mol^{2} * \mathbf{1} \cdot \mathbf{734} * \mathbf{10^{-6}}} \int_{0}^{x} \frac{dx}{(1-x)^{2} (\frac{1-x}{1+2x})^{-\mathbf{0.5}}}$$

$$W = \frac{1 * mol * gm_{cat} \cdot mol. sec * m^{6}}{sec * 50m^{6} * (133.02)^{2}mol^{2} * 1.734 * 10^{-6}} \int_{0}^{0.8} \left(\frac{\left(\frac{1-x}{1+2x}\right)^{0.5}}{(1-x)^{2}}\right) dx$$

$$W = 0.652 \int_{0}^{0.8} \frac{\left(\frac{1-x}{1+2x}\right)^{0.5}}{(1-x)^2} dx$$

 $W = 0.652(gm_{cat}) * Integral Value$

$$W = \rho_{cat} \ (1-e) * A_c * Z$$

Then find the reactor length Z.

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Homework Problems:

1-A first-order, gas-phase reaction $A \rightarrow 2B$ is performed in a PBR at 400 K and 10 atm. Feed rate is 5 mol/s containing 20% A and the rest inerts. The PBR is packed with 8 mm-diameter spherical porous particles.

The intrinsic reaction rate is given as: $r_A = 3.75 C_A \text{ mol/kg(cat).sec.}$ Bulk density of the catalyst is 2.3kg/liter. The diffusivity is 0.1 cm²/s.

a. What is the value of the internal effectiveness factor? What does it signify?

b. How much catalyst (kg) is required to obtain a conversion of 75% in the reactor?

c- what is the percentage of internal and external resistances.

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2-Ethylene oxide (EO) is a major commodity chemical, with a production of about 3 million tons/a in the US (1997). (At 1997 price levels for ethylene oxide this orresponds to a market value of about \$4 billion!) Major uses for EO are antifreeze (30%), polyester (30%), and surfactants and solvents (~ 10% each).

Your consulting company MeMyself&OthersInc. has taken on a new assignment to design a fixed-bed reactor for EO production via the catalytic reaction of ethylene with oxygen ($C_2H_4+0.5 O_2 \rightarrow EO$), using a secret (but silver-based) catalyst.

The reactor is operated isothermally at 260°C, and ethylene is fed at a rate of 200 mol/h at an inlet pressure of 10 atm. A stoichiometricamount of oxygen is added through an air feed. The reactor is a multitubularreactor with 1000 parallel tubes, each with an inner diameter of 1.5"(38.1 mm). The tubes are filled with catalyst particles (diameter = 0.25"(6.35 mm), particle density ρ_{cat} = 120 lb/ft³ = 1922 kg/m³), resulting in a bed void fraction of ε = 0.45.

The kinetics have been determined as: $-r'_{C2H4} = k'P_{C2H4}^{1/3}P_{O2}^{2/3}[mol/(lb cat .h)]$ with a rate coefficient at 260°C of k'= 4 mol/(atm.lb . cat h).

How much catalyst is needed to achieve 60% ethylene conversion? (For simplicity, assume that the properties of the reaction mixtures are at this temperature always identical to those of air.)

3- The use of a differential reactor to study the formation of methane from hydrogen and carbon monoxide over a nickel catalyst gave the following rate of formation of methane:

$$r_{CH_4} = \frac{0.0183 \, p_{H_2}^{1/2} \, p_{CO}}{1 + 1.5 \, p_{H_2}} \, , \, mole \, / \, g \, cat.s$$

Suggest a mechanism and rate-limiting step that is consistent with the experimental observation for the reaction: $CO + 3H_2 \rightarrow CH_4 + H_2O$.

It is desired to produce 20 tons/day of CH₄. Calculate the catalyst weights necessary to achieve 80% conversion in a fixed bed reactor. The feed consists of 75% H₂ and 25% CO at a temperature of 500°F and a pressure of 10 atm. Assume both molecular and atomic hydrogen are adsorbed on the surface.

4- The following second order liquid-phase catalytic reaction is conducted in an isothermal fixed-bed reactor: $A \rightarrow B$ $r = kC_A^2$

The intrinsic rate constant is 16 L/mol . s. The feed is 0.8 L/s of a solution of A with the concentration of A at 4 mol/L. Spherical catalyst pellets of radius 0.12cm are used to pack the reactor. The catalyst has a pellet density of 0.88 g/cm³, and the reactor bed density is 0.5 g/cm³. The effective diffusivity of A inside the catalyst pellet is $3.14 \times 10^{-3} \text{ cm}^2$ /s. You wish to achieve 99.9% conversion of A.

(a) First neglect both diffusional resistance and mass transfer resistance. What is the mass of catalyst required to achieve the desired conversion?

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(b) Next consider diffusional resistance but neglect mass transfer resistance. What are the Thiele modulus and effectiveness factor at the entrance of the reactor? What are the Thiele modulus and effectiveness factor at the exit of the reactor? Given these two effectiveness factors, compute an upper bound and a lower bound on the mass of catalyst required to achieve the desired conversion.

(c) Next consider both diffusional resistance and mass transfer resistance. Assume that we have estimated the mass transfer coef®cient to be $k_m = 0.35$ cm/s.

Find the effectiveness factor at the entrance of the reactor. Find the effectiveness factor at the exit of the reactor.

Given these two effectiveness factors, compute an upper bound and a lower bound on the mass of catalyst required to achieve the desired conversion.

(d) Compare your answers to parts (a)to(c). Discuss whether diffusion and/or mass transfer limitations are important in this packed bed reactor.

5- A first order heterogeneous reaction: $A \rightarrow C$ is performed catalytically in a packed bed reactor working at steady state using porous spherical catalyst particle with iameter of 0.15 cm. The diameter of the reactor is 60 cm, the catalyst density is 2.3 gm/cm³. The bed voidage is 0.3 and the porosity of the catalyst particle is 0.4. The volumetric flow rate to the reactor is 50000 cm³/sec and the reaction rate constant is 10 (cm³/gm cat. sec),and diffusion coefficient inside the pellet is 0.5 cm²/sec. The inlet concentration of A into the reactor is 8.5*10⁻² mole/cm³. Assume isothermal operation and negligible dispersion. Calculate:

- a) Thiele modulus.
- b) The effectiveness factor.
- c) The amount of the catalyst required for 85% conversion.

6-A first order reaction $A \rightarrow B$ Where $-r_A = kC_A \mod/(\text{gm. cat. sec.})$ is performed catalytically in a packed bed reactor working at steady state using non porous spherical catalyst particles with radius of 0.075 cm. The diameter of the reactor is 35 cm. The density of the catalyst is 2.2 gm/cm³ and the bed voidage is 0.28. The reaction rate constant is 0.15 (cm³)/(gm cat. sec.). The volumetric flow rate to the reactor is 20000 cm³/sec and the external mass transfer coefficient is 0.08 cm/sec. Assume isothermal operation and negligible dispersion. Calculate:

a) The total length of the reactor required for 65% conversion of A.

b) The amount of the catalyst needed for 95% conversion of A.

c) The conversion if the length of the reactor is 1 m.

7-A first order reaction: $A \rightarrow C$ is performed catalytically in a packed bed reactor working at steady state using porous spherical catalyst particle with diameter of 0.15 cm.The diameter of the reactor is 120 cm, the catalyst density is 2.0 gm/cm³. The bed voidage is 0.3 and the porosity of the catalyst particle is 0.4. The volumetric flow rate to the reactor is 20000 cm³/sec and the reaction rate constant is 1 (cm³/gm cat. sec), and diffusion coefficient inside the pellet is 2 cm²/sec. The inlet concentration of A

into the reactor is 1.5*10⁻³ mole/cm³. Assume isothermal operation and negligible dispersion.Calculate:

- a) Thiele modulus.
- b) The effectiveness factor.
- c) The length of the reactor required for 65% conversion.

d) The amount of the catalyst needed for 85% conversion

8- We want to build a packed bed reactor filled with 1.2-cm porous catalyst particles (density = 2000 kg/m³, $D_e = 2 \times 10^{-6} \text{ m}^3/\text{m}$ cat. s) to treat 1 m³/s of feed gas (1/3 A, 1/3 B, 1/3 inert) at 336 C and 1 atm to 80% conversion of A. Experiments with fine catalyst particles which are free from diffusional resistance show that

 $A + B \rightarrow R + S$, n = 2, $k' = 0.01 \text{ mol} \cdot \text{kg} \cdot \text{s}$

How much catalyst must we use?

9-In aqueous solution, and in contact with the right catalyst, reactant A is converted to product R by the elementary reaction $A \rightarrow R$. Find the mass of catalyst needed in a packed bed reactor for 90% conversion of 10⁴mol A/hr of feed having $C_{Ao}=10^3$ mol/m³. For this reaction k''' = 8 x 10⁻⁴m³/m³ bed. s and k''' = 2 m³/m³ bed. s Additional data:

Diameter of porous catalyst pellets= 6 mm

Effective diffusion coefficient of A in the pellet = $4 * 10^4 \text{ m}^3/\text{m}$ cat. s

Voidage of packed bed = 0.5

Bulk density of packed bed = 2000 kg/m^3 of bed

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10-A packed bed reactor converts A to R by a first-order catalytic reaction, $A \rightarrow R$. With 9mm pellets the reactor operates in the strong pore diffusion resistance regime and gives 63.2% conversion. If these pellets were re-placed by 18 mm pellets (to reduce pressure drop) how would this affect the conversion?

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Part Four:

- Kinetics of catalyst Poisoning.
- Kinetics of catalyst deactivation and regeneration.

4.1-Catalyst Deactivation:

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. For any catalytic process, the life of catalyst is a major economic factor. To regenerate or replace deactivated catalysts, the process needs to be shutdown and consequently production is disrupted. Subsequent separation and regeneration of catalysts also involve time and cost. Therefore, deactivation of catalysts increases the cost of production significantly. Hence, any catalytic process will be economically viable only if regenerations are required infrequently and can be done inexpensively. A catalyst can be deactivated in three ways.

I. Poisoning

II. Fouling

III. Sintering or phase transformation

I. Poisoning

Poisoning basically involve chemisorption of reactants or products or feed impurities on the active sites of the catalyst surface, thereby decreasing the number of active sites available for catalytic reactions. Since poisoning involves chemisorptions, it is known as chemical deactivation. This process can be reversible or irreversible. Compound of sulphur and other materials are frequently chemisorbed on nickel, copper and Pt catalysts. In reversible poisoning, the strength of adsorption bond is not great and activity is regained when the poison is removed from the feed. When the adsorbed material is tightly held on the active sites, poisoning is irreversible and permanent.

II. Fouling

Rapid deactivation can be caused by physical deposition of substance on the active sites of catalysts. Carbon deposition on catalysts used in petroleum industry falls in this category. Carbon covers the active site of the catalysts and may also partially plug the pore entrance. This type of deactivation is partially reversible and regeneration can be done by burning in air.

$$C \xrightarrow{air/high \ temperature} CO / CO,$$

III. Sintering or phase transformation

Because of local high temperature, support of catalysts or catalyst itself may undergo structural modification or sintering causing a reduction in specific surface area or change in chemical nature of catalytic agent so that it becomes catalytically inactive. Hence, poisoning and fouling are dependent on concentration of reactant or product or impurities. On the other hand, sintering and phase transformation may be assumed to be independent of fluid phase composition. This is also therefore known as independent deactivation. Figure 23 shows the major types of deactivation.

Major types of deactivation in heterogeneous Catalysis



Figure 23 : the major types of deactivation inhetrogenous catalysis.

Steps to reduce deactivation: Following steps can be taken to reduce the possibility of deactivation of catalysts :

- a. Removal of poison material form feed
- b. Use of hydrogen which reduces coking

c. Removal of hot spot by proper design of reactor /process control to prevent any thermal deactivation.

4.2-Mechanism of Catalysts Deactivation:

The deactivation of catalysts can occur by different mechanism as explained below :

1. Parallel deactivation

Reactant (A) produces a side product (P) which can deposit on the surface thereby deactivating it. Deposition depends on reactant concentration.



2. Series deactivation :

Reaction product (R) can decompose or react further to produce material (P) that deposits and deactivates the surface. In this case, deposition depends on product concentration.

 $A \to R \to P \downarrow$

3. Side-by-side deactivation:

In this mechanism, impurity in feed (P) deposits on the surface deactivating it. Deposition depends on concentration of impurities in the feed.

$$A \to R$$
$$P \to P \downarrow$$

4. Independent deactivation :

This catalyst decay involves structural modification or sintering of catalyst surface caused by exposure of catalysts to extreme conditions such as high temperature. This decay is dependent on time that the catalyst spends in high temperature conditions and is independent of the materials in the fluid.

4.3-Deactivation kinetics :

Activity of catalysts pellet at any time is defined as

Reaction rate can be considered as function of temperature, reactant concentration and present activity of the catalysts pellet. Therefore for n^{th} order reaction, rate can be written as

where a is the present activity of the catalyst.

Similarly, deactivation rate can be considered as function of temperature, concentration of substance that deactivates the catalyst (which can be reactant,

product or impurities) and present activity of the catalyst pellet. Hence, deactivation rate can be given as,

i = A (reactant), R (product), P(3rd substance)

Here d is called order of deactivation, k_d is deactivation rate constant and \mathbf{n}' is the concentration dependency.

Deactivation rate for different types.

1. Parallel , $A \rightarrow R + P \downarrow$

Reaction rate is $-r_A' = kC_A''a$

Deactivation rate is

$$-\frac{da}{dt} = k_d C_A^{n'} a^d$$

d = order of deactivation

2. Series $A \rightarrow R \rightarrow P \downarrow$

Reaction rate is $-r_{A}' = kC_{A}''a$

Deactivation rate is $-\frac{da}{dt} = k_d C_R^{n'} a^d$ 3. Side-by-side deactivation, $P \rightarrow P \downarrow$

Reaction rate is

$$-r_{A}' = kC_{A}^{n}a$$

Deactivation rate is

$$-\frac{da}{dt} = k_d C_P^{n'} a^d$$

4. Independent deactivation

Reaction rate is $-r'_{A} = kC''_{A}a$

Deactivation rate is $-\frac{da}{dt} = k_d a^d$

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4.3.1-Deactivation Kinetics for Sintering:

Most commonly used decay law for sintering is second order with respect to present activity.

$$\mathbf{r}_{\mathrm{d}} = -\frac{\mathrm{d}\mathbf{a}}{\mathrm{d}t} = \mathbf{k}_{\mathrm{d}} \, \mathbf{a}^2 \tag{4}$$

The k_d is the sintering decay constant. Integration with a=1 at time t=0 gives

$$\mathbf{a}(\mathbf{t}) = \frac{1}{1 + \mathbf{k}_{\mathrm{d}} \mathbf{t}} \tag{5}$$

Activity can be measured in terms of amount of sintering. If the **total active surface** area of the catalyst is S_{ao} at t = 0 and S_a at any time t, then activity can be written as

$$\mathbf{a}(\mathbf{t}) = \frac{\mathbf{S}_{\mathbf{a}}}{\mathbf{S}_{\mathbf{a}\mathbf{o}}} \tag{6}$$

From equation (5) and (6), we obtain

$$\mathbf{S}_{\mathbf{a}} = \frac{\mathbf{S}_{\mathbf{a}\mathbf{o}}}{\mathbf{1} + \mathbf{k}_{\mathbf{d}}\mathbf{t}} \tag{7}$$

The sintering decay constant k_d is given as:

 E_d is the decay activation energy. For reforming of heptanes on Pt /Al₂O₃ value of E_d is in the order of 70 kcal/mol.

4.3.2-Deactivation Kinetics for Coking or Fouling:

Various empirical relations are available for calculation of amount of coke deposited on catalyst surface after a time t.

$$C_c = At^n$$

 C_c is the concentration of carbon on the surface in g/m². The 'n' and 'A' are fouling parameter functions of feed rate. Representative value of A and n for cracking of light gas oil is 0.47 and 0.5 respectively when 't' is in minute.

The activity can be related to amount of coke deposited on the surface by following relation :

.....(9)

$$a = \frac{1}{1 + k_c C_c^p}$$

1

Substituting value of C_c from relation (9), in term of process time, activity can be expressed as shown below.

(

 $a = \frac{1}{1 + 7.6t^{1/2}}$ ∵t in seconds

Other dimensionless fouling correlations are also developed by several groups.

4.3.3-Deactivation Kinetics for Poisoning:

For petroleum feed containing trace impurities such as sulfur, the poisoning reaction can be written as $P+S \rightarrow PS$

The rate of deactivation is given as

$$\mathbf{r}_{\mathbf{d}} = -\frac{\mathbf{d}\mathbf{a}}{\mathbf{d}\mathbf{t}} = \mathbf{k}_{\mathbf{d}}^{'}\mathbf{C}_{\mathbf{p}}^{\mathbf{m}}\mathbf{a}^{\mathbf{q}} \qquad (12)$$

The C_p is the concentration of poison in feed. The 'm' and 'q' are respective orders. The rate of removal of poison from the reactant by catalyst sites is proportional to the number of sites that are not poisoned ($C_{to} - C_{ps}$) and concentration of poisons in the gas phase, C_p . The C_{ps} is the concentration of poisoned sites and C_{to} is the total number of fresh sites initially available. Then rate of removal of poison is equal to rate of formation of poisoned site and is given as

Dividing throughout by C_{to} and if 'f' is the fraction of the total number of the sites that have been poisoned then equation (13) can be written as

The fraction of sites available for adsorption (1-f) is essentially the activity a (t). Then equation (14) becomes

$$-\frac{\mathrm{d}\mathbf{a}}{\mathrm{d}\mathbf{t}} = \mathbf{a}_{\mathbf{t}}\mathbf{k}_{\mathbf{d}}\mathbf{C}_{\mathbf{p}} \tag{15}$$

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4.4-Determination of Deactivation Kinetic Parameters:

Case 1 : Consider a reaction in a mixed reactor under constant flow condition. Let **independent deactivation occur**. Assume both the main reaction and deactivation reaction to be first order with respect to activity 'a'. Then,

Reaction rate $-r_A = kC_A a$

Deactivation rate
$$-\frac{da}{dt} = k_d a$$
(16)
Integrating equation (16) gives
 $-\int_{a_0}^{a} \frac{da}{a} = k_d \int_{0}^{t} dt$
Or $[\ln a]_{a_0}^{a} = -k_d t$ a_o is initial activity
 $\ln \frac{a}{a_0} = -k_d t$ or $\frac{a}{a_0} = \exp(-k_d t)$
or $a = a_0 \exp(-k_d t)$ $a_0 = 1$
For mixed reactor, $\frac{W}{F_{A0}} = \frac{X_A}{-r_A}$
Substituting expression for rate from equation (6)
 $\frac{W}{F_{A0}} = \frac{X_A}{kC_A a}$
Now, $X_A = 1 - \frac{C_A}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}}$
Hence, substituting for X_A , $\frac{W}{F_{A0}} = \frac{X_A}{kC_A a} = \frac{C_{A0} - C_A}{kC_{A0}C_A}$
or $\frac{WkC_{A0}a}{F_{A0}} = \frac{C_{A0} - C_A}{C_A}$ or $\frac{WkC_{A0}a}{F_{A0}} = \frac{C_{A0}}{C_A} - 1$

.....(21)

Or
$$\frac{C_{A0}}{C_A} - 1 = ka \left[\frac{WC_{A0}}{F_{A0}} \right]$$
(19)

Or
$$\frac{C_{A0}}{C_A} - 1 = ka\tau_w$$
 $\because \tau_w = \frac{WC_{A0}}{F_{A0}}$(20)

 τw is called the weight time similar to space-time τ . C_A and 'a' vary with time Substituting,

 $a = \exp\left(-k_{d}t\right)$

in equation (20)

Or
$$\frac{C_{A0}}{C_A} - 1 = k\tau_{w} \exp\left(-k_d t\right)$$

Or
$$\ln\left[\frac{C_{A0}}{C_A}-1\right] = \ln\left(k\tau_w\right) - k_d t$$

Plotting $\ln \left[\frac{C_{A0}}{C_A} - 1 \right]$ versus 't' gives a straight line of slope of $-k_d$ and intercept

 $\ln(k\tau_w)$



Fig. 24. Plot to determine the rate constant and the deactivation rate constant for a reaction over deactivating catalyst. (For mixed reactor, constant flow and independent deactivation)

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Case II : Consider a reaction in a mixed reactor under changing flow condition so that concentration is constant. Let parallel deactivation occur. Assume the main reaction to be nth order and the deactivation reaction to be of first order in activity 'a'.

Parallel deactivation
A
Parallel deactivation
$$A
P \downarrow$$
Rate equation $-r_{A} = kC_{A}^{n}a$
Deactivation rate $-\frac{da}{dt} = k_{d}C_{A}^{m}a^{d}$
Since concentration is constant,
 $-r_{A} = kC_{A}^{n}a = k'a$
 $\therefore k' = kC_{A}^{n}$
 $-\frac{da}{dt} = k_{d}C_{A}^{m}a^{d} = k'_{d}a^{d}$
For mixed reactor,
 $\frac{W}{F_{A0}} = \frac{X_{A}}{-r_{A}} = \frac{X_{A}}{k'a} = \frac{C_{A0} - C_{A}}{k'aC_{A0}}$
Or
 $\frac{WC_{A0}}{F_{A0}} = \frac{C_{A0} - C_{A}}{k'a}$
Or
 $\tau_{w} = \frac{C_{A0} - C_{A}}{k'a}$
 $\therefore \tau_{w} = \frac{WC_{A0}}{F_{A0}}$
(23)
Now, $-\frac{da}{dt} = k'_{a}a^{d}$

For first order activity, d = 1Again, $a = \exp(-k_d t)$ $\therefore a_0 = 1$

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Then substituting '*a*'in equation (23)

Or
$$\ln \tau_w = \ln \left[\frac{C_{A0} - C_A}{k'} \right] + \ln \left(k'_d t \right)$$
(25)

Plotting $\ln \tau_{w}$ versus 't' gives a straight line of slope of k_{d} and intercept $\ln \left| \frac{C_{A0} - C_{A}}{k'} \right|$.



Fig. 25 . Plot to determine rate constant and deactivation rate constant for a reaction over deactivating catalysts for mixed reactor, changing flow condition and parallel deactivation

Example 1:

We plan to run an isomerization of $A \rightarrow R$ in isothermal packed bed reactor (pure A feed, F_A , = 5 kmol\hr, W = 1ton catalyst, P = 3 atm, T = 730 K). The catalyst deactivates so we plan to make 120 day runs, then regenerate the catalyst.

(a) Plot conversion and activity versus time for the run

(b) find x for the 120 day run

The rate of reaction with C_A in mol/m³ is described by

$$-r'_{\rm A} = 0.2 \ C_{\rm A}^2 \mathbf{a} \frac{\mathrm{mol} \ \mathrm{A}}{\mathrm{kg} \, \mathrm{cat} \cdot \mathrm{hr}}$$

and the rate of deactivation is given by

(a) . . .
$$-\frac{d\mathbf{a}}{dt} = 8.3125 \times 10^{-3}$$
, day⁻¹

This expression represents poisoning by a feed impurity.

(b) ...
$$-\frac{d\mathbf{a}}{dt} = 10^{-3}(C_{\rm A} + C_{\rm R})\mathbf{a}, \quad \mathrm{day}^{-1}$$

This represents poisoning by both reactant and by product, thus pore diffusion resistance does not influence the deactivation rate.

(c) . . .
$$-\frac{d\mathbf{a}}{dt} = 3.325 \, \mathbf{a}^2$$
, day^{-1}

This represents fairly strong pore diffusion resistance.

(d) . . .
$$-\frac{d\mathbf{a}}{dt} = 666.5 \, \mathbf{a}^3$$
, day^{-1}

This represents very strong pore diffusion resistance.

Solution:

In general for parts (a), (b), (c), and (d) we can write

$$-r'_{A} = 0.2 C_{A}^{2} \mathbf{a} \frac{\text{mol } A}{\text{kg cat} \cdot \text{hr}}$$

$$C_{A0} = \frac{p_{A0}}{\mathbf{R}T} = \frac{3 \text{ atm}}{\left(82.06 \times 10^{-6} \frac{\text{m}^{3} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (730 \text{ K})} = 50 \frac{\text{mol}}{\text{m}^{3}}$$

$$\tau' = \frac{WC_{A0}}{F_{A0}} = \frac{\left(1000 \text{ kg}\right) \left(50 \frac{\text{mol}}{\text{m}^{3}}\right)}{\left(5000 \frac{\text{mol}}{\text{hr}}\right)} = 10 \frac{\text{kg} \cdot \text{hr}}{\text{m}^{3}}$$

$$\int_{C_{A0}}^{C_{A}} \frac{dC_{A}}{0.2 C_{A}^{2} \mathbf{a}} = \frac{1}{0.2 \mathbf{a}} \left(\frac{1}{C_{A}} - \frac{1}{C_{A0}} \right)$$

or on rearranging

$$X_{\rm A} = 1 - \frac{C_{\rm A}}{C_{\rm A0}} = \frac{100 \, \mathbf{a}}{1 + 100 \, \mathbf{a}}$$

Let us now replace the activity term in the rate of reaction.

Part (a)

or

$$\mathbf{a} = 1 - 8.3125 \times 10^{-3} t$$

 $-\int_{1}^{\mathbf{a}} d\mathbf{a} = 8.3125 \times 10^{-3} \int_{0}^{t} dt$

evaluating X_A at various values of t gives the top most curve shown in Fig. 26.

 $x = \frac{100 * (1 - 8.3125 * 10^{-3}t)}{1 + 100 * (1 - 8.3125 * 10^{-3}t)}$ Part (b) Separating and integrating $-\frac{d\mathbf{a}}{dt} = 10^{-3}(C_{\rm A} + C_{\rm R})\mathbf{a}$ gives $\int_{a}^{1} \frac{d\mathbf{a}}{\mathbf{a}} = 0.05 \int_{0}^{t} dt$ $\mathbf{a} = e^{-0.05t}$ $x = \frac{100 * e^{-0.05t}}{1 + 100 * e^{-0.05t}}$

Part (c) Separating and integrating $-\frac{d\mathbf{a}}{dt} = 3.325 \,\mathbf{a}^2$ gives

$$\int_{1}^{a} \frac{d\mathbf{a}}{\mathbf{a}^2} = 3.325 \int_{0}^{t} dt$$

$$\mathbf{a} = \frac{1}{1+3.325 t}$$

$$x = \frac{\frac{100}{1+3.325 t}}{1+\frac{100}{1+3.325 t}}$$

Part (d) Separating and integrating $-\frac{d\mathbf{a}}{dt} = 666.5 \,\mathbf{a}^3$ gives

$$\mathbf{a} = \frac{1}{\sqrt{1 + 1333 t}}$$

$$x = \frac{100 * \frac{1}{\sqrt{1 + 1333t}}}{1 + 100 * \frac{1}{\sqrt{1 + 1333t}}}$$

From Fig. 26 we find by graphical integration that for the 120-day period, X_A .start= 0.99, X_A ,end, = 0.20 for

d = 0 the mean conversion $\overline{X}_{A} = 0.96$ d = 1 the mean conversion $\overline{\overline{X}}_{A} = 0.73$ d = 2 the mean conversion $\overline{\overline{X}}_{A} = 0.40$ d = 3 the mean conversion $\overline{\overline{X}}_{A} = 0.30$

It also clearly shows how different is the progress of the reaction with the different orders of deactivation.



Fig. 26: Decrease in conversion as a function of time for various deactivation orders.
Homework Problems:

1-Under conditions of strong pore diffusion the reaction $A \rightarrow R$ proceeds at 700°C on a slowly deactivating catalyst by a first-order rate

$$-r'_{\rm A} = 0.030 C_{\rm A} \mathbf{a}, \qquad [{\rm mol/gm} \cdot {\rm min}]$$

Deactivation is caused by strong absorption of unavoidable and irremovable trace impurities in the feed, giving third-order deactivation kinetics, or

$$-\frac{d\mathbf{a}}{dt} = 3\mathbf{a}^3, \qquad [1/day]$$

We plan to feed a packed bed reactor (W = 10 kg) with v = 100 liters\min of fresh A at 8 atm and 700°C until the catalyst activity drops to 10% of the fresh catalyst, then regenerate the catalyst and repeat the cycle,

(a) What is the run time for this operation?

(b) What is the mean conversion for the run?

2-At 730K the isomerization of $A \rightarrow R$ (rearrangement of atoms in the molecule) proceeds on a slowly deactivating catalyst with a second-order rate

$$-r'_{A} = k' C_{A}^{2} \mathbf{a} = 200 C_{A}^{2} \mathbf{a}, [\text{mol } A/\text{hr} \cdot \text{gm cat}]$$

Since reactant and product molecules are similar in structure, deactivation is caused by both A and R. With diffusional effects absent, the rate of deactivation is found to be

$$-\frac{d\mathbf{a}}{dt} = k_d (C_{\rm A} + C_{\rm R}) \mathbf{a} = 10(C_{\rm A} + C_{\rm R}) \mathbf{a}, \qquad \text{[day^{-1}]}$$

We plan to operate a packed bed reactor containing W = 1 ton of catalyst for 12 days using a steady feed of pure A, $F_{Ao} = 5$ kmol/hr at 730 K and 3 atm ($C_{Ao} = 0.05$ mol/liter).

(a) First evaluate -da/dt, τ , and then the general expression for 1 - X_A .

- (b) What is the conversion at the start of the run?
- (c) What is the conversion at the end of the run?
- (d) What is the average conversion over the 12-day run?

Relevant books:

1-Fogler, H.S. 1999. Elements of chemical reaction engineering. 3rd ed. Prentice-Hall.

2- Levenspiel, O. 1999. Chemical reaction engineering. 3rd ed. Wiley & Sons, Inc.,

3-Froment, G.F.; Bischoff, K.B.; De Wilde, J. 2011. Chemical reactor analysis and design. 3rd ed. John Wiley & Sons, Inc.

4-Missen, R.W.; Mims, C.A.; Saville, B.A. 1999. Introduction to chemical reaction engineering and kinetics. John Wiley & Sons, Inc., New York.

5-Carberry, J.J. Chemical and catalytic reaction engineering.

6-**Smith, J.M.** 1981. Chemical engineering kinetics. 3rd ed. McGraw-Hill Int. Book Co., Singapore.

7-Hill, Jr., C.G. 1977. Introduction to chemical engineering kinetics and reactor design. John Wiley & Sons.

This is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning. Winston Churchill November 10, 1942