

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – Chemical Reaction Engineering – SCHA1411

1.1 Basic Reaction Theory

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. The substance (or substances) initially involved in a chemical reaction are called reactants or reagents. Chemical reactions are usually characterized by a chemical change and they yield one or more products which usually have properties different from the reactants. Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with chemical equations which symbolically present the starting materials, end products, and sometimes intermediate products and reaction conditions.

Chemical reactions happen at a characteristic reaction rate at a given temperature and chemical concentration. Typically, reaction rates increase with increasing temperature because there is more thermal energy available to reach the activation energy necessary for breaking bonds between atoms.

1.2 Classification Of Reactions

Reactions may be classified by (a) the number of phases involved, (b) the presence or absence of

a catalyst, and (c) the nature of the overall reaction.

If all the reactants and products, and catalysts, if any, are in a single phase, the reaction is said to be homogeneous. An example is provided by the thermal cracking of ethane to ethylene

 $C2H6(g) \rightarrow C2H4(g) + H2(g)$

On the other hand, if more than one phase is involved, the reaction is said to be heterogeneous. An example is provided by the chemical vapour deposition (CVD) of Si on a substrate

 $SiH4(g) \rightarrow Si(s) + 2 H2(g)$

an enzyme called glucose isomerase catalyzes the isomerization of glucose to fructose in the liquid phase. It can be noted that this is the largest bioprocess in the chemical industry. As fructose is five times sweeter than glucose, the process is used to make high-fructose corn syrup for the soft drink industries. The overall reaction, as written, may represent either an elementary reaction or a non-elementary reaction. An example of the former is given by the gas-phase reaction

$$NO2(g) + CO(g) \rightarrow NO(g) + CO2(g)$$

Here NO is formed by the collision between molecules of NO2 and CO, and the rate expression conforms to the stoichiometry shown. On the other hand,

 $SiH4(g) \rightarrow Si(s) + 2 H2(g)$

represents a non-elementary reaction, as it actually proceeds by the sequence of reactions shown

below

 $SiH4(g) \rightarrow SiH2(g) + H2(g)$

 $SiH2(g) + * \rightarrow SiH2^*$

SiH2 * \rightarrow Si(s) + H2(g) where * represents an active site on the substrate.

Irreversible Reactions: Reactions that proceed unidirectionally under the conditions of interest

Reversible Reactions: Reactions that proceed in both forward and reverse directions under conditions of interest. Thermodynamics tells us that all reactions are reversible. However, in many cases the reactor is operated such that the rate of the reverse reaction can be considered negligible.

Homogeneous Reactions: reactions that occur in a single-phase (gas or liquid) NOx formation NO (g) + 0.5 O 2 (g) \leftrightarrow NO2 (g) Ethylene Production C 2 H 6 (g) \leftrightarrow C 2 H 4 (g) + H 2 (g) Heterogeneous Reactions: reactions that require the presence of two distinct phases Coal combustion C (s) + O 2 (g) \leftrightarrow CO 2 (g) SO 3(for sulphuric acid production) SO 2 (g) + 1/2 O 2 (g) \leftrightarrow SO 3 (g) Vanadium catalyst (s)

Single and Multiple reactions:

Single reaction: When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, then it is said to be 'single reaction'. Multiple reactions: When more than one stoichiometric equation is chosen to represent the observed changes, then more than one kinetic expression is needed to follow the changing composition of all the reaction components, it is said to be 'multiple reactions'. Multiple reactions may be classified as; Series reactions, Parallel reactions, and SeriesParallel reactions.

Elementary and Non-Elementary reactions

The reactions in which the rate equation corresponds to a stoichiometric equation are called elementary reaction. The reactions in which there is no correspondence between stoichiometry

and rate equation are known as Non-elementary reaction

1.3 Kinetic Models of Non- Elementary reactions

Free radicals, ions and polar substances, molecules, transition complexes are the various intermediates that can be formed in a non-elementary reaction.

In testing the kinetic models that involve a sequence of elementary reaction, we hypothesize the existence of two types of intermediates; Type-I: An unseen and unmeasured intermediate 'X' usually present at such small concentration that its rate of change in the mixture can be taken to be zero. Thus, we have [X] is small and d[X]/dt = 0. This is called the 'steady-state approximation'. Type-II: Where a homogeneous catalyst of initial concentration Co is present in two forms, either as free catalyst 'C' or combined in an appreciable extent to form the intermediate 'X', an accounting for the catalyst gives [Co] = [C] + [X]. We then also assume that either (dX/dt) = 0 or that the intermediate is in equilibrium with its reactants. Using the above

two types of approach, we can test the kinetic model or search a good mechanism; Trial and error procedure is involved in searching for a good mechanism.

1.4 Reaction rate and kinetics

Reaction rate

The rate expression provides information about the rate at which a reactant is consumed. Consider a single phase reaction $aA + b B \rightarrow rR + Ss$. Rate of reaction is defined as number of moles of reactant disappearing per unit volume per unit time

- rA = -1 dNA = (amount of A disappearing), mol ------V dt (volume) (time) $m^3.s$

In addition, the rates of reaction of all materials are related by

- rA = -rB = rR = rS

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a b c d

Rate constant k

When the rate expression for a homogeneous chemical reaction is written in the form

 $- rA = kCA^{a}CB^{b}....CD^{d}$, a+b+....+d = n

The dimensions of the rate constant k for the nth order reaction are

(time) ⁻¹(concentration)¹⁻ⁿ

Which for a first order reaction becomes $(time)^{-1}$

1.5 Factors affecting rate of reaction

Many variables affect the rate of reaction of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables. In heterogeneous systems, material may have to move from phase to phase during reaction; hence, the rate of mass transfer can be important. In addition, the rate of heat transfer may also become a factor. In short, the variables affecting the rate of the reaction are (1) temperature (2) Pressure and (3) Composition of materials involved.

1.6 Various forms of rate equation

Based on unit volume of the reaction mixture



Based on unit mass in fluid-solid system

-	$1 dN_i$	moles i formed
r; =	\overline{V} , dt	(volume of solid) (time)

Based on unit surface of solid in fluid-solid system or unit interfacial area in two fluid systems

	$1 dN_i$	moles i formed
$r_i = 1$	V, dt	(volume of reactor) (time)

Based on unit volume of solid in fluid-solid system

r'i =	$1 dN_i$	moles i formed
	W dt	(mass of solid) (time)

Based on unit volume of reactor when different from unit volume of the reaction mixture

	$1 dN_i$	moles i formed
r; =	S dt	(surface) (time)

Rates defined on various basis are interchangeable and the following may be shown

 $\begin{pmatrix} \text{volume} \\ \text{of fluid} \end{pmatrix} r_i = \begin{pmatrix} \text{mass of} \\ \text{solid} \end{pmatrix} r'_i = \begin{pmatrix} \text{surface} \\ \text{of solid} \end{pmatrix} r''_i = \begin{pmatrix} \text{volume} \\ \text{of reactor} \end{pmatrix} r''_i$

$Vr_i = Wr_i' = Sr_i'' = V_sr_i''' = V_rr_i'''$

Power law kinetics is simply put rate is proportional to concentration of species 1 to the power q 1 concentration of species 2 to the power q 2. So, products of all the, such C 1 raise to q 1 C 2 raise to q 2, up to C N raise to raise to q n. In a compact form, we can express this as rate equal to K, K is that proportionality constant, product of C j rise to q j, j going from 1 to N. So, q j is the order of the reaction with respect to species A j; and this is the simplest form of form of power law power law kinetics. Now, we call this q j as order with respect to A j and if you sum up all these q j s, we get q, what we call as overall overall order. reaction of hydrogen iodide getting decomposed to H 2 plus I 2. Now, it turns out for this particular reaction, the rate of reaction is proportional to concentration of hydrogen iodide raise to power 2. So, clearly in this case, q is 2 there is only one species in the reactant side, so our q j and q r q r are same. So, this is the this is the order of the reaction, so q can be integer. Let us take another example, decomposition of acetaldehyde to give us methane and carbon monoxide. Now, it turns out the rate of these reactions is proportional to concentration of acetaldehyde raise to power 3 by 2. So, q in this case is 3 by 2, or in other words, orders can be integers, they can be even fractions.

1.7 Molecularity

It is the number of molecules taking part in the reaction

e.g. $A \rightarrow C$: Unimolecular reaction

 $A+B \rightarrow C$: Bimolecular reaction

1.8 Order

It is defined as the sum of the powers to which the concentration terms are raised. The overall kinetic order of a reaction is defined by how many concentrations appear on the right side of the rate expression. The order of the reaction with respect to a particular species is defined by whether that species appears one or more times. For example, if the right side of the rate law is [A]^m[B]ⁿ, then the overall order of the reaction is m+n and the reaction is m'th order with respect to [A] and n'th order with respect to [B]. Zeroth order means that the reaction rate does not change as the concentration of a species is changed. There are no biochemical reactions that are zeroth order overall.

e.g. $A+B \rightarrow C$

-rA = kCACB

n (order) = 1 + 1 = 2

1.9 Concentration dependent term of rate equation

Rate of reaction is defined as number of moles of reactant disappearing per unit volume per unit

time

- rA = -1 dNA

V dt

If constant volume systems are considered, the rate of reaction is modified to

- rA = - dCA

dt

The definition of rate of a chemical reaction describing change in molar concentration with respect to time, i.e., is not general and valid only when the volume of the mixture does not change during the course of the reaction. This may be only true for liquid phase reactions where volume changes are not significant. The volume of a gas also changes due to changes in operating conditions (temperature and pressure) in addition to changes in number of moles.

1.10 Rate equation in terms of partial pressure

For isothermal (elementary) gas reactions where the number of moles of material ' to The changes during reaction, the relation between the total pressure of the system ' changing concentration or partial pressure of any of the reaction component is r R + s S + ... a A + b B+ ... o)] - n) (For the component 'A', pA = CA R T = pAo - [(a/ o)] - n) (For the component 'R', pR = CR R T = pRo + [(r/ And the rate of the reaction, for any component 'i', is given by ri = (1/RT) (dpi/dt)

1.12 Effect of temperature on reaction

Temperature dependency from Arrhenius law

For many reactions and particularly elementary reactions, the rate expression can be written as a



roduct of a temperature . The excess energy of the reactants required to dissociate into products is known as activation energy. The temperature dependency on the reaction rate constant is given by Arrhenius Law. That is, k = ko e-E/RT Where k = rate constant, k0 = frequency factor, E = Activation energy The temperature dependence of the rate constant k is usually fitted by the Arrhenius equation . Arrhenius equation is frequently applied to approximate the temperature dependency of reaction rate and the rate constant or velocity constant, k, is related to temperature, T, by the following expression:

 $k = k0e^{-E/RT}$

Where, k0 = pre-exponential factor and has units similar to that of k. Ea = activation energy,

J·mol-1

where the pre-exponential factor k0 and the activation energy E are treated as constants and T is

the absolute temperature. If a plot of ln k versus 1/T shows a significant curvature, the rate constant k is a function of temperature

 $k = k0 e^{-Ea/RT}$

The higher the temperature the more molecules that have enough energy to make it over the barrier Arrhenius Plot $k = A \exp(-Ea/RT) \ln k = \ln A - Ea/RT$ straight line plot y = b + mx y = $\ln k x = 1/T b = \ln A m = -Ea/R$ Plot $\ln k vs 1/T$, slope = -Ea/R intercept = $\ln A$. A plot of $\ln k vs$ 1/T will be straight line, the slope of which is Ea /R. The units of the slope are K. A large slope of Arrhenius plot means large value of Ea and vice versa. Reactions having large value of Ea are more temperature sensitive while with low value of Ea are less temperature dependent.

Transition state theory

Transition state theory (TST) explains the reaction rates of elementary chemical reactions. The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes. Describes the flow of systems from reactants-to-products over potential energy surfaces. Predicts the rate of an elementary equation in term of reactant concentration.

 $k = T A e^{-Ea/RT}$

Collision theory This theory was proposed by Trautz (1916) and Lewis (1918) for gas phase reactions. It is based on the kinetic theory of dilute gases. Consider an elementary reaction of the form $A1 + A2 \rightarrow$ products The reaction rate, i.e the number of molecules of A1 consumed per unit volume per unit time is assumed to be equal to the number of collisions per unit volume per unit time between molecules of A1 and A2. The latter may be estimated as follows. Using the Maxwell-Boltzmann velocity distribution for each species, the activation energy can be found from

 $k = T \frac{1/2}{2} A e^{-Ea/RT}$

1.13 Constant volume reactions

- 1. Integral method
- 2. Differential method

Method of analysis of data

1.13.1 Integral method

General Procedure

The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is shown in the figure. It should be noted that the integral method is especially useful for fitting



1.13.2 Differential method

Plot the concentration versus time data and then carefully draw a smooth curve to represent the

data. This curve will most likely not pass through all experimental points. Determine the slope of the curve at suitably selected concentration values. These slopes are rates of the reactant at particular concentration. Search for a rate expression to represent this rate versus concentration data either by fitting and testing a particular rate equation or by trail and error method or by testing the nth order equation.



1.14 Irreversible Unimolecular-type first order reaction

First order (unimolecular) reaction:

Suppose we wish to test the first-order rate equation of the following type, for this reaction.

Reaction: $A \rightarrow B$

Rate Law: -d[A]/dt = k[A]

Integrated solution: $\int d[A]/[A] = -k \int dt \ln [A] = -kt + \ln [Ao] [A] = [Ao] e^{-kt}$

Separating and integrating we obtain a plot of In (1 - XA) or In (CA/CAo) vs. t, a straight line

through the origin for this form of rate of equation. If the experimental data seems to be better fitted by a curve than by a straight line, try another rate form because the first-order reaction does not satisfactorily fit the data.

Fractional conversion XA

Fractional conversion of a reactant A is defined as fractional reactant converted into product at

any time. It is given by the equation, XA = (NAO - NA) / NAO Where 'NAO' is the initial no. of moles of reactant 'A' at t = 0. 'NA' is the remaining no. of moles of reactant at any time 't' in the reaction.

1.15 Irreversible Unimolecular-type second order reaction

Second-order reaction (dimerization) (like molecules)

Reaction: $2A \rightarrow Product$

Rate Law: $- d[A]/dt = k[A]^2$

Integrated solution: $\int d[A]/[A]^2 = -k \int dt 1/[A] = k (t) + 1/[A0] [A] = A0/(A0kt + 1)$

The equation is a hyperbolic equation, and second-order, dimerization kinetics are often called hyperbolic kinetics.

Bimolecular reactions with different reactants: (unlike molecules)

Reaction: $A+B \rightarrow AB$

Rate Law: -d[A]/dt = -d[B]/dt = k[A][B]

Integrated solution:

$$-rA = CAO dXA/dt = k(CAO-CAOXA)(CBO-CBOXA)$$

Let M= CBO/CAO be the initial molar ratio of reactants , we obtain

 $-rA = CAO dXA/dt = kCAO^{2}(1-XA)(M-XA)$

after breakdown into partial fractions, integration and rearrangement, the final result in a number

of different forms is

 $\ln (1-XB / 1-XA) = \ln (M-XA/M(1-XA)) = \ln CBCAO/CBOCA = \ln CB/MCA = CAO (M-1)kt=(CBO-CAO)kt$

 $M \neq 1$

A linear plot will be obtained between the concentration function and time for this second order rate law.

1.16 Half life

The half-life (t 1/2) for a reaction is the time required for half of the reactants to convert to products.

For a first-order reaction, t 1/2 is a constant and can be calculated from the rate constant as:

 $t 1/2 = -\ln(0.5)/k = 0.693/k$

1.17 Pseudo First order reaction

A second order rate equation which follows the first order rate equation is defined as pseudo First

order reaction. Example: Ester hydrolysis. CH 3COOH + C 2H 5OHCH3 COO C2 H5 + H 2O (A) (B) (C) (D) When C BO >>C Ao, Concentration of H 2O is very large, -rA = -dCA/dt = k 'CA

1.18 Zero order reaction

When the rate of the reaction is independent of the concentration of the reactants, it is called as Zero order reaction. Example: Decomposition of HI

1.19 Third-order reaction

An irreversible trimolecular-type third-order reaction may fall on two categories; Products with corresponding rate equation(1) The reaction A + B + D -rA = -(dCA/dt) = k CA CB CD. If

CDo is much greater than both CAo and CBo, the reaction becomes second order. Products with

corresponding rate equation(2) The reaction A + 2B - rA = -(dCA/dt) = k CA CB 2.

1.20 nth order

The empirical rate equation of nth order, -rA = -dCA/dt = k CA n (constant volume). Separating the variables and integrating, we get CA 1-n - CAo 1-n = (n - 1) k t. Case i) n>1, CAo 1-n = (1 -n) k t. The slope is (1 - n) k is negative Or the time decreases. Case ii) n

1.21 Steady-State approximation

The kinetics of reactions of this type can also be also analyzed by writing the overall expression for the rate of change of B and setting this equal to 0. By doing this, we are making the assumption that the concentration of B rapidly reaches a constant, steady-state value that does not change appreciably during the reaction. d[B]/dt = k1[A] - k-1[B] - k2[B] = k1[A] - (k-1+k2)[B] = 0 (k-1+k2)[B] = k1[A] [B] = (k1)/(k-1 + k2) [A] substituting

into d[C]/dt = k2[B] gives: d[C]/dt = (k1k2)/(k-1 + k2) [A] now if k-1 >> k2 d[C]/dt \approx (k1 k2)/(k-1) [A], if k2 >> k-1 d[C]/dt \approx (k1k2)/(k2) [A] = k1[A]

Limiting reactant

Usually in a reaction, one of the reactants is present in excess to that required stoichiometrically. If the reactants are added in stoichiometric amounts, there is no point using the concept of limiting reactant. The limiting reactant is the one which is consumed first and may be indicated by dividing the number of moles of each reactant in feed to the corresponding stoichiometric amount (form a balanced chemical equation) of the reactant. The reactant with the lowest ratio is the limiting reactant and will be the first to fully consumed in the reaction, if the reaction goes to completion.

Constant volume method: It refers to the volume of reaction mixture, and not the volume of reactor. It actually means a constant density reaction system, that is, the composition of reaction mixture is constant. Most of the liquid phase as well as gas phase reactions occurring in a constant volume bomb fall in this class. In a constant volume system, the measure of reaction rate of component 'i' (reactant 4 or product) becomes ri = (1 / V) (dNi / dt) = dCi / dt. Conversion of reactant 'A' in this method is given by XA = 1 – (CA/CAo). Variable volume method: It actually means the composition of reaction mixture varies with time by the presence of inerts. Gas phase reactions involving the presence of inerts or of impure reactants occurringin a reactor fall in this class. The measure of reaction rate of component 'i' (reactant or product), in this method, i) [d (ln V) / dt).becomes ri = (Cio /In variable volume system, the fractional change in volume of the system between the initial and final stage of the reaction will be accounted. Thus, conversion of reactant A (CA/CAo)].'A' becomes XA = <math>[1 - (CA/CAo)] / [1 + 'A(CA/CAo)]



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Reactor Design for Single Reactions

2.1 CLASSIFICATION OF REACTORS

Reactors are classified based on

1. Method of operation: Batch or Continuous reactor

2. Phases: Homogeneous or Heterogeneous reactor

2. 2 REACTOR TYPES

Equipment in which homogeneous reactions are effected can be one of three general types : the batch , the steady –state flow and the un-steady-state flow or semibatch reactor. The batch reactor is simple, needs little supporting equipment and is therefore ideal for small scale

experimental studies on reaction kinetics. Industrially it is used when relatively small amounts of material are to be treated. The steady state flow reactor is ideal for industrial purposes when large quantities of material are to be processed and when the rate of the reaction is fairly high to extremely high. Extremely good product quality control can be obtained. This is a reactor which is widely used in the oil industry. The semibatch reactor is a flexible system but is more difficult to analyze than the other reactor types. It offers good control of reaction speed because the reaction proceeds as reactants are added. Such reactors are used in a variety of applications from the calorimetric titrations in the laboratory to the large open hearth furnaces for steel production.



2.3 Reactor Design

The starting point for all design is the material balance expressed for any reactant

2.3.1 Material balance

Rate of reactant flow into element of volume =rate of reactant flow out of element of volume + rate of reactant loss due to chemical reaction within the element of volume + rate of accumulation of reactant in element of volume.

In non isothermal operations energy balance must be used in conjunction with material balances

2.3.2 Energy balance

Rate of heat flow into element of volume =rate of heat flow out of element of volume + rate of disappearance of heat by reaction within the element of volume + rate of accumulation of heat in element of volume.

2.3.3. Factors to be considered for design of reactor

The different factors required for reactor design are (i) Size of reactor (ii) Type of reactor (iii)

Time or duration of reaction (iv) Temperature & Composition of reacting material in the reactor (v) Heat removal or added and (vi) Flow pattern of fluid in the reactor.

2.4 Ideal Reactors

Ideal reactors (BR, PFR, and MFR) are relatively easy to treat. In addition, one or other usually represents the best way of contacting the reactants – no matter what the operation. For these reason, we often try to design real reactors so that their flows approach these ideals.

2.4.1 Ideal Batch Reactor



A batch reactor (BR) is one in which reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady state operation where composition changes with time; however at any instant the composition throughout the reactor is uniform. The advantages of a batch reactor are (i) small instrumentation cost and (ii) flexibility of operation. A batch reactor has the disadvantages of (i) high labour (ii) poor quality control of the product and (iii) considerable shutdown time has taken to empty, clean out and refill.

Making a material balance for component A. Noting that no fluid enters or leaves the reaction

mixture

Input = output + disappearance + accumulation (1)

Input = 0

Output = 0

Disappearance of A by reaction moles/time $= (-r_A)V$

Accumulation of A by reaction moles/time = dNA/dt

By replacing these two terms

 $(-r_A)V = N_{AO} dX_A/dt$

Rearranging and integrating gives

 $t = N_{AO} \int dX_A / (-r_A) V$

 $t = CAO \int dXA/(-rA) = - \int dCA/(-rA)$ FOR $\epsilon A = 0$

2.4.2 Space time and space velocity

Space velocity: It is the reciprocal of space time and applied in the analysis of continuous flow reactors such as plug flow reactor and CSTR. It is defined as the number of rector volumes of a feed at specified conditions which can be treated in unit time. A space velocity of 10 h - 1 means that ten reactor volumes of the feed at specified conditions are treated in a reactor per hour.

Space time and space velocity are the proper performance measures of flow reactors.

Space time

 $\tau = 1/s =$ time required to process one reactor volume of feed measured at specified conditions (time)

Space velocity

s= $1/\tau$ = number of reactor volumes of feed at specified conditions which can be treated in unit time (time⁻¹)

$$\tau = VCAO/FAO = 1/s$$

Holding time: It is the mean residence time of flowing material in the reactor. It is given by the expression t = CAo + d XA)/] / [(-rA) (1 + AXA)

For constant density systems (all liquids and constant density gases) $t = \tau$ Where 'V' is the

volume of the reactor and 'v' is the volumetric flow rate of reacting fluid

For constant density systems, the performance equation for Batch reactor and Plug flow reactor are identical.

2.5 Steady state mixed flow reactor or Continuous stirred tank reactor (CSTR)



Mixed flow reactor (MFR) is also called as back mix reactor or continuous stirred rank reactor (CSTR) or constant flow stirred tank reactor (CFSTR). In this reactor, the contents are well stirred and uniform throughout. The exit stream from the reactor has the same composition as the fluid within the reactor.

Since the composition is uniform throughout, the accounting can be made about the reactor as a

whole.

Input = output + disappearance + accumulation (2)

Accumulation = 0

Input of A.moles /time = F_{AO}

Output of A.moles /time = $F_A = F_{AO}$ (1-X_A)

Disappearance of A by reaction moles/time $= (-r_A)V$

Introducing all these terms in eqn 2

 $F_{AO} X_A = (-r_A)V$

Which on rearrangement becomes

 $V/\ F_{AO}=\ \tau \ / \ C_{AO}= X_A \ / \ (\ \text{-r}_A)$

2.6 Steady state Plug flow reactor or Tubular reactor



Plug flow reactor (PFR) is also referred as slug flow, piston flow, ideal tubular, and unmixed flow reactor. It specifically refers to the pattern of flow as plug flow. It is characterized by the fact that the flow of fluid through the reactor is orderly no element of fluid overtaking or mixing with any other element ahead or behind. Actually, there may be lateral mixing of fluid in a PFR; however, there must be no mixing or diffusion along the flow path. The necessary and sufficient condition for plug flow is the residence time in the reactor to be the same for all elements of fluid

Input = output + disappearance + accumulation (3)

Accumulation = 0

Input of A.moles /time = F_{AO} Output of A.moles /time = F_A + d F_A

Disappearance of A by reaction moles/time = $(-r_A)dV$

Introducing all these terms in eqn 3

 $F_{\mathbf{A}} = F_{\mathbf{A}} + d F_{\mathbf{A}} + (-r_{\mathbf{A}})dV$

Noting that

 $d F_A = d [F_A (1-X_A)] = - F_{AO} dX_A$

we obtain on replacement

 $F_{AO} dX_A = (-r_A)dV$

Grouping the terms accordingly and integrating

V/ $F_{AO} = \tau / C_{AO} = \int dX_A / (-r_A)$

ideal reactors are based on simple models of flow patterns and mixing in the reaction vessel. In

an ideal batch reactor, the concentration and temperature fields are assumed to be spatially uniform. In practice, the condition can be approximately realized by vigorous agitation or stirring. In the absence of stirring, beautiful spatial patterns, caused by an interaction between diffusion and reactions, may develop in some systems. All the elements of the fluid spend the same amount of time in the reactor, and hence have the same residence time. From the viewpoint of thermodynamics, a batch reactor represents a closed system. The steady states of the batch reactor correspond to states of reaction equilibria. Batch reactors are often used in the pharmaceutical industry, where small volumes of high-value products are made.

The ideal continuous stirred tank reactor (CSTR) like in an ideal batch reactor, the concentration and temperature fields in an ideal CSTR are spatially uniform. As there are no spatial gradients, the species concentrations in the exit stream are identical to the corresponding values in the reactor. On the other hand, the species concentrations in the inlet stream are in general different from those in the reactor. Unlike the batch reactor, the CSTR is an open system as it can exchange heat and mass with the surroundings. Hence it operates away from equilibrium, and steady states are usually not states of reaction equilibria. On account of the assumption of perfect mixing, the sequence in which fluid elements leave the reactor is uncorrelated with the sequence in which they enter. As shown later, this leads to a distribution of residence times for the fluid leaving the reactor. These reactors are widely used for polymerization reactions such as the polymerization of styrene, production of explosives, synthetic rubber, etc. Compared to tubular reactors, CSTRs are easier to clean and permit better control of the temperature. (c) The plug flow reactor (PFR) The PFR is an idealization of a tubular reactor. The velocity, temperature, and concentration fields are assumed to be uniform across the cross section of the reactor. In practice, this situation can be approximately realized for the case of turbulent flow through a tube with a large ratio of the length to the diameter. The latter condition ensures that axial mixing has a negligible effect on the conversion. In a PFR, there is perfect mixing in the radial or transverse direction. Further, there is no mixing or diffusion in the axial direction. Like a CSTR, the PFR also represents an open system, and hence steady states are not states of reaction equilibrium. Owing to the assumption of plug flow, all the fluid elements have the same residence time. The velocity of the fluid is often treated as a constant, but this assumption must be relaxed when the density of the fluid changes significantly along the length of the tube. The steady state equations for a PFR are similar in form to the dynamic equations for an ideal batch reactor. In many cases, the results for the latter can be translated into results for a PFR operating at a steady state. Tubular reactors are used for many gas phase and liquid phase reactions, such as the oxidation of NO and the synthesis of NH3. These reactors are often modelled as PFRs, but more detailed models involving complications such as radial gradients, may be required in some cases.

Plug flow and mixed flow reactor design

Mixed flow reactor design

Applying mass balance performance equation for mixed flow reactor

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}$$
$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}$$

Plug flow reactor design

Performance equation for plug flow reactor

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{AV}} \frac{dX_A}{-r_A}$$
$$\tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0} \int_0^{X_{AV}} \frac{dX_A}{-r_A}$$





2.7 Steady state reactor

Reactors those in which the properties of the system do not change with time is said to be a steady state reactor. Example: Continuous stirred Tank reactor, plug flow reactor. Total mass inflow = Total mass outflow

2.8 Unsteady state reactor

Reactors are those in which the properties of the system changes with time and rate of reaction decreases with time expect for zero order reaction are said to be unsteady state reactor. Example: Batch reactor, Semi-batch reactor. There is accumulation in these reactors. Accumulation = input - output + generation - consumption.

2.9 Semi batch reactor



It is an unsteady state reactor. Reactors which are partially batch and partially continuous are referred to as semi-batch reactor. The semi batch reactors offers good control of reaction speed, because the reaction proceeds as reactants are added. Types: (i) volume changes but composition is unchanged (ii) composition changes but volume is constant.

2.10 Recycle reactor



In some reaction system, it is advantageous to divide the product stream and a part returned to reactor as recycle to increase the conversion rate. These reactors are called recycle reactors. The recycling provides a means for obtaining various degree of backmixing. Recycle ratio 'R' can be defined as the ratio of the volume fluid returned to the reactor entrance to the volume of fluid leaving the system or reactor. Significance: Recycle ratio can be made to vary from zero to infinity. Reflection suggests that as the recycle ratio is raised, the behavior shifts from plug flow (R = 0) to). mixed flow (R =).), the recycle reactor. When the recycle ratio 'R' becomes or tends to infinity (R= behaves like a CSTR. When material is to be processed to some fixed final conversion in a recycle reactor, there must be a particular recycle ratio 'R' that minimizes the reactor volume or space time. That recycle ratio is said to be optimum and the operation is said

The actual conversion at inlet is given by:

to

$$X_{A1} = \frac{1 - C_{A1}/C_{A0}}{1 + \varepsilon_A C_{A1}/C_{A0}}$$

The concentration at inlet to the reactor is given by

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + Rv_f} = \frac{F_{A0} + RF_{A0}(1 - X_{Af})}{v_0 + Rv_0(1 + \varepsilon_A X_{Af})} = C_{A0} \left(\frac{1 + R - RX_{Af}}{1 + R + R\varepsilon_A X_{Af}}\right)$$

So finally we get the following results:

$$X_{\rm A1} = \left(\frac{\boldsymbol{R}}{\boldsymbol{R}+1}\right) X_{\rm A3}$$

The final equation for any expansion factor value is:

$$\frac{V}{F_{A0}} = (\mathbf{R}+1) \int_{\left(\frac{\mathbf{R}}{\mathbf{R}+1}\right) X_{Af}}^{X_{Af}} \frac{dX_{A}}{-r_{A}} \quad . \quad . \text{ any } \varepsilon_{A}$$

Also in terms of concentration,

$$\tau = \frac{C_{A0}V}{F_{A0}} = -(\mathbf{R}+1) \int_{\frac{C_{A0}+\mathbf{R}C_{Af}}{\mathbf{R}+1}}^{C_{Af}} \frac{dC_{A}}{-r_{A}} \dots \varepsilon_{A} = 0$$

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UNIT – III - Chemical Reaction Engineering – SCHA1411

DESIGN OF MULTIPLE REACTORS FOR SINGLE REACTIONS

There are many ways of processing a fluid: in a single batch or flow reactor, in a chain of reactors possibly with interstage feed injection or heating and in a reactor with recycle of the product stream using various feed ratios and conditions. The reactor system selected will influence the economics of the process by dictating the size of the units needed and by fixing the ratio of products formed. The first factor, reactor size, may well vary a hundredfold among competing designs while the second factor, product distribution, is usually of prime consideration where it can be varied and controlled. For single reactions product distribution is fixed; hence, the important factor in comparing designs is the reactor size. The size comparison of various single and multiple ideal reactor systems is considered.

3.1 SIZE COMPARISON OF SINGLE REACTORS

3.1.1 Batch Reactor

The batch reactor has the advantage of small instrumentation cost and flexibility of operation (may be shut down easily and quickly). It has the disadvantage of high labor and handling cost, often considerable shutdown time to empty, clean out, and refill, and poorer quality control of the product. Hence it may be generalized to state that the batch reactor is well suited to produce small amounts of material and to produce many different products from one piece of equipment. On the other hand, for the chemical treatment of materials in large amounts the continuous process is nearly always found to be more economical.

3.1.2 Mixed Versus Plug Flow Reactors, First- and Second-Order Reactions

For a given duty the ratio of sizes of mixed and plug flow reactors will depend on the extent of reaction, the stoichiometry, and the form of the rate equation.

- $r_A = -1 dN_A$

 $\dots = kC_A^n$



To provide a quick comparison of the performance of plug flow with mixed flow reactors, the performance graph is used. For identical feed composition *CAo* and flow rate *FA*, the ordinate of this figure gives directly the volume ratio required for any specified conversion.

1. For any particular duty and for all positive reaction orders the mixed reactor is always larger than the plug flow reactor. The ratio of volumes increases with reaction order.

2. When conversion is small, the reactor performance is only slightly affected by flow type. The performance ratio increases very rapidly at high conversion; consequently, a proper representation of the flow becomes very important in this range of conversion.

3. Density variation during reaction affects design; however, it is normally of secondary importance compared to the difference in flow type. Dashed lines represent fixed values of the dimensionless reaction rate group, defined as $k\tau$ for first-order reaction

 $kC_{A0}\tau$ for second-order reaction

With these lines we can compare different reactor types, reactor sizes, and conversion levels. Second-order reactions of two components and of the type behave as second-order reactions of one component when the reactant ratio is unity. Thus

-rA = kCACB = kc; when M = 1

On the other hand, when a large excess of reactant B is used then its concentration does not change appreciably (CB = CBO) and the reaction approaches first-order behavior with respect to the limiting component **A**, or

-rA = kCACB = (kCBO)C = A krCA when M + 1

Thus terms of the limiting component A, the size ratio of mixed to plug flow reactors is represented by the region between the first-order and the second-order curves.


For reactions with arbitrary but known rate the performance capabilities of mixed and plug flow reactors are best illustrated in above figure. The ratio of shaded and of hatched areas gives the ratio of space-times needed in these two reactors. The rate curve drawn in above figure is typical of the large class of reactions whose rate decreases continually on approach to equilibrium (this includes all nth-order reactions, n > 0). For such reactions it can be seen that mixed flow always needs a larger volume than does plug flow for any given duty.

3.2 Plug Flow Reactors in Series and / or in Parallel

Consider N plug flow reactors connected in series, and let X_1, X_2, \ldots, X_N , be the fractional

conversion of component A leaving reactor 1, 2, ..., N. Basing the material balance on the feed

rate of A to the first reactor, we find for the

 $V_i/F_O = \tau_i/C_{AO} = \int dX / (-r)$ or for the N reactors in series

 $V/F_0 = \Sigma V_i / F_{0} = \int dX / (-r_)$

Hence, N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V.

3.2.1 Operating A Number Of Plug Flow Reactors

The reactor setup shown in Figure consists of three plug flow reactors in two parallel branches. Branch D has a reactor of volume 50 liters followed by a reactor of volume 30 liters. Branch E has a reactor of volume 40 liters. What fraction of the feed should go to branch D?



Branch D consists of two reactors in series; hence, it may be considered to be a single reactor of volume

 $V_D = 50 + 30 = 80$ liters

Now for reactors in parallel V/F must be identical if the conversion is to be the same in each branch. Therefore, two-thirds of the feed must be fed to branch D.

3.3 Equal-Size Mixed Flow Reactors in Series



In plug flow, the concentration of reactant decreases progressively through the system; in mixed flow, the concentration drops immediately to a low value. Because of this fact, a plug flow reactor is more efficient than a mixed flow reactor for reactions whose rates increase with reactant concentration, such as nth-order irreversible reactions, n > 0. Consider a system of N mixed flow reactors connected in series. Though the concentration is uniform in each reactor, there is, nevertheless, a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, illustrated in above figure, suggests that the larger the number of units in series, the closer should the behavior of the system approach plug flow. This will be shown to be so. Quantitatively evaluate the behavior of a series of N equal-size mixed flow reactors. Density changes will be assumed to be negligible; hence $\rho = 0$. As a rule, with mixed flow reactors it is more convenient to develop the necessary equations in terms of concentrations rather than fractional conversions.

3.4 Comparison Charts

At present 90% of reactant A is converted into product by a second-order reaction in a single mixed flow reactor. We plan to place a second reactor similar to theone being used in series with it.

(a) For the same treatment rate as that used at present, how will this additionaffect the conversion of reactant?

For the same 90% conversion, by how much can the treatment rate be increased?



(*a*) *Find the conversion for the same treatment rate.* For the single reactor at 90% conversion we have from chart

$$kCo\tau = 90$$

For the two reactors the space-time or holding time is doubled; hence, the operation will be represented by the dashed line of chart where

kCoτ= 180

This line cuts the N = 2 line at a conversion X = 97.4%, point a.

(b) Find the treatment rate for the same conversion. Staying on the 90% conversion

line, we find for N = 2 that

 $kCo\tau = 27.5$, point b

Comparing the value of the reaction rate group for N = 1 and N = 2, we find Since $V_2 = 2V_1$ the ratio of flow rates becomes

Thus, the treatment rate can be raised to 6.6 times the original.



3.5 Mixed Flow Reactors of Different Sizes in Series

For arbitrary kinetics in mixed flow reactors of different size, two types of questions may be asked: how to find the outlet conversion from a given reactor system, and the inverse question, how to find the best setup to achieve a given conversion. Different procedures are used for these two problems.

3.5.1 Finding the Conversion in a Given System

A graphical procedure for finding the outlet composition from a series of mixed flow reactors of various sizes for reactions with negligible density change has been presented by Jones (1951). All that is needed is an r versus C curve for component A to represent the reaction rate at various concentrations. It is illustrated by the use of this method by considering three mixed flow reactors in series with volumes, feed rates, concentrations, space-times (equal to residence timesbecause $\rho = O$), and volumetric flow rates as shown in figure below. Now from equation noting that $\rho = 0$, we may write for component A in the first reactor



$$\tau_1 = V_1 / v = C_0 - C_1 / (-r_1) - 1 / \tau_1 = (-r_1) / C_1 - C_0$$

For *i* th reactor

 $-1/\tau_{i} = (-r_{i})/C_{i}-C_{i-1}$



Plot the C versus r curve for component A and it is as shown in figure above. To find the conditions in the first reactor note that the inlet concentration Co is known (point L), that C, and (-r), correspond to a point on the curve to be found (point M), and that the slope of the line LM = MNINL = (-r), l (C, -Co) = -(l/rl) from equation. Hence, from Co draw a line of slope -(l/r) until it cuts the rate curve; this gives C1. Similarly, we find from equation, that a line of slope -(1/r2) from point N cuts the curve at P, giving the concentration C2 of material leaving the second reactor. This procedure is then repeated as many times as needed. With slight modification this graphical method can be extended to reactions in which density changes are appreciable.

3.5.2 Determining the Best System for a Given Conversion

To find the minimum size of two mixed flow reactors in series to achieve a specified conversion of feed which reacts with arbitrary but known kinetics, the following procedure is followed. The basic performance expressions, from equations, give, in turn, for the first reactor



and for the second reactor

τ_{2} / Co = X ₂₋ X ₁ / (-r₂)

as the intermediate conversion *XI* changes, so does the size ratio of the units (represented by the two shaded areas) as well as the total volume of the two vessels required (the total area shaded). Figure shows that the total reactor volume is as small as possible (total shaded area is minimized) when the rectangle KLMN is as large as possible. This brings us to the problem of choosing *XI* (or point M on the curve) so as to maximize the area of this rectangle. This is done according to Maximization of Rectangles concept. In the below figure, construct a rectangle between the x-y axes and touching the arbitrary curve at point M(x, y). The area of the rectangle is then

A = xy

This area is maximized when

da = 0 = xdy + ydx





In words, this condition means that the area is maximized when M is at that point where the slope of the curve equals the slope of the diagonal NL of the rectangle. Depending on the shape of the curve, there may be more than one or there may be no "best" point. However, for nth-order kinetics, n > 0, there always is just one "best" point. The optimum size ratio of the two reactors is achieved where the slope of the rate curve at M equals the diagonal NL. The best value of M is

shown in figure, and this determines the intermediate conversion *X*, as well as the size of units needed. The optimum size ratio for two mixed flow reactors in series is found in general to be dependent on the kinetics of the reaction and on the conversion level. For the special case of first-order reactions equal-size reactors are best; for reaction orders n > 1 the smaller reactor should come first; for n < 1 the larger should come first. However, Szepe and Levenspiel (1964) show that the advantage of the minimum size system over the equal-size system is quite small, only a few percent at most. Hence, overall economic consideration would nearly always recommend using equal-size units.

3.6 Best Arrangement of a Set of Ideal Reactors



For the most effective use of a given set of ideal reactors we have the following general rules: 1. For a reaction whose rate-concentration curve rises monotonically (any nth-order reaction, n >

0) the reactors should be connected in series. They should be ordered so as to keep the concentration of reactant as high as possible if the rate-concentration curve is concave (n > I), and as low as possible if the curve is convex (n < 1). As an example, for the case of above figure the ordering of units should be plug, small mixed, large mixed, for n > 1; the reverse order should be used when n < 1.

2. For reactions where the rate-concentration curve passes through a maximum or minimum the arrangement of units depends on the actual shape of curve, the conversion level desired, and the units available. No simple rules can be suggested.

3. Whatever may be the kinetics and the reactor system, an examination of the l/(-r) vs. CA curve is a good way to find the best arrangement of units.



SCHOOL OF BIO AND CHEMICAL ENGINEERING

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UNIT – IV - Chemical Reaction Engineering – SCHA1411

Unit I – Non-Ideal Reactors

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

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

Ideal Reactors

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

Non-ideal reactors (real reactors)

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

The deviation from ideal flow patterns may be caused by

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



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

Factors that make up the contacting or flow pattern are:

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

Residence Time Distribution Function

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



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

RTD Measurement

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

Characteristics of chemical tracer:

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

Experimental Methods for Finding E

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



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

1.The Pulse Input Experiment



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

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

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

 $\Delta \mathbf{M} = \mathbf{C} \ \upsilon \ \Delta t \tag{1}$ $\upsilon \text{ is the volumetric flow rate of the effluent from the vessel}$ $\Delta \mathbf{M} \text{ is the amount of material that has spent an amount of time between t and } \Delta t \text{ in the vessel}$

Eqn (1) / M

 $\frac{\Delta \mathbf{M}}{\mathbf{M}} = \frac{\mathbf{C} \,\upsilon}{\mathbf{M}} \,\Delta \mathbf{t} = \frac{\mathbf{C}}{\mathbf{M}/\upsilon} \,\Delta \mathbf{t} \tag{2}$

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

 $\Delta M / M$ is the fraction of material that has residence time

between t and t+ Δt in the vessel

Let us define E is

$$E = \frac{C \upsilon}{M} = \frac{C}{M/\upsilon}$$
(3)
$$\frac{\Delta M}{M} = E \Delta t$$
(4)

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

Eqn (1) may be rewritten as

$$\int_{0}^{M} dM = \int_{0}^{\infty} C \upsilon dt$$
(5)
$$\int_{0}^{M} dM = \upsilon \int_{0}^{\infty} C dt$$
(6)

$$\mathbf{M}/\upsilon = \int_{0}^{\infty} \mathbf{C} \, \mathbf{dt} \tag{7}$$

Combining equations (3) and (7)

$$\mathbf{E} = \frac{\mathbf{C}}{\int_{0}^{\infty} \mathbf{C} \, \mathbf{dt}}$$
(8)
$$\int_{0}^{\infty} \mathbf{C} \, \mathbf{dt} = \sum_{0}^{\infty} \mathbf{C}_{i} \, \Delta \mathbf{t}_{i} = \text{Area under the } \mathbf{C} \, \mathbf{curve} = \mathbf{M} / \upsilon$$

$$\begin{pmatrix} \text{Area under the} \\ C_{\text{pulse}} \text{ curve} \end{pmatrix}: \quad \mathbf{A} = \int_{0}^{\infty} C \, dt \cong \sum_{i} C_{i} \Delta t_{i} = \frac{M}{v} \qquad \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^{3}}\right]$$
$$\begin{pmatrix} \text{Mean of the} \\ C_{\text{pulse}} \text{ curve} \end{pmatrix}: \quad \overline{t} = \frac{\int_{0}^{\infty} tC \, dt}{\int_{0}^{\infty} C \, dt} \cong \frac{\sum_{i} t_{i} C_{i} \Delta t_{i}}{\sum_{i} C_{i} \Delta t_{i}} = \frac{V}{v} \quad [\text{s}]$$

E curve from C curve





Transforming an E curve into E_{θ} curve

We have another RTD function \mathbf{E}_{θ} . Here time is measured in terms of mean residence time $\theta = t/\overline{t}$. Thus



Figure — Transforming an E curve into an E_{θ} curve.

2. The Step Experiment

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



Figure — Information obtainable from a step tracer experiment.

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

$$\begin{pmatrix} \text{shaded area} \\ \hline \end{array} \end{pmatrix} = C_{\max} \overline{t} = \frac{\mathbf{m}V}{v^2} \left[\frac{\mathbf{kg} \cdot \mathbf{s}^2}{\mathbf{m}^3} \right]$$

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



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

Relationship between the F and E curves

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

$$\mathbf{F} = \int_{0}^{t} \mathbf{E} \, \mathbf{dt} \qquad (1) \qquad \left(\because \int_{0}^{t} \mathbf{E} \, \mathbf{dt} + \int_{t}^{\infty} \mathbf{E} \, \mathbf{dt} = 1 = \int_{0}^{\infty} \mathbf{E} \, \mathbf{dt} \right)$$

 $1 - \mathbf{F} = \int_{t}^{\infty} \mathbf{E} \, \mathbf{dt} = \begin{pmatrix} \text{fraction of the effluent stream that has} \\ \text{been in the vessel for longer than time t} \end{pmatrix}$ (2)

$$\int_{t}^{\infty} \mathbf{E} \, d\mathbf{t} = 1 - \int_{0}^{t} \mathbf{E} \, d\mathbf{t}$$
(3)
$$\int_{t}^{\infty} \mathbf{E} \, d\mathbf{t} = 1 - \mathbf{F}$$
(4)

F is the cummulative RTD function

On differentiating eqn (1) with respect to t, we get $\frac{dF}{dt} = E$

This is the relationship b/w E and F



Figure — Relationship between the E and F curves.



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

Conversion in non-ideal flow reactors

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

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

States of aggregation of the flowing stream

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

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







Figure — Examples of macro- and microfluid behavior.

Early and late mixing of fluids

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



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





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

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

Late mixing favors reactions with n>1

Early mixing favors reactions with n<1

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

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

$$\begin{pmatrix} \text{mean concentration} \\ \text{of reactant} \\ \text{in exit stream} \end{pmatrix} = \sum_{\substack{\text{all elements} \\ \text{of exit stream}}} \begin{pmatrix} \text{concentration of} \\ \text{reactant remaining} \\ \text{in an element of} \\ \text{age between } t \\ \text{and } t + dt \end{pmatrix} \begin{pmatrix} \text{fraction of exit} \\ \text{stream which is} \\ \text{of age between } t \\ \text{and } t + dt \end{pmatrix}$$

$$\left(\frac{\overline{C}_{\rm A}}{\overline{C}_{\rm A0}}\right)_{\rm at\ exit} = \int_0^\infty \left(\frac{\overline{C}_{\rm A}}{\overline{C}_{\rm A0}}\right)_{\rm for\ an\ element\ or\ little} \cdot \mathbf{E}\ dt$$

or in terms of conversions

$$\overline{X}_{\mathsf{A}} = \int_0^\infty (X_{\mathsf{A}})_{\mathsf{element}} \cdot \mathbf{E} \, dt$$

or in a form suitable for numerical integration

$$\frac{\overline{C}_{A}}{C_{A0}} = \sum_{\substack{\text{all age} \\ \text{intervals}}} \left(\frac{C_{A}}{C_{A0}}\right)_{\text{element}} \cdot \mathbf{E} \,\Delta t$$

• for first-order reactions

$$\left(\frac{C_{\rm A}}{C_{\rm A0}}\right)_{\rm element} = e^{-kt}$$

- for second-order reactions
- for an *n*th-order reaction

$$\binom{C_{A0}}{element} = \frac{1}{1 + kC_{A0}t}$$
$$\binom{\frac{C_{A}}{C_{A0}}}{\binom{C_{A0}}{element}} = [1 + (n - 1)C_{A0}^{n-1}kt]^{1/1-n}$$

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SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 5 CATALYTIC REACTIONS SCHA1411

Catalytic Reaction Kinetic Model

Introduction:

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

A(fluid) + $bB(Solid) \rightarrow fluid products$	(1)
\rightarrow Solid products	(2)
\rightarrow fluid and solid products	(3)

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

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

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

Similarly, iron pyrites reacts as follows:

$$4\text{FeS}_2(s) + 11\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s) + 8\text{SO}_2(g)$$

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

$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(g)$$

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

 $C(s) + O_2(g) \rightarrow CO_2(g)$ $2C(s) + O_2(g) \rightarrow 2CO(g)$ $C(s) + CO_2(g) \rightarrow 2CO(g)$

With steam, water gas is obtained by the reactions-

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$

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

Selection of a Model

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

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

Progressive-Conversion Model (PCM):

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



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

Shrinking-Core Model:

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





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

SHRINKING-CORE MODEL FOR SPHERICAL PARTICLES OF UNCHANGING SIZE:

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

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



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

- *Step 1*. Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.
- *Step 2*. Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.
- Step 3. Reaction of gaseous A with solid at this reaction surface.
- *Step 4*. Diffusion of gaseous products through the ash back to the exterior surface of the solid.
- Step 5. Diffusion of gaseous products through the gas film back into the main body of fluid.
The above mentioned steps can vary according to the reactions. For example, if there is no gaseous products generation then step 4 & 5 is neglected and does not contribute towards resistance to the reaction. In the analysis of determining kinetic model we will only consider the resistances from step 1, 2 & 3.

1. Diffusion through gas film controls:

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



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

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

$$dN_{\rm B} = bdN_{\rm A}$$

$$-\frac{1}{S_{ex}}\frac{dN_{\rm B}}{dt} = -\frac{1}{4\pi R^2}\frac{dN_{\rm B}}{dt} = -\frac{b}{4\pi R^2}\frac{dN_{\rm A}}{dt} = bk_g(C_{\rm Ag} - C_{\rm As}) = bk_gC_{\rm Ag} = \text{constant}$$
(4)

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

$$N_{\rm B} = \rho_{\rm B} V = \left(\frac{\text{moles B}}{\mathrm{m}^3 \, \text{solid}}\right) \,(\mathrm{m}^3 \, \text{solid})$$
 ------ (5)

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

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

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

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

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

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

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

$$1 - X_{\rm B} = \left(\frac{\text{volume of unreacted core}}{\text{total volume of particle}}\right) = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi R^3} = \left(\frac{r_c}{R}\right)^3 \qquad \dots \dots (10)$$

Therefore,

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_{\rm B} \tag{11}$$

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



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



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

2. Diffusion through Ash Layer Controls:

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

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



controlling resistance.

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

$$-\frac{dN_{\rm A}}{dt} = 4\pi r^2 Q_{\rm A} = 4\pi R^2 Q_{\rm As} = 4\pi r_c^2 Q_{\rm Ac} = \text{constant} \qquad \dots \dots (12)$$

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

$$Q_{\rm A} = \mathscr{D}_e \frac{dC_{\rm A}}{dr} \tag{13}$$

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

Combining equations 12 & 13 for any r,

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

$$-\frac{dN_{\rm A}}{dt}\int_{R}^{r_c}\frac{dr}{r^2} = 4\pi \mathscr{D}_e \int_{C_{\rm Ag}=C_{\rm As}}^{C_{\rm Ac}=0} dC_{\rm A}$$

or,

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

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

$$-\rho_{\rm B} \int_{r_c=R}^{r_c} \left(\frac{1}{r_c} - \frac{1}{R}\right) r_c^2 \, dr_c = b \mathscr{D}_e C_{\rm Ag} \int_0^t dt$$

or

$$t = \frac{\rho_{\rm B}R^2}{6b\mathscr{D}_e C_{\rm Ag}} \left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 \right] \quad \dots \dots (16)$$

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

$$\boldsymbol{\tau} = \frac{\rho_{\rm B} R^2}{6b \mathcal{D}_e C_{\rm Ag}} \tag{17}$$

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

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

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

3. Chemical Reaction Controls:

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



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

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

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

which on integration becomes:

$$-\rho_{\rm B} \int_{R}^{r_c} dr_c = bk'' C_{\rm Ag} \int_{0}^{t} dt$$

or

$$t = \frac{\rho_{\rm B}}{bk'' C_{\rm Ag}} (R - r_c) \tag{21}$$

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

$$\boldsymbol{\tau} = \frac{\rho_{\rm B}R}{bk''C_{\rm Ag}} \tag{22}$$

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

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_{\rm B})^{1/3} \tag{23}$$

This result is plotted in figures. 2.12 & 2.13.

RATE OF REACTION FOR SHRINKING SPHERICAL PARTICLES

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

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

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

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

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



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

1. Chemical Reaction Control:

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

2. Gas Film Diffusion Controls:

Film resistance at the surface of a particle is dependent on numerous factors, such as the relative velocity between particle and fluid, size of particle, and fluid properties. These have been correlated for various ways of contacting fluid with solid, such as packed beds, fluidized beds, and solids in free fall. As an example, for mass transfer of a component of mole fraction y in a fluid to free-falling solids Froessling (1938) gives –

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

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

$$k_g \sim \frac{1}{d_p}$$
 for small d_p and u ------ (25)
 $k_g \sim \frac{u^{1/2}}{d_p^{1/2}}$ for large d_p and u ------ (26)

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

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

$$dN_{\rm B} = \rho_{\rm B} \, dV = 4\pi \rho_{\rm B} R^2 \, dR$$

Thus, similar to equation 7, we have

Since in the Stokes regime equation 24 reduces to

$$k_g = \frac{2\mathscr{D}}{d_p} = \frac{\mathscr{D}}{R} \tag{28}$$

combining equation 27 & 28 and integrating

$$\int_{R_0}^{R} R \, dR = \frac{bC_{Ag}\mathscr{D}}{\rho_{B}} \int_{0}^{t} dt$$

or,

$$t = \frac{\rho_{\rm B} R_0^2}{2b C_{\rm Ag} \mathscr{D}} \left[1 - \left(\frac{R}{R_0}\right)^2 \right]$$

The time for complete disappearance of a particle is thus

$$\boldsymbol{\tau} = \frac{\rho_{\rm B} R_0^2}{2b C_{\rm Ag} \mathscr{D}} \tag{29}$$

and on combining we get

$$\frac{t}{\tau} = 1 - \left(\frac{R}{R_0}\right)^2 = 1 - (1 - X_{\rm B})^{2/3}$$
 (30)

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

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

-		Film Diffusion Controls		Ash Diffusion Controls		Reaction Controls	
	Flat plate $X_{\rm R} = 1 - \frac{1}{2}$	$\frac{t}{\tau} = X_{\rm B}$		$\frac{t}{\tau} = X_{\rm B}^2$		$\frac{t}{\tau} = X_{\rm B}$	
	L = half thickness	$\boldsymbol{\tau} = \frac{\rho_{\rm B}L}{bk_g C_{\rm Ag}}$		$\boldsymbol{\tau} = \frac{\rho_{\rm B} L^2}{2b \mathscr{D}_e C_{\rm Ag}}$		$\boldsymbol{\tau} = \frac{\rho_{\rm B}L}{bk''C_{\rm Ag}}$	
	Cylinder $X_{\rm B} = 1 - \left(\frac{r_c}{R}\right)^2$	$\frac{t}{\tau} = X_{\rm B}$		$\frac{t}{\tau} = X_{\rm B} + (1 - X_{\rm B}) \ln(1 - X_{\rm B})$		$\frac{t}{\tau} = 1 - (1 - X_{\rm B})^{1/2}$	
		$\boldsymbol{\tau} = \frac{\rho_{\rm B}R}{2bk_g C_{\rm Ag}}$		$\boldsymbol{\tau} = \frac{\rho_{\rm B} R^2}{4b \mathscr{D}_e C_{\rm Ag}}$		$\boldsymbol{\tau} = \frac{\rho_{\rm B}R}{bk''C_{\rm Ag}}$	
	Sphere $X_{\rm B} = 1 - \left(\frac{r_c}{R}\right)^3$	$\frac{t}{\tau} = X_{\rm B}$	(11)	$\frac{t}{\tau} = 1 - 3(1 - X_{\rm B})^{2/3} + 2(1 - X_{\rm B})$	(18)	$\frac{t}{\tau} = 1 - (1 - X_{\rm B})^{1/3}$	(23)
		$\boldsymbol{\tau} = \frac{\rho_{\rm B}R}{3bk_g C_{\rm Ag}}$	(10)	$\boldsymbol{\tau} = \frac{\rho_{\rm B} R^2}{6b \mathscr{D}_e C_{\rm Ag}}$	(17)	$\boldsymbol{\tau} = \frac{\rho_{\rm B}R}{bk''C_{\rm Ag}}$	(22)
	Small particle Stokes regime	$\frac{t}{\tau} = 1 - (1 - X_{\rm B})^{2/3}$	(30)	Net englischie		$\frac{t}{\tau} = 1 - (1 - X_{\rm B})^{1/3}$	
		$\boldsymbol{\tau} = \frac{\rho_{\rm B} R_0^2}{2b \mathscr{D} C_{\rm Ag}}$	(29)	Not applicable		$\boldsymbol{\tau} = \frac{\rho_{\rm B} R_0}{b k'' C_{\rm Ag}}$	
	Large particle (u = constant)	$\frac{t}{\tau} = 1 - (1 - X_{\rm B})^{1/2}$	(31)	Not oppliaghle		$\frac{t}{\tau} = 1 - (1 - X_{\rm B})^{1/3}$	
		$\boldsymbol{\tau} = (\text{const}) \frac{R_0^{3/2}}{C_{\text{Ag}}}$		not applicable		$\boldsymbol{\tau} = \frac{\rho_{\rm B}R}{bk''C_{\rm Ag}}$	

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

Shrinking Sphere

DETERMINATION OF THE RATE-CONTROLLING STEP

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

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

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

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

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

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

CATALYSTS AND CATALYTIC REACTIONS

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

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



Figure 3.1 Comparison of activation energies of exothermic catalytic and noncatalytic reactions

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

below.

$$C_2H_5OH \xrightarrow{Boron\ Phospate} C_2H_4 + C_2H_5OC_2H_5$$
$$C_2H_5OH \xrightarrow{Mo_2C/Carbon} H_2 + C_2H_4O$$

Types of catalytic reactions

Catalytic reactions can be divided into two main types -

1. Heterogeneous

2. Homogeneous

Heterogeneous catalysis

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

Homogeneous catalysis

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

SURFACE AREA AND ADSORPTION

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

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

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

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

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

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

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

Table 3.1 Physical vs Chemical Adsorption

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

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

Adsorption Isotherms

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



Figure 3.2 Five types of isotherms for adsorption.

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

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

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

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

Freundlich Adsorption Isotherm

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

$$x/m = K C_e^n \tag{3.1}$$

 $\begin{array}{ll} \mbox{Where,} & \mbox{K and n are Freundlich coefficients} \\ & \mbox{x = weight of adsorbate adsorbed on m unit weight of adsorbent} \\ & \mbox{C}_e \mbox{= equilibrium concentration of adsorbate} \end{array}$

From equation (3.1), we get

$$log(x/m) = logK + n log C_e$$
(3.2)

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

Langmuir Adsorption Isotherm

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

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

2. Each site on the surface of the adsorbent can hold one adsorbate molecule.

3. The heat of adsorption is the same for each site and is independent of θ .

4. There is no interaction between molecules on different sites.

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

$$r_a = k_a p(1 - \theta) \tag{3.3}$$

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

$$r_a = k_a \theta \tag{3.4}$$

At equilibrium,

Rate of adsorption = Rate of desorption

$$k_{a}p(1-\theta) = k_{d}\theta$$
$$\theta = \frac{k_{a}p}{k_{d} + k_{a}p} = \frac{Kp}{1+Kp} = \frac{v}{v_{m}}$$
(3.5)

Where,

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

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

$$r_a = k_C C_g (\bar{C}_m - C) \tag{3.6}$$

Where is the rate constant for the catalyst and is the concentration of absorbable component in the gas. Similarly, Eq.3.4 becomes

$$r_a = k_c' C \qquad (3.7)$$

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

$$\theta = \frac{\bar{C}}{\bar{C}_m} = \frac{K_c C_g}{1 + K_c C_g} \tag{3.8}$$

Where $K_c = k_c / k_c$ '

Rearranging equation (3.8), we get

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

(3.9)

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

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

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

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

(3.28)

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

CATALYST PREPARATION

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

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

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

Precipitation or gel formation

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

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

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

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

Impregnation

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

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

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

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

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

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