GATEFLIX

CHEMICAL REACTION ENGINEERING

For

CHEMICAL ENGINEERING

CHEMICAL REACTION ENGINEERING

SYLLABUS

Theories of reaction rates; kinetics of homogeneous reactions, interpretation of kinetic data, single and multiple reactions in ideal reactors, non-ideal reactors; residence time distribution, single parameter model; non-isothermal reactors; kinetics of heterogeneous catalytic reactions; diffusion effects in catalysis

ANALYSIS OF GATE PAPERS

Exam Year	Total
2001	24
2002	24
2003	15
2004	21
2005	17
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1 CHEMICAL REACTION KINETICS

1.1 INTRODUCTION

Chemical reaction engineering subject was developed with an aim of learning that how to SELECT, SIZE and determine the OPTIMAL CONDITIONS for a reactor whose purpose is to produce a specific chemical product. The word KINETICS is related to determining how fast or how slow the reaction occurs. We are interested in determining the speed of a chemical reaction because it will affect the size (volume) of the reactor required. For example if the speed of the reaction is high it will take less time (which is proportional to volume which we will understand later) to reach to a specific value of conversion.

But it is not only the speed which matters. The initial task in approaching the description of a chemically reacting system is to understand the answer to the question that what changes are going to occur.
For example, nitrogen (N_2) and hydrogen (H_2) are reacted over an iron catalyst to give ammonia (NH_3):

$N_2 + 3H_2 \longrightarrow 2NH_3$

Generally at the exit of the reactor fifty percent of nitrogen is converted. We can expect that production of ammonia can be increased significantly by adding a catalyst (lets say). But then THERMODYNAMICS tells us that we cannot improve the conversions significantly unless we change the conditions of temperature & pressure. Thus first of all we should identify the constraints imposed by thermodynamics on the reaction.

1.2 HOW A REACTION PROCEEDS

Let's take the simple example of ammonia synthesis
$N_2 + 3H_2 \longrightarrow 2NH_3$

Suppose initially we have 10 moles of nitrogen and hydrogen each and no moles of product.

The coefficient of reactants and products in the reaction are called STOICHIOMETRIC COEFFICIENT.

	N_2	$3H_2$	$2NH_3$
t = 0:	10	10	0
$t = t_1$:	9	7	2
$t = t_2$:	8	4	4
$t = t_3$:	7	1	6
$t = t_4$	(7-1/3)	0	(6 + 2/3)

We can have the following conclusions

- The total mass during a reaction remains constant
- Mass of a species and moles of a species change during the reaction
- The reactant which gets consumed first is called the LIMITING REACTANT while the other

reactant is called the EXCESS REACTANT.

- Most of the reaction does not go to completion, they attain equilibrium somewhere before the completion.
- All the stoichiometric calculations should be done on the basis of limiting reactant only.

1.2.1 Identifying the limiting reactant

- Divide the initial moles of the reactant with its stoichiometric coefficient.
- The reactant for which the above value is less becomes the limiting reactant.
- If the reactants are present in stoichiometric proportion or stoichiometric ratio i.e., the ratio of initial moles of reactants to their corresponding stoichiometric coefficient are equal, then none of the reactants are limiting. We can also say that both of them are limiting reactants.

1.2.2 Conversion / Fractional conversion

- Conversion is only defined for reactants and never for products.
- Conversion of reactant A is defined as

$$X_A = \frac{N_{A_o} - N_A}{N_{A_o}} \text{ or } X_A = \frac{F_{A_o} - F_A}{F_{A_o}}$$

- Here N_{A_o} is the initial moles of A and N_A is the moles of A left at the time when we want to calculate conversion.

F_{A_o} & F_A have the same meaning in terms of flow rates.

- Conversion of all the reactants can be found, but because we do the stoichiometric calculations on the basis of the limiting reactant, hence it is usually provided for the limiting reactant.

- For a general reaction

$aA + bB \rightarrow cC + dD$ where we have N_{A_o} moles of A, N_{B_o} moles of B, N_{C_o} moles of C & N_{D_o} moles of D initially.
By using the reaction stoichiometry and assuming that A is the limiting reactant whose conversion is known, we can write the following equations

$$N_A = N_{A_o}(1 - X_A)$$

$$N_B = N_{B_0} - \frac{b}{a} N_{A_o} X_A$$

$$N_C = N_{C_0} + \frac{c}{a} N_{A_o} X_A$$

$$N_D = N_{D_o} + \frac{d}{a} N_{A_o} X_A$$

- If conversion of one reactant is known and the stoichiometry is known, we can find all other moles.
- The relation between conversions of two reactants is given by

$$X_B = \frac{bN_{A_o}}{aN_{B_0}} X_A$$

- The above equation suggests that if the reactants are present in the stoichiometric proportion then the conversion of both the reactants are same.

1.3 RATES OF A REACTION

- The rate of a reaction can be average rate or instantaneous rate. Average rate is defined between two instants of time while instantaneous rate is defined at a particular instant.
- For the reaction $aA+bB \rightarrow cC+dD$

$$(-r_A)=\frac{-1dN_A}{Vdt}$$

$$(-r_B)=\frac{-1dN_B}{Vdt}$$

$$(r_C)=\frac{1dN_C}{Vdt}$$

$$(r_D)=\frac{1dN_D}{Vdt}$$

- The negative sign in the case of reactants indicates that they are being consumed. However the negative sign on the left side is only for notation, it should never be used for mathematical calculations.
- In the above equations, V denote the volume of reaction mixture. It is usual practice to find the rates in homogenous systems on the basis of volume of reaction mixture.
- The above rates are related as

$$\frac{(-r_A)}{a}=\frac{(-r_B)}{b}=\frac{(r_C)}{c}=\frac{(r_D)}{d}$$

- Rates depends upon the concentration of the reacting species as well as the temperature. Some other factors like catalyst can also affect the rate of reaction.

1.4 THE RATE LAW

- Rate law is an expression which is obtained from experimental results.
- Rate law has a general form of

$$rate=k\{f(T)only\}*g\{Concentration\}$$

$$rate=k\,C_A^{\alpha}C_B^{\beta}$$

- k is called the rate constant or the specific reaction rate and it is a function of temperature only.
- $\alpha \& \beta$ are called order of the reaction with respect to A & B respectively.
- The overall order of the reaction is denoted by n and n = $\alpha+\beta$
- The units of rate constant is given by $\left(\frac{mol}{L}\right)^{1-n} s^{-1}$ if concentration is expressed in mol/L and time in seconds.
- Since order of a reaction is determined from the rate law, order of a reaction is an experimental quantity.
- Radioactive decay is an example of first order reaction.
- The rate law of a reaction is independent of the way in which the reaction is written.

1.4.1 ELEMENTARY & NON-ELEMENTARY REACTIONS

- The reactions which take place in a single step only are called elementary reactions.
- For an elementary reaction, there is a direct correspondence between the order w.r.t a reactant and its stoichiometric coefficient.
- For elementary reactions α = a & β = b. The overall order of the elementary reaction is hence equal to a+b.

- Non-elementary reactions takes place in more than one steps. One of these steps is the slowest step which is the rate determining step also.
- The rate law of a non-elementary reaction is written from the rate determining step.
- Just by looking at the reaction, we cannot say whether the reaction is elementary or not.

1.4.2 ORDER AND MOLECULARITY OF A REACTION.

- Molecularity is only defined for elementary reactions.
- Molecularity of an elementary reaction is the number of molecules colliding to form products.
- The value of molecularity cannot be zero, negative or fraction.
- However order of a reaction can be zero, negative or fraction.
- For an elementary reaction, order of the reaction is equal to the molecularity of the reaction.

1.5 TYPES OF REACTION SYSTEM

In chemical reaction engineering we have two types of reaction systems.

(1) Constant volume reaction system (CVRS)

(2) Variable volume reaction system (VVRS)

In CVRS, the volume of reaction mixture remains constant with conversion or with reaction time. This constant value of volume is equal to the initial volume of the reaction mixture.

In VVRS, the volume of reaction mixture changes as reaction proceeds. The volume of reaction mixture may increase or decrease with conversion. In both cases it is called variable volume reaction system.

- All the liquid and aqueous phases reactions, irrespective of stoichiometric coefficients are considered as CVRS.
- If the reaction takes place in gas phase then we have to check whether the reaction is CVRS or VVRS
- For a gas phase reaction, if sum or stoichiometric coefficients of reactants and products is same, then it is constant volume reaction system.
- For a gas phase reaction, if sum or stoichiometric coefficients of reactants and products is different, then it is variable volume reaction system.

1.5.1 FRACTIONAL VOLUME CHANGE

To give a qualitative meaning to change in volume during the reaction we have introduced ε, which is called fractional volume change. It is defined as

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

Similarly we can define $\varepsilon_B = \frac{V_{X_B=1} - V_{X_B=0}}{V_{X_B=0}}$

- ε is only defined for reactants because its definition is based on the conversion of the reactants.
- The value of ε indicates whether the volume of reaction mixture is constant or changing and hence it

tells about the volume change quantitatively.

- If ε =0 there is no change in volume and hence the system is CVRS. While if $\varepsilon \neq 0$, there is change in volume and hence the system is VVRS.
- If ε is positive, there is an increase in volume with the reaction, while if ε is negative there is a decrease in volume of the reaction mixture with reaction.
- There is no need to find the value of ε for aqueous and liquid phase reaction irrespective of nature of stoichiometric coefficients.
- The value of ε is always calculated for complete conversion of the reactant, irrespective of the actual conversion. Hence we can say that the value of ε is independent of actual conversion.

Since at constant pressure and temperature, volume is directly proportional to the number of moles, we can also define the value of ε as

$\varepsilon_A = \dfrac{N_{T|X_B=1} - N_{T|X_B=0}}{N_{T|X_B=0}}$ where N_T denotes the total moles of reaction mixture. Similarly ε_B can be defined on the basis of total moles.

1.5.2 CALCULATION OF ε

Let's consider the following example of gas phase reaction.

$2A + 3B \rightarrow C + D$

$N_{Ao} = 50$

$N_{Bo} = 50$

Species	N_i@ X_A=0	N_i@ X_A=1
A	50	0
B	50	-25
C	0	25
D	0	25
TOTAL	100	25

- Without knowing the actual conversion we can calculate the value of ε.

Hence according to the definition of ε

$$\varepsilon_A = \frac{25-100}{100} = -0.75$$

Similarly, for the same reaction and initial feed

Species	N_i@ X_B=0	N_i@ X_B=1
A	50	0
B	50	50-(100/3)
C	0	50/3
D	0	50/3
TOTAL	100	50

$$\varepsilon_B = \frac{50-100}{100} = -0.5$$

With any of the values we can say that the volume of reaction mixture decreases with time or with conversion.

1.5.3 RELATION BETWEEN VOLUME OF REACTION MIXTURE AND ε_A

At constant temperature and pressure and assuming that the gaseous reaction mixture obeys ideal gas law, we have the following relations

$V = V_o(1+\varepsilon_A X_A)$ & $V = V_o(1+\varepsilon_B X_B)$

For the same conditions we can write the above equations in the form of total moles also

$$- N_T = N_{To}(1+\varepsilon_A X_A) \;\&\; N_T = N_{To}(1+\varepsilon_B X_B)$$

The above equations also shows that total volume of reaction mixture is a linear function of conversion.

However, if ideal gas law is not obeyed, then we have the following relation

$$V = V_o(1+\varepsilon_A X_A)\frac{P_o T}{P T_o}$$

- Hence from the above discussion it should be clear that the value of fractional volume change depends upon the reaction stoichiometry and the feed concentration.

1.6 RELATIONS FOR CVRS & VVRS

When there is no volume change during the reaction, all the relations which are valid for moles of species or molar flowrates, are also valid for concentration of species.

But when there is a volume change during the reactions, we should be careful while writing different relations.

For constant volume systems

$$N_T = N_{To}$$
$$V = V_o$$
$$\varepsilon_A = 0$$
$$N_A = N_{A_o}(1-X_A)$$
$$C_A = C_{A_o}(1-X_A)$$
$$dC_A = -C_{A_o}dX_A$$
$$(-r_A) = -\frac{dC_A}{dt} = \frac{C_{A_o}dX_A}{dt}$$

Constant volume systems are also called constant density systems.

For variable volume systems because volume of the system changes with the reaction and moles of species are also changing during the reaction there is no direct relationship between moles and concentrations. Hence different relations will be used. Variable volume problems are also called variable density problems.

$$N_T = N_{To}(1+\varepsilon_A X_A)$$
$$V = V_o(1+\varepsilon_A X_A)\frac{P_o T}{P T_o}$$
$$\varepsilon_A \neq 0$$
$$N_A = N_{A_o}(1-X_A)$$
$$C_A = \frac{C_{A_o}(1-X_A)}{(1+\varepsilon_A X_A)}$$
$$(-r_A) = C_{A_o}\frac{dX_A}{(1+\varepsilon_A X_A)dt}$$

1.7 KINETIC EQUATIONS FOR CONSTANT VOLUME REACTION SYSTEM

The rate equations of the form $\frac{-dC_A}{dt} = kC_A^n$ is called differential rate equation. This equation has to be integrated to obtain integrated rate equation or kinetic equation for different orders of reactions for both constant volume problems and variable volume problems.

In the beginning we will start with constant volume reaction systems of different orders but with one type of reactant only.

1.7.1 UNIMOLECULAR ZERO ORDER REACTIONS (CVRS)

$$A \xrightarrow{k} \text{Products}$$

$$\frac{-dC_A}{dt} = k$$

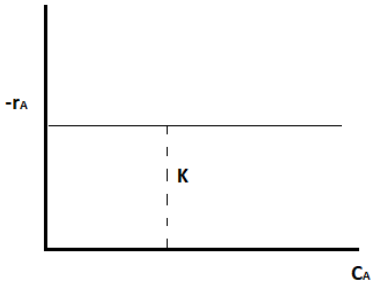
$$-dC_A = kdt$$

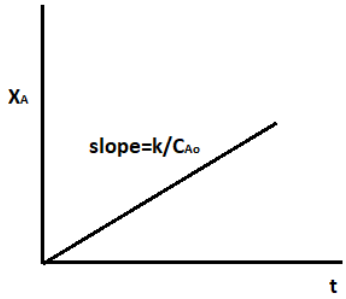
$$\int_{C_{A_o}}^{C_A} -dC_A = k\int_0^t dt$$

$$C_{A_o} - C_A = kt$$

$$C_{A_o} X_A = kt$$

- In a zero order reaction the rate remains constant with conversion or time.
- A zero order reaction can go to completion in finite time.
- The time of completion of a zero order reaction is given by $t = \frac{C_{A_o}}{k}$
- The conversion obtained in a zero order reaction in a given time interval depends upon initial concentration.
- The following plots can be obtained from above equations.





1.7.2 FIRST ORDER REACTIONS

$$A \xrightarrow{k} \text{Products}$$

$$\frac{-dC_A}{dt} = kC_A$$

$$\frac{-dC_A}{C_A} = kdt$$

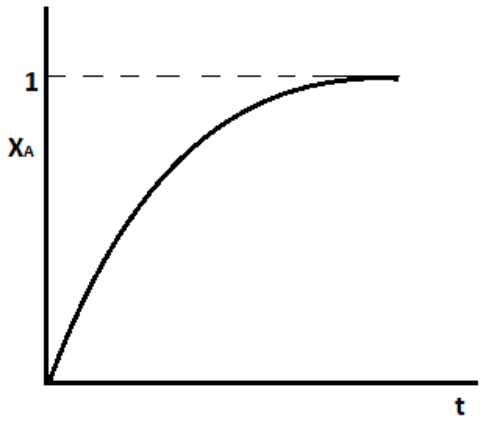
$$\int_{C_{A_o}}^{C_A} \frac{-dC_A}{C_A} = k\int_0^t dt$$

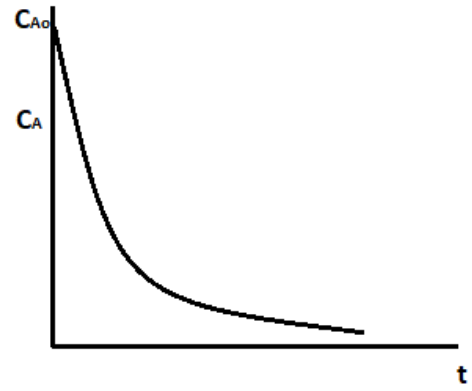
$$C_A = C_{A_o} e^{-kt}$$

$$\ln(1 - X_A) = -kt$$

- It shows that rate of a first order reaction decreases exponentially with time.
- The conversion of a first order reaction increases exponentially with time.
- A first order reaction never goes to completion in finite time.
- The conversion obtained for a first order reaction in a given time is independent of initial concentration.
- Rate also decreases exponentially for a first order reaction.

The following plots can be obtained from the above equations.





1.7.3 SECOND ORDER REACTION

$$A \xrightarrow{k} \text{Pr}oducts$$

$$\frac{-dC_A}{dt} = kC_A^2$$

$$\frac{-dC_A}{C_A^2} = kdt$$

$$\int_{C_{A_o}}^{C_A} \frac{-dC_A}{C_A^2} = k\int_0^t dt$$

$$\frac{1}{C_A} - \frac{1}{C_{A_o}} = kt$$

$$\frac{X_A}{1-X_A} = kC_{A_o}t$$

- A second order reaction also never goes to completion in finite time.
- The conversion achieved in a given time interval depends upon the initial concentration.

For nth order CVRS we can write the general equation of integrated rate expression, which is given by

$$\frac{1}{C_A^{n-1}} - \frac{1}{C_{A_o}^{n-1}} = (n-1)kt\,;n \neq 1$$

1.7.4 SECOND ORDER BIMOLECULAR REACTION (CVRS)

$$A + B \xrightarrow{k} \text{Pr}oducts$$

$$\frac{-dC_A}{dt} = kC_AC_B$$

Let $\frac{C_{Bo}}{C_{Ao}} = M$

$$\frac{-dC_A}{dt} = kC_{A_o}(1-X_A)(C_{B_o} - C_{Ao}X_A)$$

$$\frac{C_{Ao}dX_A}{dt} = kC_{Ao}^2(1-X_A)(M-X_A)$$

After integrating the above expression, we get

$$\ln\frac{M-X_A}{M(1-X_A)} = C_{A_o}(M-1)kt\,;M \neq 1$$

- If M=1 i.e, the reactants are present in stoichiometric proportion, then it can be easily proved that the integrated rate expression will be same as that of second order uni-molecular reaction.

1.7.5 IRREVERSIBLE PARALLEL REACTIONS

Consider the reactant A reacting by two paths where both paths are elementary. These reactions are considered under the category of multiple reactions. Because we have considered both reactions to be elementary, both of them are of first order.

Also because of the stoichiometry we can say that

$$C_{A_o} = C_A + C_R + C_S$$

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A + k_2 C_A = (k_1 + k_2) C_A$$

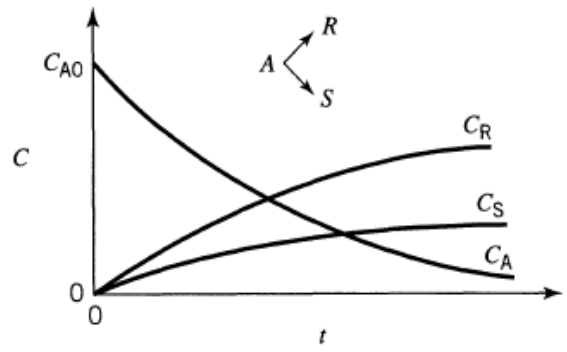
$$r_R = \frac{dC_R}{dt} = k_1 C_A$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A$$

Integrating the above equation gives

$$C_A = C_{A_o} e^{-(k_1 + k_2)t}$$

The concentration profile for this parallel react ion can be shown as



For parallel reactions we can also write

$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$ which on integrating gives

$$\frac{C_R - C_{Ro}}{C_S - C_{So}} = \frac{k_1}{k_2}$$

1.7.6 IRREVERSIBLE SERIES REACTIONS

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

$$(-r_A) = \frac{-dC_A}{dt} = k_1 C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R$$

For the first reaction the relation is same as of a first order reaction and is given by

$$C_A = C_{A_o} e^{-kt}$$

If the value of C_A is substituted in the second differential equation, we get a linear differential equation in C_R

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A_o} e^{-k_1 t}$$

The equation can be solved to give C_R

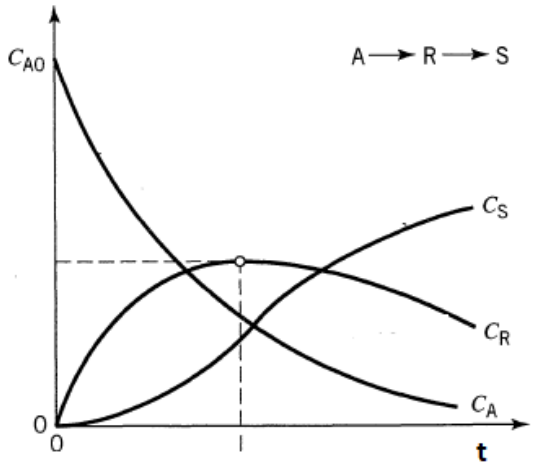
$$C_R = C_{A_o} k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right)$$

Now by using the condition

$C_{A_o} = C_A + C_R + C_S$, we can calculate C_S

$$C_S = C_{A_o} \left(1 + \frac{k_2 e^{-k_1 t}}{k_1 - k_2} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right)$$

The concentration profiles can be shown as



The concentration of R passes through a maxima. The time at which concentration of R is maximum can be obtained by differentiating the expression of C_R with respect to time and equating it to zero.

$$t_{max} = \frac{1}{k_{log\,mean}} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}$$

1.7.7 FIRST ORDER REVERSIBLE REACTION

Let us consider the elementary first order reversible reaction $A \Leftrightarrow B$.

$$-\frac{dC_A}{dt} = C_{A_o}\frac{dX_A}{dt} = k_1 C_A - k_2 C_B$$

$$= k_1 C_{A_o}(1 - X_A) - k_2(C_{B_o} + C_{A_o} X_A)$$

$$= \frac{dX_A}{dt} = k_1 C_{A_o}[(1 - X_A) - \frac{k_2}{k_1}(M + X_A)]$$

For reversible reactions, we can also define the equilibrium constant K_C as $\frac{k_1}{k_2}$ and equilibrium conversion $X_{A_e} = \frac{M + X_{Ae}}{1 - X_{Ae}}$, where $M = \frac{C_{Bo}}{C_{Ao}}$

Substituting the relations for equilibrium conversion and M in the differential equation, we obtain the following equation

$$\frac{dX_A}{dt} = \frac{k_1(M+1)}{M + X_{Ae}}(X_{Ae} - X_A) \text{ and}$$

integrating,

$$-\ln(1 - \frac{X_A}{X_{Ae}}) = \frac{M+1}{M + X_{Ae}} k_1 t$$ which is the final integrated rate expression. Note that this result is only valid for the given order and given stoichiometry.

1.7.8 AUTOCATALYTIC REACTIONS

A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction. The simplest such reaction is $A + R \rightarrow R + R$.

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R$$

According to the reaction stoichiometry, total moles of reactants and products remains constant.

$$C_o = C_A + C_R = C_{Ao} + C_{Ro}$$

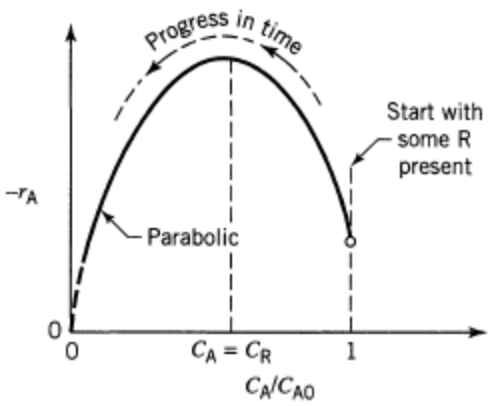
$$-r_A = -\frac{dC_A}{dt} = kC_A(C_o - C_A)$$

$$-\frac{dC_A}{C_A(C_o - C_A)} = -\frac{1}{C_o}\left(\frac{dC_A}{C_A} + \frac{dC_A}{C_o - C_A}\right) = kdt$$

After integration it yields, assuming M is the initial ratio of the reactants R to A.

$$\ln \frac{M + X_A}{M(1 - X_A)} = C_{Ao}(M+1)kt$$

- For an autocatalytic reaction to proceed, there must be some amount of R present initially. As more R is formed, the rate increases. But, we know that as A is also getting consumed, the rate must fall to zero after some time. Hence the rate curve passes through a maxima.



1.8 KINETIC EQUATIONS FOR VARIABLE DENSITY SYSTEMS

For zero order variable volume reaction systems we can write

$\frac{C_{Ao}dX_A}{(1+\varepsilon_A X_A)dt} = k$ Which on integration gives

$$\frac{\ln(1+\varepsilon_A X_A)}{\varepsilon_A} = \frac{kt}{C_{Ao}}$$

- For first order reactions, it can be easily proved that the kinetic equation for variable volume reaction system is same as of constant volume reaction system.

1.9 HALF -LIFE OF A REACTION

The time required for a reaction to reach 50% conversion is known as half-life of the reaction. For ease of analysis, we will only discuss constant volume reaction system for calculation of half-life.

The expression of half-life can be easily obtained by substituting, $C_A = \frac{C_{A0}}{2} or\ X_A = 0.5$ in the kinetic equations developed earlier.

- Hence for a zero order reaction half-life is given by $t_{1/2} = \frac{C_{A0}}{2k}$.
- Half-life of a first order reaction is $t_{1/2} = \frac{0.693}{k}$.
- Half-life of a first order reaction is independent of initial concentration while for a zero order reaction, it depends upon initial concentration.
- From the kinetics of nth order system, it can be easily derived that Half-life of nth order system is given by $t_{1/2} = \frac{(0.5)^{1-n}-1}{k(n-1)}C_{Ao}^{1-n}$.
- We can also say that half-life of a reaction is directly proportional to C_{Ao}^{1-n}. This relation can be used to determine the order of the reaction.

Similar to half-life, we can also define fractional life of a reactant. If X denotes the fraction of A reacted, F denotes the fraction of A remaining. Hence X+F = 1. Fractional life is the time taken by the reaction such that fraction F of reactant is remaining. Hence fractional life for nth order reaction is given by $t_F = \frac{(F)^{1-n}-1}{k(n-1)}C_{Ao}^{1-n}$.

- Fractional life of a reactant is directly proportional to $(F)^{1-n}-1$.
- Above relation can also be used to determine the order of a reaction.

1.10 TEMPERATURE DEPENDENCY OF RATE

The rate constant present in the rate law depends upon temperature only. The effect of temperature on rate constant and hence on the rate of reaction is given by many theories. The most accepted theory is the Arrhenius theory which relates k with T as

$k = k_o e^{\frac{-E_a}{RT}}$

where E_a is the activation energy.

- Ko is called pre-exponential factor and assumed to be independent of temperature.
- The activation energy of a reaction is always positive and is also assumed to be independent of temperature.
- The relation clearly shows that with increase in temperature, rate constant increases and hence rate increases.

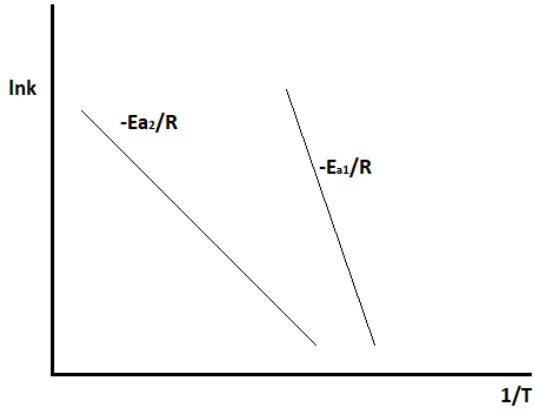
The Arrhenius relation can be written in a different form for two values of temperatures

$\ln\frac{k_2}{k_1}=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ where k_1 and k_2 are the rate constants at T_1 & T_2.

- Other theories were also given for the reaction rates. According to collision theory the rate constant is related to temperature as $k=k_oT^{\frac{1}{2}}e^{\frac{-E_a}{RT}}$
- According to transition state theory the rate constant is given by $k=k_oTe^{\frac{-E_a}{RT}}$
- By default Arrhenius theory should be used for solving numerical problems unless specified.

On taking log on both sides of Arrhenius theory, $\ln k=\ln k_o-\frac{E_a}{RT}$. If we plot ln(k) vs 1/T , it will be a straight line of slope $\frac{E_a}{R}$.

If we consider two different reactions of activation energy E_{a1} & E_{a2} such that $E_{a1}>E_{a2}$, then the plot shows that reactions with higher activation energy are more temperature sensitive. It means that if temperature is increased, the rate constant of both reactions will increase , the increase for reaction 1 will be more than increase for reaction 2.



GATE QUESTIONS

1. The reaction rate constants at two different temperatures T_1 and T_2 are related by

(a) $ln\left(\frac{k_2}{k_1}\right)=\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

(b) $ln\left(\frac{k_2}{k_1}\right)=\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

(c) $\exp\left(\frac{k_2}{k_1}\right)=\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

(d) $\exp\left(\frac{k_2}{k_1}\right)=\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

(GATE 2001)

2. The conversion for a second order, irreversible reaction (constant volume) $A \xrightarrow{k_2} B$, in batch mode is given by

(a) $\frac{1}{1+k_2C_{A_0}t}$ (b) $\frac{k_2C_{A_0}t}{1+k_2C_{A_0}t}$

(c) $\frac{(k_2C_{A_0}t)^2}{1+k_2C_{A_0}t}$ (d) $\frac{k_2C_{A_0}t}{\left(1+k_2C_{A_0}t\right)^2}$

(GATE 2001)

3. The following half-life data are available for the irreversible liquid phase reaction, $A \rightarrow$ products:

Initial concentration (kmol/m^3)	Half-life (min)
2	2
8	1

The overall order of the reaction is

(a)0.5 (b)1

(c)1.5 (d)2

(GATE 2001)

4. In the hydro dealkylation of toluene to benzene, the following reactions occur

$$C_7H_8+H_2 \rightarrow C_6H_6+CH_4$$
$$2C_6H_6+ \rightarrow C_{12}H_{10}+H_2$$

Toluene and hydrogen are fed to a reactor in a molar ratio 1:5 80% of the toluene gets converted and the selectivity of benzene (defined as moles of benzene formed /per moles of toluene converted) is 90% .the fractional conversion of hydrogen is

(a)0.16 (b)0.144

(c)0.152 (d)0.136

(GATE 2002)

5.The extent of a reaction is

(a) Different for reactants and products

(b) Dimensionless

(c) Dependent on the stoichiometric coefficients

(d) all of the above

(GATE 2002)

6. For an isothermal second order aqueous phase reaction $A \rightarrow B$, the ratio of the time required for 90% conversion to the time required for 45% conversion is

(a) 2 (b) 4

(c) 11 (d) 22

(GATE 2004)

7. The rate of ammonia synthesis for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is given by $r = 0.8P_{N_2}P_{H_2}^3 - 0.6P_{NH_3}^2$. If the reaction is represented as, $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons \frac{1}{2}NH_3$, the rate of ammonia synthesis is

(a) $r = 0.8P_{N_2}^{0.5}P_{H_2}^{1.5} - 0.6P_{NH_3}$

(b) $r = 0.8P_{N_2}P_{H_2}^3 - 0.6P_{NH_3}^2$

(c) $r = 0.5\left(0.8P_{N_2}P_{H_2}^3 - 0.6P_{NH_3}^2\right)$

(d) $r = 0.5\left(0.8P_{N_2}^{0.5}P_{H_2}^{1.5} - 0.6P_{NH_3}\right)$

(GATE 2004)

8. The rate expression for the gaseous phase reaction $CO + 2H_2 \rightleftharpoons CH_3OH$ is given by $r = k_1 p_{CO}^{\alpha} p_{H_2}^{\beta} - k_2 p_{CH_3OH}^{\gamma}$

(a) $\alpha = 1, \beta = 1, \gamma = 1$

(b) $\alpha = 1, \beta = 2, \gamma = 1$

(c) $\alpha = 1/3, \beta = 2/3, \gamma = 1$

(d) $\alpha = 1/2, \beta = 1, \gamma = 1/2$

(GATE 2004)

9. The rate expression for the reaction of A is given by $-r_A = \frac{k_1 C_A^2}{1 + k_2 C_A^{1/2}}$. The units of k_1 and k_2 are respectively

(a) $(mol^{-1}m^3s^{-1}), (mol^{-1/2}m^{3/2})$

(b) $(mol^{-1}m^3s^{-1}), (mol^{1/2}m^{3/2})$

(c) $(molm^{-3}s^{-1}), (mol^{1/2}m^{-3/2}s^{-1})$

(d) $(mol^{-1}m^{-3}s^{-1}), (mol^{-1/2}m^{3/2}s^{-1/2})$

(GATE 2005)

10. Which is the correct statement from the following statements on the Arrhenius model of the rate constant $k = Ae^{-E/RT}$

(a) A is always dimensionless

(b) for two reaction 1 and 2, if $A_1 = A_2$ and $E_1 > E_2$, then $k_1(t) > k_2(t)$

(c) for a given reaction, the percentage change of k with respect to temperature is higher at lower temperatures

(d) the percentage change of k with respect to temperature is higher for higher A. **(GATE 2005)**

11. For the liquid phase reaction $S \rightarrow P$, in a series of experiments in a batch reactor, the half-life $(t_{1/2})$ was found to be inversely proportional to the square root of the initial concentration of A. The order of the reaction is

(a) $\frac{3}{2}$ (b) 1

(c) $+\frac{1}{2}$ (d) $-\frac{1}{2}$

(GATE 2005)

12. For the reaction $2R + S \rightarrow T$, the rates of formation r_R, r_S and r_T of the substances R, S and T respectively, are related by

(a) $2r_R = r_S = r_T$ (b) $2r_R = r_S = -r_T$

(c) $r_R = 2r_S = 2r_T$ (d) $r_R = 2r_S = -2r_T$

(GATE 2005)

13 .The rate, at which an antiviral drug acts, increases with its concentration in the blood C, according to the equation

$$r = \frac{kC}{C_{50} + C}$$

Where C_{50} is the concentration at which the rate is 50% of the maximum rate K. Often the concentration C_{90} of the maximum, is measured instead of C_{50}. The rate equation then becomes

(a) $r = \frac{1.8kC}{C_{90} + C}$ (b) $r = \frac{kC}{\left(\frac{C_{90}}{9} + C\right)}$

(c) $r = \frac{kC}{C_{90}}$ (d) $r = \frac{0.9\ kC}{C_{90}}$

(GATE 2006)

14.For a homogenous reaction system, where

C_i - is the concentration of i at time t

N_i is the number of moles of i at time t

V is the reaction volume at time t

t is the reaction time,

The rate of reaction for species j is defined as

(a) $\frac{dC_j}{dt}$ (b) $-\left(\frac{dC_j}{dt}\right)$

(c) $\frac{1}{v}\frac{dN_j}{dt}$ (d) $-\left(\frac{1}{v}\frac{dN_j}{dt}\right)$

(GATE 2009)

15. The half-life of a first order liquid phase reaction in 30 sec. Then the rate constant in min^{-1} is

(a) 0.0231 (b) 0.602

(c) 1.386 (d) 2.0

(GATE 2009)

16 .The half-life of an nth order reaction in a batch reactor depends

(a) only on the rate constant

(b) on the rate constant and the order of the reaction

(c) On the rate constant and the initial reactant concentration

(d) On the rate constant, initial concentration and the order of the reaction **(GATE 2012)**

17. The gas phase decomposition of azomethane to give ethane nitrogen takes place according to the following sequence of elementary reaction.

$$(CH_3)_2N_2 + (CH_3)N_2 \rightarrow K_1(CH_3)_2N_2 + \left[(CH_3)_2N_2\right]^*$$

$$\left[(CH_3)N_2\right]^* + (CH_3)_2N_2 \rightarrow K_2(CH_3)_2N_2 + (CH_3)_2N_2$$

$$\left[(CH_3)_2N_2\right]^* \rightarrow K_3C_2H_6 + N_2$$

using the pseudo-state-approximation for $\left[(CH_3)_2N_2\right]^*$, the order with respect to azomethane in the rate expression for the formation of ethane, in the limit of high concentrations of azomethane, is

(a) 0 (b) 1

(c) 3 (d)2

(GATE 2013)

18. A homogeneous reaction $(R \rightarrow P)$ occurs in a batch reactor. The conversion of the reactant R is 67% after 10 minutes and 80% after 20 minutes. The equation for this reaction is

(a) $-r_R = k$ (b) $-r_R = kC_R^2$

(c) $-r_R = kC_R^3$ (d) $-r_R = kC_R^{0.5}$

(GATE 2014)

19.An irreversible, homogeneous reaction $A \rightarrow$ Products, has the rate expression:

$Rate = \frac{2C_A^2 + 0.1C_A}{1+50C_A}$, where C_A the concentration of A is C_A varies in the range 0.5-50 mol/m^3.For very high concentration of A, the reaction order tends to:

(a) 0 (b) 1

(c) 1.5 (d)2

(GATE 2015)

20.For which reaction order, the half-life of the full lifetime (time for 100% conversion) of the reactant?

(a) Zero order (b) Half order

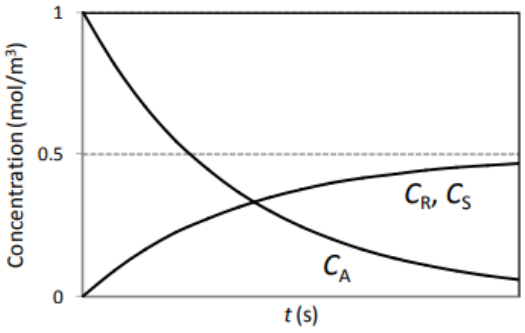
(c) First order (d) Second order

(GATE 2015)

21. Hydrogen iodide decomposes through the reaction $2HI \rightleftharpoons H_2 + I_2$.the value of the universal gas constant R is 8.314 $J\,mol^{-1}K^{-1}$. the activation energy for the forward reaction is 184000J mol^{-1} . ratio (rounded off to the first decimal place) of the forward reaction rate at 600 K to that at 550 K is_____

(GATE 2016)

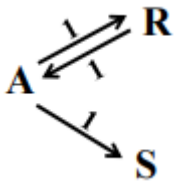
22. The variations of the concentrations (C_A, C_R and C_S) for three species (A,R and S) with time, in an isothermal homogeneous batch reactor are shown in the figure below.



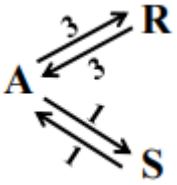
Select the reaction scheme that correctly represents the above plot. The numbers in the reaction schemes shown below, represent the first order rate constants in unit of s^{-1}.

(GATE 2016)

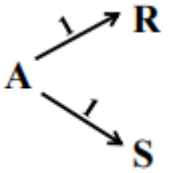
(a)



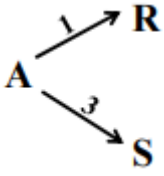
(b)



(c)



(d)



23. For a non-catalytic homogeneous reaction $A \rightarrow B$, the rate expression at 300 K is $-r_A(molm^{-3}s^{-1}) = \frac{10C_A}{1+5C_A}$,where C_A is the concentration of A (in mol/m^3). Theoretically, the upper limit for the magnitude of the reaction rate ($-r_A$ in $molm^3s^{-1}$, rounded off to the first decimal place) at 300 K is_____

(GATE 2016)

24. For a chemical reaction. The ratio of rate constant at 500 K to that at 400 K is 2.5. given R=8.314 J $mol^{-1}K^{-1}$,the value of activation energy (in kJ/mol) is

(a) 10.5 (b)12.0

(c)15.2 (d)18.4

(GATE 2018)

ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(B)	(B)	(C)	(C)	(D)	(C)	(B)	(A)	(A)	(C)
11	12	13	14	15	16	17	18	19	20
(A)	(D)	(B)	(C)	(C)	(D)	(B)	(B)	(B)	(A)
21	22	23	24						
(28.5)	(C)	(2)	(C)						

EXPLANATIONS

1.Solution:- (b)

Assuming Arrhenius law

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

$$\frac{k_1}{k_2} = e^{\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

Or

$$ln\left(\frac{k_1}{k_2}\right) = -\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Or

$$ln\left(\frac{k_1}{k_2}\right) = \frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Or

2.Solution:- (b)

The rate equation for second order reaction can be written as

$$\frac{-dC_{A0}}{dt} = k_2 C_A^2$$

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A^{\,2}} = \int_0^t k_2 dt$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = k_2 t$$

$$\frac{1}{C_A(1-X_A)} - \frac{1}{C_{A0}} = k_2 t$$

$$\frac{X_A}{C_{A0}(1-X_A)} = k_2 t$$

$$X_A = (1-X_A)k_2 C_{A0} t$$

$$X_A = \frac{k_2 C_{A0} t}{1+k_2 C_{A0} t}$$

3. Solution:- (c)

For nth order, $-\frac{dC_A}{dt} = kC_A^n ...(1)$

$$-\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^n} = \int_0^t kdt$$

$$C_A^{1-n} - C_{A_0}^{1-n} = k(n-1)t$$

For half-life, $t = t_{1/2}$ and $C_A = \frac{C_{A_0}}{2}$

$$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)} C_{A_0}^{1-n} ...(2)$$

Putting values from given data,

$$2 = \frac{(2^{n-1}-1)}{k(n-1)} \times 2^{1-n} ....(3)$$

And $1 = \frac{(2^{n-1}-1)}{k(n-1)} \times 8^{1-n} ....(4)$

Dividing Equation (4) by Equation (3),

$$\frac{1}{2} = \left(\frac{8}{2}\right)^{1-n}$$

$$\frac{1}{2} = 4^{1-n} \Rightarrow n = 1.5$$

4. Solution:- (c)

$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$

Initial moles a 5a 0 0

After 80% a(1-0.8) 5a-0.8a 0.8a 0.8 a

And $2C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2$

0.8a-2b b

Given, $\frac{\text{Moles Of benzene formed}}{\text{Moles of toluene converted}} = 0.9$

$\frac{0.8a - 2b}{0.8a} = 0.9$

Or $b = 0.04a$

Fractional conversion of hydrogen

$= \frac{0.8a - b}{5a} = \frac{0.8a - 0.04a}{5a} = 0.152$

5.Solution:(d)

All options are true

6. Solution:- (c)

$A \rightarrow B$

For second order reaction,

$(-r_A) = \frac{-dC_A}{dt} = kC_A^2$

$C_A = C_{A_0}(1 - X_A)$

Since, $\therefore C_{A_0}\frac{dX_A}{dt} = kC_{A_0}^2(1 - X_A)^2$

$\int_0^{X_A} \frac{dX_A}{(1 - X_A)^2} = kC_{A_0}\int_0^t dt$

$\left[\frac{1}{1 - X_A}\right]_0^{X_A} = kC_{A_0}t$

Or $t = \frac{1}{kC_{A_0}}\left(\frac{1}{1 - X_A}\right)$

Time required for 90% conversion, $t_{90} = \frac{1}{kC_{A_0}}\left(\frac{0.9}{1 - 09}\right) = \frac{9}{kC_{A_0}}$

Time required for 45% conversion, $t_{45} = \frac{45}{55}.\frac{1}{kC_{A_0}}$

Thus, $t_{45} = \frac{t_{90}}{t_{45}} = 9 \times \frac{55}{45} = 11$

7.Solution:(b)

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$r = 0.8p_{N_2}p^3NH_3 - 0.6p^2NH_3$

The rate of the reaction does not change even if we change the stoichiometric coefficient by a certain factor.

$\therefore For, \frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$

The rate of reaction remains same.

8.Solution :(b)

$CO + 2H_2 \rightleftharpoons CH_3OH$

The rate of reaction

$r = k_1 p_{CO}^{\alpha} p_{H_2}^{\beta} - k_2 p_{CH_3OH}^{\gamma}$

For this gas phase reaction α, β and γ should be in proportion to their respective stoichiometric coefficients.

Thus, $\alpha : \beta : \gamma = 1 : 2 : 1$

$\therefore \alpha : \beta : \gamma \neq 1 : 1 : 1$

9. Solution:- (a)

Given, $-r_A = \dfrac{k_1 C_A^2}{1 + k_2 C_A^{1/2}}$

Or $(-r_A) + (-r_A) k_2 C_A^{1/2} = k_1 C_A^2$

Each term in this equation will have same unit, i.e, $(-r_A)$

The unit of $(-r_A) = \dfrac{mol}{m^3 - s}$

$\therefore$ unit of $k_1 C_A^2 = \dfrac{mol}{m^3 - s}$

Or $k_1 = \left(\dfrac{mol}{m^3 - s}\right)\left(\dfrac{m^3}{mol}\right)^2$

Or $k_1 = mol^{-1} m^3 s^{-1}$

Now, unit of $(-r_A)$ $k_2 C_A^{1/2}$ = unit of $(-r_A)$

Or $k_2 \left(\dfrac{mol}{m^3}\right)^{1/2} = 1$

Or $k_2 = mol^{-1/2} m^{3/2}$

10.Solution:- (c)

The rate constant from Arrhenius model

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

Option (a)

$e^{-E/RT}$ is dimensionless.

$\therefore$ Units of K and A are same.

$\therefore$ A is not dimensionless.

Option(b) If $A_1 = A_2$

$\dfrac{k_1}{k_2} = e^{\frac{1}{RT}(E_1 - E_2)}$

11.Solution:- (a)

$A \rightarrow P$

For nth order reaction, the rate equation is

$\dfrac{-dC_A}{dt} = kC_A^n$

Or $C_A^{1-n} - C_{A0}^{1-n} = (n-1)t$

At half-life, $C_A = C_{A0/2}$

$\therefore t_{1/2} = \dfrac{2^{n-1} - 1}{k(n-1)} C_{A0}^{1-n}$

Now, check for all options given,

$n = \dfrac{3}{2}$

$t_{1/2}\, \alpha\, C_{A0}^{-1/2}\, \alpha\, \dfrac{1}{\sqrt{C_{A0}}}$

$\therefore n = \dfrac{3}{2}$ is correct answer.

12.Solution: (d)

$2R + S \rightarrow T$

The rates can be written for different substance as $r_R = 2r_S = -2r_T$

13. Solution:- (b) Given, $r = \dfrac{kC}{C_{50} + C}$...(1)

Also, $r_{\max} = k$ and $r_{90} = 0.9k$

Or $\dfrac{kC_{90}}{C_{50} + C_{90}} = 0.9k$

or $kC_{90} = 0.9k(C_{50} + C_{90})$

$C_{90} = 9C_{50}$.....(2)

From Eqs. (1) and (2)

$$r = \frac{kC}{\frac{C_{90}}{9} + C}$$

14.Solution:- (c)

$$\text{Rate of reaction} = \frac{1}{V}.\frac{dN_j}{dt}$$

Option(b) is also rate of reaction but for liquid phase reaction only.

15.Solution: (c)

For first order reaction

$$t_{1/2}\frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}}, = 30s = \frac{1}{2}$$

$$= 1.386\,\text{min}^{-1}$$

16. Solution:- (d)

For nth order reaction, $-\frac{dC}{dt} = kC^n$

Or $\int_{C_o}^{C}\frac{dC}{C^n} = \int_0^t -kdt$

Or $\frac{1}{1-n}\left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}}\right] = -kt$

For half-life, $t = t_{1/2}, C = \frac{C_0}{2}$

$$\frac{1}{C_0^{n-1}}.\frac{1}{(n-1)}(2^{n-1}-1) = kt_{1/2}$$

It can be seen that the half-life depends on rate constant(k), initial concentration

(C_0) and order of the reaction (n).

17. Solution:- (b)

$[C_2H_6]$ depends on $\left[(CH_3)_2N_2\right]^*$ which in turn depends on $\left[(CH_3)_2N_2\right]$. the ratio of all concentration is one. The order of reaction w.r.t $(CH_3)_2N_2$ is 1

18. Solution:- (b)

For ideal batch reaction

$$A = \int_{C_{A0}}^{C_A}\frac{dC_A}{-\gamma a} = \int_{C_{A0}}^{C_A}\frac{dC_A}{KC_A^n}$$

$$C_A = C_{A0}(1-X_A)$$

$$dC_A = -C_{A0}dX_A$$

$$t = -C_{A0}\int\frac{dX_A}{KC_{A0}^n(1-X_A)^n} = -\frac{C_{A0}^{1-n}}{K}\int_0^{X_A}\frac{dX_A}{(1-X_A)^n}$$

$$t = \frac{C_{A0}^{1-n}}{K}\left[\frac{(1-X_A)^{1-n}}{1-n}\right]^{X_A}$$

$$t = \frac{C_{A0}^{1-n}}{K}\left[\frac{(1-X_A)^{1-n}-1}{1-n}\right]$$

For reaction $R \to P$;

X_A =0.67, t =10 minutes

X_A = 0.08, t = 20minutes

$$10 = C_{A0}^{1-n}\left[\frac{0.33^{1-n}-1}{1-n}\right]\text{\_\_\_\_(1)}$$

$$20 = \frac{C_{A0}^{1-n}}{K}\left[\frac{0.2^{1-n}-1}{1-n}\right]\text{\_\_\_\_\_(2)}$$

Dividing equation (1) by equation (2) =

$$\frac{1}{2} = \frac{0.33^{1-n}-1}{0.2^{1-n}-1}$$

Solving we get $n = 2 \Rightarrow So, -\gamma_R = KC_R^2$

19.Solution: (b)

$$Rate = \frac{2C_A^2 + 0.1C_A}{1 + 50C_A}$$

$$0.5 < C_A < 50(mol/m^3)$$

For very high value of C_A (say $(50 mol/m^3)$

$$0.1C_A << 2C_A^2$$

$$and\, 50C_A >> 1$$

$$so, that = \frac{2C_A^2}{50C_A} = \frac{1}{25}C_A$$

So reaction order is one

20.Solution: (a)

For zero order reaction

$$\frac{dC_A}{dt} kC_A^0 = k$$

Where k=rate constant

$$C_{A0} - C_A = kt$$

For, full life time C_A=0

$$t = \frac{C_{A0}}{K}$$

And for half life

$$C_A = \frac{C_{A0}}{2}, So\ t_{\frac{1}{2}} = \frac{C_{A0}}{2k}$$

$$So, t = 2t_{\frac{1}{2}}$$

21.Solution:

$$ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\frac{k_2}{k_1} = 28.5$$

22. Solution:- (c)

23.Solution:

$$-r_a = \frac{10C_A}{1 + 5C_A}$$

$$@\, high C_A - r_A = \frac{10C_A}{5C_A} = 2$$

$$@\, low C_A - r_A = \frac{10C_A}{1} = 10C_A$$

$$= 10C_A\ ;\ 0\left[low C_A\right]$$

Upper limit $-r_A = 2$

24. Solution:- (c)

$$\ln\frac{k_2}{k_1} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln(2.5) = \frac{E_a}{8.314}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$E_a = 15.24$ kj/mol

2 DESIGN OF ISOTHERMAL IDEAL SINGLE REACTORS

2.1 INTRODUCTION

So far we were dealing with kinetics, i.e., how much time reaction will take to reach a particular conversion. But the question is which reactor is suitable for the operation. The reaction should be carried out in batch mode or continuous mode or semi-batch mode. In this chapter we will deal with choice and design of reactors. Design means sizing the reactor or finding the volume of reactor required for a given conversion .To find the volume of the reactor required, design equation or performance equation will be derived.

The performance equation of a reactor can be derived by writing material balance on any of the reactants or products. Because we are dealing with isothermal reactors in this chapter, so energy balance is not required. The general equation of material balance on a species A is given by

$$(moles\ A\ in) - (moles\ A\ out)$$
$$-(moles\ A\ reacted)$$
$$+(moles\ A\ generated) = (Accumulation\ of\ moles\ of\ A)$$

In this chapter we will deal with three types of reactors

(i) Batch reactors & semi-batch reactors

(ii) Continuous Stirred Tank Reactors

(iii) Plug Flow Reactors

2.2 IDEAL BATCH REACTORS

- The batch reactors are used in those cases where we have to produce less amount of products.
- In batch reactors there is no continuous inlet of reactants and no continuous outlet of products.
- All the reactants are charged at once and they are allowed to react for some time. Once desired conversion is achieved, the products are discharged at once.
- Since no continuous input or output is there, the IN and OUT terms of material balance are ZERO.
- In batch reactors we talk in terms of amount of substance, not in terms of flow rates of species.
- A batch reactor is considered to be uniformly or perfectly mixed but the conditions inside the reactor changes with time and hence it is an unsteady-state reactor.
- However the total mass inside the reactor remains constant, the species mass changes with time. Similarly other properties in the reactor also change with time.

Hence the material balance becomes,

$0 + 0 - (-r_A)V + 0 = \frac{dN_A}{dt}$ where V is the volume of reaction mixture. Integrating,

$$dt = \frac{-dN_A}{(-r_A)V}$$

$$\int_0^t dt = \int_0^{X_A} \frac{-dN_A}{VkC_{Ao}^n(1-X_A)^n}$$

The above integration has to be solved and it relates the time required to achieve a given conversion in the batch reactor.

For constant volume reactions and for variable volume reaction systems (batch reactor) the value of V has to be substituted and the integral has to be solved.

For constant volume batch reactors the above integral reduces to

$$\frac{t}{C_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$t = C_{Ao} \int_0^{X_A} \frac{dX_A}{kC_{Ao}^n(1-X_A)^n}$$

For variable volume batch reactors, the volume has to be kept inside the integral

$$dt = \frac{-dN_A}{(-r_A)V}$$

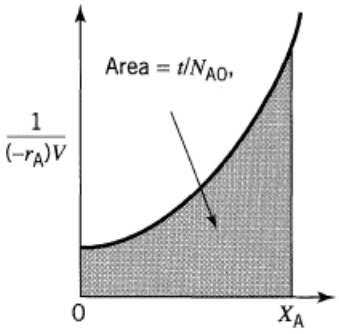
$$t = N_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)V}$$

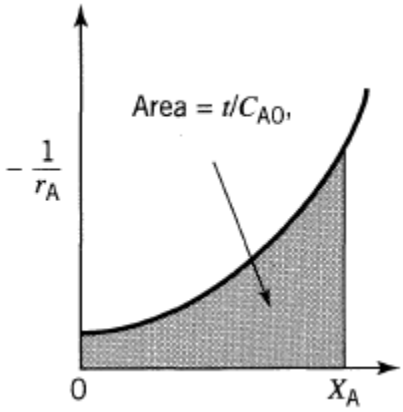
- A very important conclusion for batch reactors is the design or performance equation of batch reactors is same as the kinetic equations.
- It means that when we integrate the above equations for different orders and different systems (CVRS & VVRS) , we will obtain the same equations that we have obtained for kinetic equations.
- Hence all the previously derived equations can be used for the reactions taking place in a batch reactor.

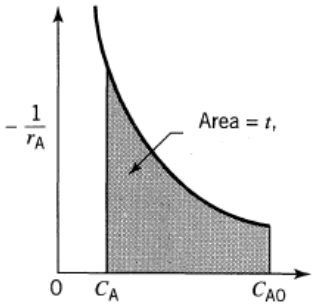
2.2.1 PERFORMANCE CURVES OF BATCH REACTORS

Performance curves are the plots between

$$\frac{1}{-r_A} Vs\, X_A \; or \; \frac{1}{-r_A} Vs\, C_A .$$







- For batch reactors , the shaded area (area under the curve) gives indication of how much time should be given to the reactants to achieve desired conversion.

2.3 CONTINUOUS REACTORS

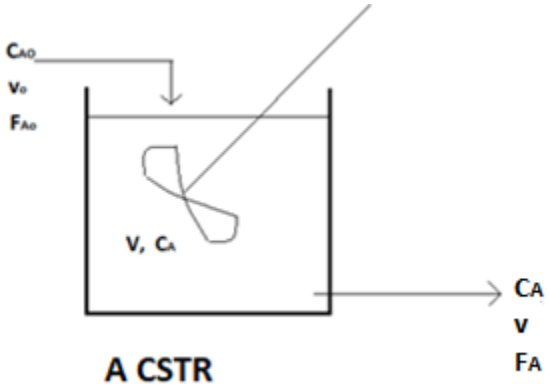
- The reactors where there is a continuous inlet stream of reactants and product is also withdrawn continuously are continuous reactors.
- In continuous reactors we can talk in terms of flow rates.
- Flow rates can be molar flow rates, mass flow rates, or volumetric flowrates.
- Continuous reactors can also be operated at unsteady state, but we always do the analysis of these reactors at steady state only. However the reactors may or may not be uniform.
- For continuous reactors we define two terms, **space time τ and space velocity $\frac{1}{\tau}$.**
- Space time is the time required to process one reactor volume. The space time has the units of time.
- $\tau = \frac{V_R}{v_o}$ where V_R is the reactor volume and v_0 is the inlet volumetric flowrate. Space time is always calculated at the inlet conditions and it is independent of what is happening inside the reactor.
- The reciprocal of space time is called space velocity and defined as the number of reactor volumes processed per unit time.
- Space time and space velocity are only defined for flow reactors and not for batch reactors.
- The average residence time $\bar{t}$ can also be defined for flow reactors. It can be understood as the ratio of volume of the reactor to the average volumetric flowrate.
- During gas phase reactions there may be increase or decrease in total moles and due to this the volumetric flowrate also increases and decreases which affects the average residence time.
- Hence for constant volume systems where volumetric flowrate at the inlet and inside the reactor are same, the value of space time and average residence time should be same.
- For variable volume systems, the volumetric flow rates inside the reactors may be less or more than that of the inlet, therefore space time and residence time are different.
- The above discussion suggests that for those gas phase reactions where there is increase in moles with reactions, average residence time should be less than space time and vice versa.

2.3.1 IDEAL MIXED FLOW REACTORS

The mixed flow reactors are also known as continuous stirred tank reactors (CSTR), and Constant flow stirred tank reactors (CFSTR). The ideal mixed flow reactors has the following characteristics

- The contents of the reactor are perfectly mixed and hence they are uniform in composition.
- Analysis of MFR is done at steady state.
- The composition and properties of exit stream of the MFR is same as that of the properties of the mixture inside the reactor.
- In a MFR there is a step change in properties of the inlet stream. Its concentration decreases suddenly as it enters the reactor. Similarly there is step change in properties like temperature, volumetric flowrates etc.

For a reaction $A \rightarrow \text{Pr}oducts$, the material balance becomes



$$F_{Ao} - F_A - (-r_A)V - 0 = 0$$
$$F_{Ao} - F_{A0}(1 - X_A) - (-r_A)V = 0$$
$$F_{Ao}X_A = (-r_A)V$$
$$\frac{V_M}{F_{Ao}} = \frac{X_A}{-r_A}$$

In the above equation V_M denotes the volume of the MFR required to achieve a conversion X_A.

Because the material balance was written on the basis of molar flow rates and molar flow rates are independent of change in volume, hence the equation can be used for both constant and variable volume systems.

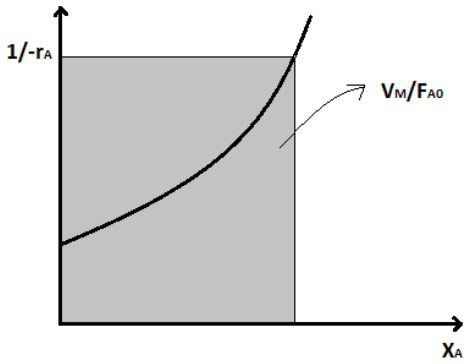
However if we substitute the value of X_A

$$X_A = 1 - \frac{C_A}{C_{Ao}}$$
$$\frac{V_M}{\upsilon} = \frac{C_{A0} - C_A}{-r_A}$$
$$\tau_M = \frac{C_{A0} - C_A}{-r_A}$$

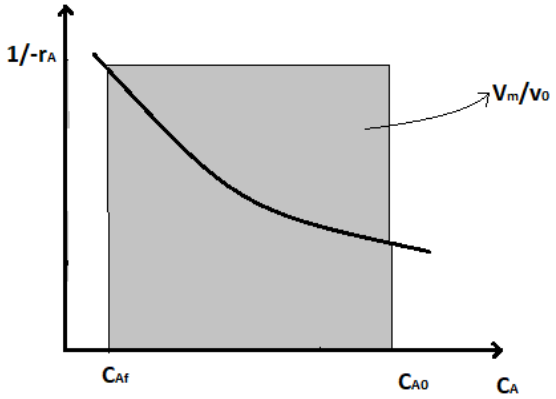
This equation can only be applied to constant volume systems. We can observe from the above equations that conversion achieved is proportional to the volume of the reactor. Higher the volume more is the conversion if rest everything remains same.

2.3.2 PERFORMANCE CURVES

Using the general equation $\frac{V_M}{F_{Ao}} = \frac{X_A}{-r_A}$



We do not consider the area of the curve for a MFR. We consider the area of the rectangle. This rectangle is completed according to the final conversion achieved in the reactor. For constant volume systems the performance curve becomes



- While solving problems on mixed flow reactors the value of rate has to be substituted in the design equation.
- The rate in the design equation should always be calculated according to the exit conversion.

For CVRS $\frac{V_M}{F_{Ao}} = \frac{X_A}{kC_{Ao}^n(1-X_A)^n}$

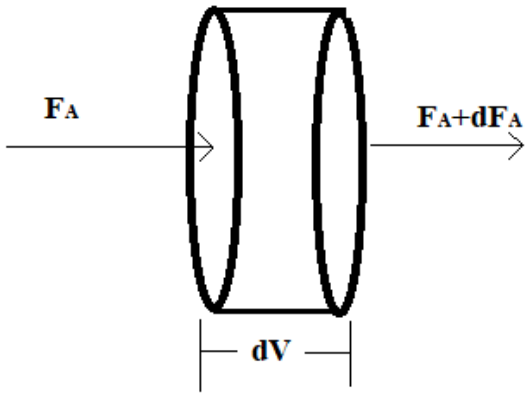
For VVRS $\frac{V_M}{F_{Ao}} = \frac{X_A(1+\varepsilon_A X_A)^n}{kC_{Ao}^n(1-X_A)^n}$

2.3.4 IDEAL PLUG FLOW REACTORS

Plug flow reactors are also called tubular reactors or unmixed reactors or piston flow reactor.

- In an ideal PFR there is no axial mixing. The liquid elements enter as a plug and the successive plugs are not mixed with each other.
- There is infinite radial mixing inside the PFR.
- Hence in an ideal PFR there will be concentration gradient in the axial direction while no concentration gradient in the radial direction.
- Each plug of liquid enters the reactor and spends same time inside the reactor.
- At a given time, there are many such plugs inside the PFR. Each plug is having a different concentration of reactants because they have spent different time inside the reactor. Hence the plug flow reactor is non-uniform.
- But if we consider a fixed location inside the reactor, then at that location concentration of any plug will be same.
- Any property, concentration or temperature or conversion changes gradually in a PFR.

Since the PFR is non-uniform, we cannot select the entire reactor as the control volume for writing the material balance equation. So we will select a thin strip of reactor of volume dV to write the balance and then integrate it over the entire volume of the reactor



$$F_A-(F_A+dF_A)-(-r_A)dV+0=0$$

Q $dF_A=-F_{Ao}dX_A$

$$\therefore \frac{dV}{F_{Ao}}=\frac{dX_A}{-r_A}$$

$$\int_0^{V_P}\frac{dV}{F_{Ao}}=\int_0^{X_A}\frac{dX_A}{-r_A}$$

$$\frac{V_P}{F_{Ao}}=\int_0^{X_A}\frac{dX_A}{-r_A}=\frac{\tau_P}{C_{A0}}=\int_0^{X_A}\frac{dX_A}{-r_A}$$

The above equation can be solved for different orders. Hence for constant volume reaction systems and first order systems,

$$\frac{\tau_P}{C_{Ao}}=\int_0^{XlA}\frac{dX_A}{kC_{Ao}(1-X_A)}$$

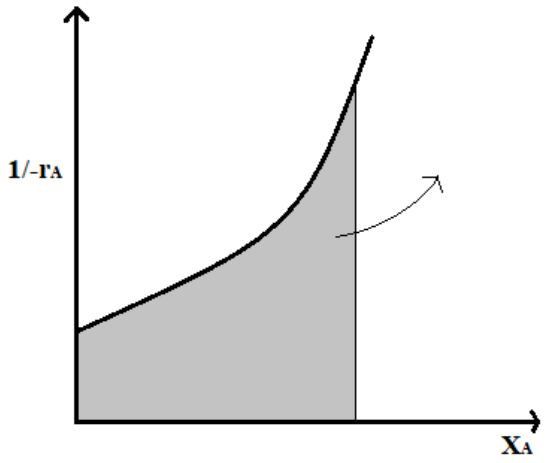
$$k\tau_P=\int_0^{X_A}\frac{dX_A}{1-X_A}$$

$$k\tau_P=-\ln(1-X_A)$$

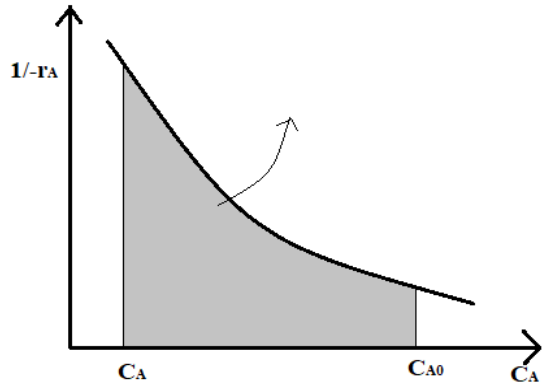
- We observe that the design equation of PFR for constant volume reaction systems is same as the kinetic equation if we replace t in kinetic equation with τ_P.
- But for variable volume reaction systems there is no direct correspondence between kinetic equation and design equation.
- Hence for solving problems on constant volume reaction systems in plug flow reactors, there is no need to solve the integral and the kinetic equations can be used directly.

2.3.5 PERFORMANCE CURVES

Using the equations developed we can plot the following curves



Because of the integral in the design equation, the area under the curve is calculated. For constant volume reaction systems, the performance curve takes the following form.



2.3.6 SPACE TIME AND MEAN RESIDENCE TIME

For both CSTR and PFR, space time is calculated by dividing the volume of the reactor by inlet volumetric flowrate. For constant volume reactions the volumetric flowrate does not change inside the reactor and hence mean residence time remains same as that of space time for both the reactors.

For variable volume reaction in a CSTR, there is sudden expansion or contraction. The volumetric flowrate inside the MFR is

different from the inlet volumetric flowrate, but remains at a constant value inside the reactor. This value of flowrate inside the reactor is also same as that of exit volumetric flow rate. Hence for this case average residence time can be found by dividing the reactor volume by exit volumetric flowrate.

For variable volume reaction in a PFR the volumetric flowrate within the reactor is different than the inlet volumetric flowrate. But the flowrates inside the PFR are not constant. It decreases or increases gradually and hence average residence time in a PFR can be derived as

$$\bar{t} = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}$$

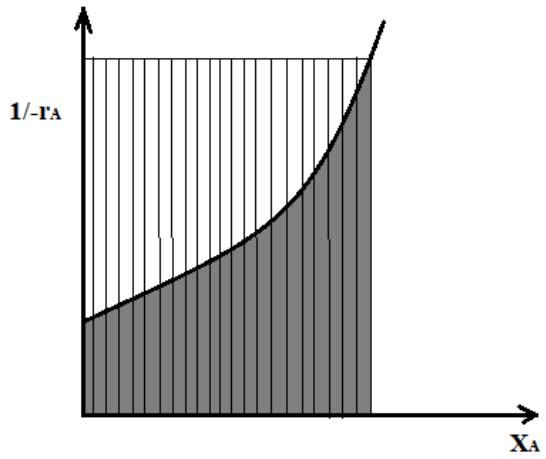
If there is increase in number of moles during a gas phase reaction, volumetric flowrate will increase with conversion and hence average residence time will be less than the space time and vice-versa.

This statement is only valid for gas phase reactions when ideal gas assumption is valid.

2.3.7 SELECTION OF REACTORS

Here we have to make a selection between ideal CSTR and ideal PFR. The selection criteria is to minimize the volume of reactor for a given conversion or to maximize the conversion for a given reactor volume. The type of reactor suitable for a reaction is decided according to order of the reaction. That reactor is selected for which the area of the performance curve (area under the curve for PFR & area of the rectangle for CSTR) is minimum.

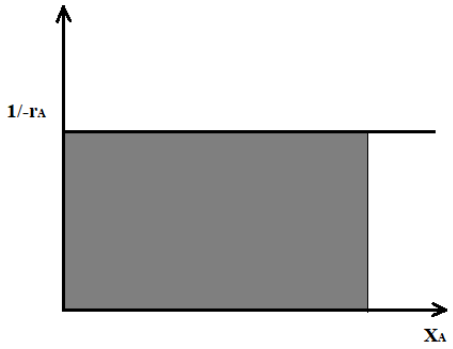
For positive order reactions,



It is clear that the area under the curve is less than the area of the rectangle for a given conversion.

- Hence for positive order reactions and for a fixed conversion, the volume required by a CSTR is more than the volume required by a PFR.
- For a positive order reactions and for fixed volume of reactors, a PFR always gives higher conversion than a CSTR.
- For positive order reactions, a PFR should be selected.

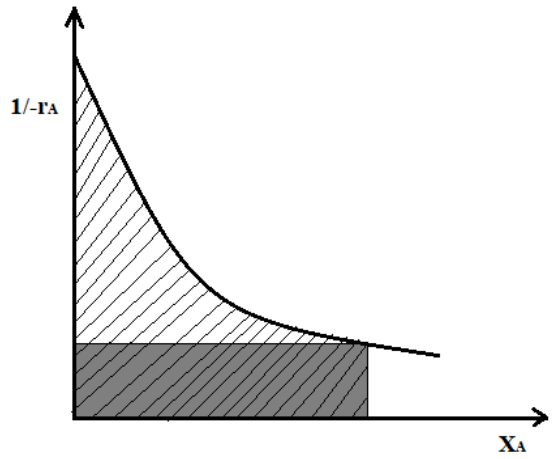
For zero order reactions, $\frac{1}{-r_A} vs\ X_A$ is



We observe that for a zero order reaction, the area under the curve as well as the area of rectangle are same. Hence for a given

conversion the volume of PFR & CSTR required will be same.

For negative order reactions,



Area for CSTR is less than area for PFR.

- Therefore for negative order reactions & for a given conversion, volume of PFR required is more than the volume of CSTR required.
- For a negative order reaction, and fixed volume of reactors, CSTR will give higher conversions than PFR.
- In this case CSTR should be preferred.

We can summarize the selection of reactors as

$n > 0$ select PFR

$n = 0$ type of reactor doesn't matter

$n < 0$ select CSTR

where n is the order of reaction.

GATE QUESTIONS

1.The first order series reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ is conducted in a batch reactor. The initial concentration of A, B and C (C_{A0}, C_{B0}, C_{C0} respectively) are all non-zero. The variation of C_B with reaction time will not show a maximum, if

(a) $K_2 C_{B0} > K_1 C_{A0}$ (b) $K_1 C_{A0} > K_2 C_{B0}$

(c) $C_{B0} > C_{A0}$ (d) $C_{A0} > C_{B0}$

(GATE 2001)

2. The first-order, gas phase reaction $A \xrightarrow{k_1} 2B$ is conducted isothermally in batch mode. The rate of change of conversion with time is given by

(a) $\frac{dX_A}{dt} = k_1(1-X_A)^2(1+2X_A)$

(b) $\frac{dX_A}{dt} = k_1(1-X_A)(1+0.5X_A)$

(c) $\frac{dX_A}{dt} = k_1(1-X_A)$

(d) $\frac{dX_A}{dt} = \frac{k_1(1-X_A)}{(1+X_A)}$

(GATE 2001)

3. An elementary liquid phase decomposition reaction $A \rightarrow 2B$ is to be carried out in a CSTR .the design equation is

(a) $k\tau = \frac{X_A}{(1-X_A)}$

(b) $k\tau = \frac{X_A(1+X_A)}{(1-X_A)}$

(c) $k\tau = \frac{X_A}{(1-X_A)^2}$

(d) $k\tau C_{Ao} = \frac{X_A/(1+X_A)^2}{(1-X_A)^2}$

(GATE 2003)

4. A pollutant P degrades according to first order kinetics. An aqueous stream containing P at 2 kmol/m^3 and volumetric flow the 1 m^3/h requires a mixed flow reactor of volume V to bring down the pollutant level to 0.5 kmol/m^3. The inlet concentration of the pollutant is now doubled and the volumetric flow rate is tripled. If the pollutant level is to be brought down to the same level of 0.5 kmol/m^3, the volume of the mixed flow reactor should be increased by a factor of

(a) 7 (b) 6

(c) 3 (d) 7/3

(GATE 2004)

5. An isothermal aqueous phase reversible reaction $P \leftrightarrow R$ is to be carried out in a mixed flow reactor. The reaction rate in (kmol/m^3-h) is given by r=0.5 C_P-0.125 C_R. A stream containing only P enters the reactor. The residence time required (in hour) for 40% conversion of P is

(a) 0.80 (b) 1.33

(c) 1.60 (d) 2.67

(GATE 2004)

6. A second order liquid phase reaction $A \rightarrow B$ is carried out in a mixed flow reactor operated in semi-batch mode (no exit stream). The reactant A at concentration C_{AF} is fed to the reaction at a volumetric flow rate of F. The volume of the reacting mixture is V and the density of the liquid mixture is constant. The mass balance for A is

(a) $\frac{d(VC_A)}{dt} = -F(C_{AF} - C_A) - KC_A^2V$

(b) $\frac{d(VC_A)}{dt} = F(C_{AF} - C_A) - KC_A^2V$

(c) $\frac{d(VC_A)}{dt} = -FC_A - KC_A^2V$

(d) $\frac{d(VC_A)}{dt} = FC_{AF} - KC_A^2V$

(GATE 2004)

7. The following gas phase reaction is taking place in a plug flow reactor,

$A + \frac{1}{2}B \rightarrow C$

A stoichiometric mixture of A and B at 300 K is fed to the rector. At 1 m along the length of reactor, the temperature is 360 K. The pressure drop is negligible and an ideal gas behaviour can be assumed. Identify the correct expression relating the concentration of A at the inlet (C_{A0}), concentration of A at exit (C_A) and the corresponding conversion of $A(X)$.

(a) $C_A = 1.2C_{A0}\frac{(1-X)}{(1-0.33X)}$

(b) $C_A = 1.2C_{A0}\frac{(1-X)}{(1-0.5X)}$

(c) $C_A = 0.83C_{A0}\frac{(1-X)}{(1-0.33X)}$

(d) $C_A = 0.83C_{A0}\frac{(1-X)}{(1-0.5X)}$

(GATE 2004)

8. The rate of the liquid phase reversible reaction $A \rightleftharpoons 2B$ in (kmol/m^3) at 298 ^0K, is $-r_A = 0.02C_A - 0.01C_B$, where the concentrations C_A and C_B are expressed in (kmol/m^3). What is the maximum limiting conversion of A achievable in an isothermal CSTR at 298K, assuming pure A is fed at the in inlet?

(a) 1 (b) 2/3

(c) 1/2 (d) 1/3

(GATE 2005)

9. An irreversible gas phase reaction $A \rightarrow 5B$ is conducted in an isothermal batch reactor at constant pressure in the presence of an inert. The feed contains no B. If the volume of the gas at complete conversion must not exceed three time the initial volume, the minimum mol % of the inert in the feed must be

(a) zero (b) 20

(c) 33 (d) 50

(GATE 2006)

10. A first order reversible reaction $A \rightleftharpoons B$ occurs in a batch reactor. The exponential decay of the concentration of A has the time constant

(a) $\frac{1}{k_1}$ (b) $\frac{1}{k_2}$

(c) $\frac{1}{k_1 - k_2}$ (d) $\frac{1}{k_1 + k_2}$

(GATE 2006)

11. A well-stirred reaction vessel is operated as a semi batch reactor in which it is proposed to conduct a liquid phase first order reaction of the type $A \rightarrow B$. The reactor is fed with the reactant A at a constant rate of 1 L/min having feed concentration equal to 1 mol/L. The reactor is initially empty. Given k=1 min^{-1}, the conversion of reactant A based on moles of A fed at t=2 min is

(a) 0.136 (b) 0.43

(c) 0.57 (d) 0.86

(GATE 2007)

12. The gas phase reaction $A + 3B \rightarrow 2C$ is conducted in a PFR at constant temperature and pressure, the PFR achieves a conversion of 20% of A. The feed is a mixture of A, B and an inert I. It is found that the concentration of A remains the same throughout the reactor.

Which one of the following ratios of inlet molar rate $(F_A, in : F_B, in : F_I, in)$ is consistent with this observation? Assume the reaction mixture is an ideal gas mixture.

(a) 2:3:0 (b) 2:2:1

(c)3:2:1 (d)1:2:1

(GATE 2008)

13. The elementary liquid phase series parallel reaction scheme

$A \rightarrow B \rightarrow C$ $A \rightarrow R$

Is to be carried out in the an isothermal CSTR. The rate laws are given by

$r_R = k' C_A$

$r_B = kC_A - kC_B$

Feed is pure A. The space time of the CSTR which results in the maximum exit concentration of B is given by

(a) $\frac{1}{\sqrt{kk'}}$ (b) $\frac{1}{\sqrt{k'\left(k + k'\right)}}$

(c) $\frac{1}{\sqrt{\left(k + k'\right)}}$ (d) $\frac{1}{\sqrt{k\left(k + k'\right)}}$

(GATE 2008)

14. The liquid phase reaction $A \rightarrow$ Products is governed by the kinetics, $(-r_A) = kC_A^{1/2}$. if the reaction undergoes 75% conversion of A in 10 min in an isothermal batch reactor, the time (in min) for complete conversion of A is

(a) 40/3 (b) 20

(c) 30 (d) infinite

(GATE 2008)

16. An isothermal liquid phase zero order reaction $A \rightarrow B (k = 0.5 mol/m^3 - s)$ is carried out in a batch reactor. The initial concentration of A is $2 mol/m^3$. At 3 seconds from the start of the reaction, the concentration of A in mol/m^3 is

(a) 0.8 mol/m^3 (b) 0.0 mol/m^3

(c) 0.5 mol/m^3 (d) 0.1 mol/m^3

(GATE 2013)

17. In order to achieve the same conversion under identical reaction conditions and feed flow rate for a non-autocatalytic reaction of positive order, the volume of an ideal CSTR is

(a) Always greater than that of an ideal PFR

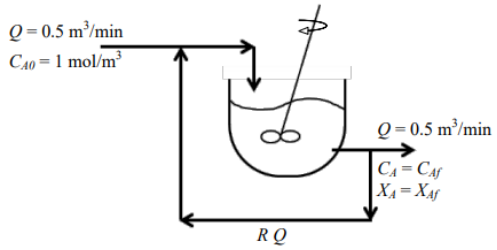
(b) Always smaller than that of an ideal PFR

(c) Same as that of an ideal PFR

(d) Smaller than that of an ideal PFR only for first order reaction

(GATE 2014)

18. An isothermal steady state mixed flow reactor (CSTR) of $1\,m^3$ volume is used to carry out the first order liquid-phase reaction $A \rightarrow$ products. Fresh feed at a volumetric flow rate of Q containing reactant A at a concentration C_{Ao} mixes with the recycle stream at a volumetric flow rate RQ as shown in the figure below.



It is observed that when the recycle ratio R=0.5, the exit conversion $X_{Af} = 50\%$ when the recycle ratio is increased to R=2, the new exit conversion (in percent) will be:

(a) 50.0 (b)54.3

(c) 58.7 (d)63.2

(GATE 2015)

19. The liquid phase reversible reaction $A \rightleftharpoons B$ is carried out in an isothermal CSTR operating under steady state conditions. The inlet stream does not contain B and the concentration of A in the inlet stream is 10mol/lit. The concentrations of A at the reactor exit, for residence times of 1 s and 5 s are 8 mol/lit. And 5mol/lit, respectively. Assume the forward and backward reactions are elementary following the first order rate law. Also assume that the system has constant molar density. The rate constant of the forward reaction (in s^{-1}, rounded off to the third decimal place) is _____

(GATE 2016)

20. The following liquid phase second order reaction is carried out in an isothermal CSTR at steady state

$$A \rightarrow R(-r_A) = 0.005C_A^2 mol/m^2\,\text{hr}$$

Where C_A is the concentration of reactant in the CSTR. The reactor volume is $2m^3$. The inlet flow rate is $0.5\ m^3/\text{hr}$ and the inlet concentration conversion rounded to 2 decimal place is_____

(GATE 2017)

21. The elementary second -order liquid phase reaction $A + B \rightarrow C + D$ is carried out in an isothermal plug flow reactor of $2m^3$ volume. The inlet volumetric flow rate is $10m^3$/h. The initial concentrations of both A and B are $2kmol/m^3$. The rate constant is given as $2.5\,m^3\ kmol^{-1}h^{-1}$. The percentage conversion of A is _____

(GATE 2018)

ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(A)	(C)	(A)	(C)	(C)	(D)	(C)	(C)	(D)	(D)
11	12	13	14	15	16	17	18	19	20
(C)	(C)	(D)	(B)	(A)	(C)	(A)	(A)	(0.267)	(0.80)
21									
(50%)									

EXPLANATIONS

1.Solution:- (a)

$r_B = k_1 C_A - k_2 C_B$

The concentration and rate of reactant B is related as per Eq.(1) the concentration of B will increase as A react to form B and then concentration of B will decrease as B reacts to form C. Thus, it shows a maximum point in between. But concentration of B will not show a maximum, if rate of disappearance of B is higher than formation, i.e, when

$K_2 C_{B_0} > K_1 C_{A_0}$

2.Solution:- (c)

$-r_A = -\frac{dC_A}{dt} = k_1 C_A,$

For batch reactor, first order reaction

$$-\frac{dC_{A_0}(1-X_A)}{dt} = k_1 C_{A_0}(1-X_A)$$

$$\frac{dX_A}{dt} = k_1(1-X_A)$$

3. Solution: (a)

For CSTR,

Input = output+ disappearance + Accumulation

$$F_{A0} = F_{A0}(1-X_A) + (-r_A)V$$

$$F_{A0}X_A = (-r_A)V$$

$$\tau = \frac{1}{s} = \frac{C_{A0}V}{F_{A0}}$$

$$\therefore \frac{F_{A0}}{V} = \frac{C_{A0}}{\tau} = \frac{(-r_A)}{X_A}$$

$$\frac{C_{A0}}{\tau} = \frac{KC_{A0}(1-X_A)}{X_A}$$

$$\therefore \tau k = \frac{X_A}{1-X_A}$$

4. Solution: (c)

For case (1),

Given , $C_{A_0} = 2kmol/m^3$

$V_o = 1\ m^3/h$

$C_A = 0.5\ kmol/m^3$

For MFR, $\frac{V}{F_{A_0}} = \frac{X_A}{(-r_A)}$

Or $\frac{V}{V_o C_{A_0}} = \frac{X_A}{kC_A}$...(1)

First order kinetics.

Here, $X_A = 1 - \frac{C_A}{C_{A_0}} 0.75$

$$\therefore \frac{V}{1\times 2} = \frac{0.75}{k\times 0.5}$$

Or $kV = 3$....(2)

For case (2), $C'_{A_0} = 4m^3/m^3, V'_o = 3m^3/h$

$C_{A_0}^{'}$ =0.5 $kmol/m^3$

Here, $X_A^{'}$ =0.875

And from Eq.(1),

$$\frac{V'}{3\times 4}=\frac{0.875}{k\times 0.5}$$
$$kV'=21...(3)$$

From Eqn. (2) and (3),

$$\frac{V'}{V}=7$$

5. Solution:- (c)

P $\rightleftharpoons$ R

Initial moles, C_{p_0} 0

After 40%

conversion, C_{p_0} (1-0.4) $0.4\,C_{p_0}$

For MFR, $\frac{V}{F_P}=\frac{X_P}{(-r_P)}$

$$\frac{V}{V_oC_P}=\frac{X_P}{0.5C_P-0.125C_R}$$

Or $$\frac{\tau}{C_{p_o}}=\frac{0.4}{0.5\times 0.6C_{p_o}-0.125\times 4C_{p_o}}$$
$$\tau=1.6\ h$$

6.Solution:- (d)

$A\rightarrow B$

$(-r_A)=kC_A^2$, second order reaction

Applying material balance for A,

Input = Output + Reaction + Accumulation

$$F_{A_0}=0+(-r_A)V+\frac{dN_A}{dt}$$

Or $$V_0C_{A_0}=kC_A^2V+\frac{d(C_AV)}{dt}$$

Here, it is given that V_0 =F and $C_{A_0}=C_{A_F}$

$$\therefore \frac{d(VC_A)}{dt}=FC_{A_F}-kC_A^2V$$

7.Solution:- (c)

$$A + \frac{1}{2}B \rightarrow C$$

Initial moles, 1 0.5 0

Here, $\varepsilon_A=\frac{1-\left(1+\frac{1}{2}\right)}{\left(1+\frac{1}{2}\right)}=-\frac{1}{3}$

Volume at point Q,

$$v_A=v_o\left(1+\varepsilon_AX_A\right)$$
$$v_1=v_o\left(1-\frac{1}{3}X_A\right)$$

But the temperature is changing. Thus we need to find the volumetric flowrate at Q with temperature $T_1=360k$.

With constant pressure

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}\cos^{-1}\theta$$
$$\frac{V_0(1-\frac{1}{3}X_A)}{300}=\frac{V_2}{360}$$
$$V_2=1.2V_0(1-\frac{1}{3}X_A)$$

Thus the concentration at point Q ,

$$C_A = \frac{N_A}{V_2} = \frac{N_{A0}(1-X_A)}{1.2V_o(1-0.33X_A)}$$

$$C_A = 0.83C_{Ao}\left(\frac{1-X_A}{1-0.33X_A}\right)$$

8.Solution: (c)

$$A \rightleftharpoons 2B$$

Initial moles 1 0

At equilibrium, $1-X_e$ $2X_e$

Given, $-r_A = 0.02C_A - 0.01C_B$

For maximum limiting conversion of A, reaction should be in equilibrium. At equilibrium, rate of forward reaction = Rate of backward reaction

Or $0.02C_{Ae} - 0.01C_{Be} = 0$

Or $0.02(1-X_e) - 0.01(2X_e) = 0$

$$X_e = \frac{1}{2}$$

With constant pressure,

$$\frac{v_1}{T_1} = \frac{v_2}{T_2}$$

$$\therefore \frac{V_0(1-\frac{1}{3}X_A)}{300} = \frac{V_2}{360}$$

Or $V_2 = 1.2V_0(1-\frac{1}{3}X_A)$

Thus, the concentration at point Q, $C_A = \frac{N_A}{V_2}$

$$C_A = \frac{N_{A_0}(1-X_A)}{1.2V_0(1-0.33X_A)}$$

$$C_A = 0.83C_{A_0}\left(\frac{1-X_A}{1-0.33X_A}\right)$$

9. Solution:- (d)

$A \rightarrow 5B$

Let initial number of moles of A in the feed= n_A

Initial moles of inert in the feed = n_1

After complete conversion,

Total number of moles $= n_B + n_I$
$= 5n_A + n_I$

Given, $\frac{V_{final}}{V_{initial}} = 3$

$$\therefore \frac{5n_A + n_I}{n_A + n_I} = 3$$

$$n_A = n_I$$

Thus, minimum mole percent of the inert in the feed $= \frac{n_I}{n_A + n_I} \times 100 = 50\%$

10. Solution: (d)

The rate of reaction

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = k_1C_A - k_2C_B$$

$$\therefore C_{A0}\frac{dX_A}{dt} = k_1C_{A0}(1-X_A) - k_2(C_{B0} + C_{A0}X_A)$$

$$= k_1C_{A0} - k_2C_{B0} - (k_1+k_2)C_{A0}X_A \ldots(1)$$

At equilibrium, $X_A = X_{Ae}$

$$\frac{dX_{Ae}}{dt} = 0$$

$\therefore k_1 C_{A0} - k_2 C_{B0} = (k_1 + k_2) C_{A0} X_{Ae} ...(2)$

From Eqs.(1) and (2),

$$C_{A0} \frac{dX_A}{dt} = (k_1 + k_2) C_{A0} \left(X_{A0} - X_A \right)$$

$$\frac{dX_A}{\left(X_{Ae} - X_A \right)} = (k_1 + k_2) dt$$

Integrating,

$$\int_0^{X_A} \frac{dX_A}{\left(X_{Ae} - X_A \right)} = \int_0^t (k_1 + k_2) dt$$

$$\left[-In(X_{Ae} - X_A) \right]_0^{X_A} = (k_1 + k_2) t$$

$$ln\left(\frac{X_{Ae} - X_A}{X_{Ae}} \right) = -(k_1 + k_2) t$$

$$\frac{X_{Ae} - X_A}{X_{Ae}} = e^{-(k_1 + k_2) t} = e^{-t/\tau}$$

$\therefore$ Time constant for different substances as $\tau = \dfrac{1}{k_1 + k_2}$

11. Solution: (c)

Semi-batch reactor is shown in the figure.

$A \rightarrow B$

Given, $V_0 = 1\, L / \min$

Initial volume $V_0 = 0$

$k = 1 \min^{-1}$

$-r_A = kC_A$ (first order reaction)

Since, the reactor is being filled continuously, the volume changes with time and at any time t, V (t) can be found from overall mass balance of all species.

Rate in = Rate out + Generation +Accumulation

$$\rho_0 V_0 = 0 + 0 + \frac{d}{dt}(\rho_0 V)$$

$$\frac{dV}{dt} = V_0$$

$$V = V_0 t + C_1$$

$$t = 0, V = 0$$

$$\therefore C_1 = 0$$

Thus, $V = V_0 t ...(1)$

Now, applying material balance for A,

Input =Output +Reaction +Accumulation

$$F_{A_0} = 0 + (-r_A) V + \frac{dN}{dt}$$

$$V_0 C_{A_0} = k C_A V + \frac{d(C_A V)}{dt}$$

Or $$V_0 C_{A_0} = k C_A V_0 t + \frac{dC_A}{dt} + C_A . \frac{dV}{dt}$$

Or $$V_0 C_{A_0} = k C_A V_0 t + V_0 \frac{dC_A}{dt} + C_A . V_0$$

Or $$\frac{dC_A}{dt} + \left(\frac{1 + kt}{t} \right) C_A = \frac{C_{A_0}}{t} ...(2)$$

We need to solve this equation.

Integration factor $= \exp\left[\int \left(\dfrac{1 + kt}{t} \right) dt \right] = \exp(kt + Int) = te^{kt}$

Solution of Eq. (2) can be written as

$$C_A te^{kt} = \int \frac{C_{A_0}}{t} te^{kt} dt + C_2$$

$$C_A te^{kt} = \frac{C_{A_0}}{K} e^{kt} + C_2 ...(3)$$

At, $t = 0, C_A = 0$

$$C_2 = -\frac{C_{A_0}}{K}$$

From Eq. (3), $C_A t e^{kt} = \frac{C_{A_0}}{K}(e^{kt} - 1)$

$$\frac{C_A}{C_{A_0}} = \frac{1}{kt}(1 - e^{-kt})$$

Or $1 - X_A = \frac{1}{kt}(1 - e^{-kt})$

Putting values, k= 1 min^{-1}, t=2 min

$1 - X_A = 0.43$

$X_A = 0.57$

12. Solution:- (c)

	A	+	3B	→	2C	+	Inert
Initial	$(F_{A,in})$		$(F_{B,in})$		0		$(F_{I,in})$
After	$F_{A,in} \times 0.8$		$F_{B,in} - 0.6\,F_{A,in}$		$(0.4F_{A,in})$		

Initial concentration of A, $\frac{F_{A,in}}{F_{A,in} + F_{B,in} + F_{l,in}}$

Concentration of A after 20% conversion

$$\frac{0.8F_{A,in}}{0.6F_{A,in} + F_{B,in} + F_{l,in}}$$

Given, the concentration of A remains same throughout the reactor.

$$\therefore \frac{F_{A,in}}{F_{A,in} + F_{B,in} + F_{l,in}} = \frac{8.0F_{A,in}}{0.6F_{A,in} + F_{B,in} + F_{l,in}}$$

$$0.2F_{A,in} = 0.2F_{B,in} + 0.2F_{l,in}$$

Or $F_{A,in} = F_{B,in} + F_{l,in}$

Thus, according to option (c), it satisfies this result

$\therefore F_{A,in} : F_{B,in} : F_{l,in} = 3:2:1$

13. Solution:- (d)

$A \rightarrow B \rightarrow C$

$A \rightarrow R$

Given, $r_R = k'C_A$ and $r_B = kC_A - kC_B$

$\therefore (-r_A) = kC_A + k'C_A = (k + k')C_A$

Applying material balance for B.

$FC_{B_0} + (r_B)V = FC_B$

$(kC_A - kC_B)\tau = C_B \qquad (as \frac{V}{F} = \tau)$

$$C_B = \frac{kC_A\tau}{1 + k\tau}$$

$$C_B = \frac{kC_A\tau}{(1 + k\tau)\left[1 + (k + k')\tau\right]}$$

For maximum exit concentration of B, $\frac{dC_B}{d\tau} = 0$

$$kC_{A_0}(1 + k\tau)\left[1 + (k + k')\tau\right] -$$
$$k\tau C_{A_0}\left[(1 + k\tau)(k + k') + k\left[1 + (k + k')\tau\right]\right] = 0$$

$$1 + k(k + k')\tau^2 + (2k + k^1)\tau =$$
$$(k + k')\tau + k(k + k')\tau^2$$
$$+k\tau + k(k + k')\tau^2$$
$$or\ k(k + k')\tau^2 = 1$$
$$\tau = \frac{1}{\sqrt{k(k + k')}}$$

14. Solution:- (b)

$A \rightarrow$ product

$-r_A = kC_A^{1/2}$

For isothermal batch reactor

$$-\frac{dC_A}{dt} = (-r_A)$$

$$-\frac{dC_A}{dt} = k\sqrt{C_A} \ldots (1)$$

We have, $X_A = 1 - \frac{C_A}{C_{A_0}}$

$\therefore C_{A_0} dX_A = -dC_A$

From Eq. (1),

$$C_{A_0}\frac{dX_A}{dt} = k\sqrt{C_{A_0}(1-X_A)}$$

$$\sqrt{C_{A_0}} \cdot \frac{dX_A}{\sqrt{1-X_A}} = kdt \ldots (2)$$

Or $\sqrt{C_{A_0}} \cdot \int_0^{0.75} \frac{dX_A}{\sqrt{1-X_A}} = \int_0^{10} kdt$

$$\sqrt{C_{A_0}} \cdot \left[-2\sqrt{1-X_A}\right]_0^{0.75} = 10$$

$$\sqrt{C_{A_0}}\left[-1+2\right] = 10k$$

Or $\frac{\sqrt{C_{A_0}}}{k} = 10 \ldots (3)$

Now, again from Eq.(2)

$$\sqrt{C_{A_0}} \cdot \int_0^1 \frac{dX_A}{\sqrt{1-X_A}} = \int_0^t kdt$$

$$\frac{\sqrt{C_{A_0}}}{k} = \left[-2\sqrt{1-X_A}\right]_0^1 = t$$

$t = 10 \times 2$

$t = 20 \min$

15. Solution:- (a)

For autocatalytic reaction, $A + R \rightarrow R + R$

Initially, the reaction rate will be rapid due to production of R then with fall in concentration of a, the rate will be declining.

Thus, the curve will look like as given below.

16.Solution: (c)

For batch reactor zero order reaction

$$\frac{dc_A}{dt} = K$$

$$or \int_c^{c_A} dc_A = -\int_0^t dt$$

$c_A - c_{A0} = -kt$

$= 2 - 0.5 \times 3 = 0.5 mol/m^3$

17.Solution:(a)

$For CSTR. volume V = \frac{F_{A0} X_A}{-r_A}$

$For PFR volume V = F_{A0} \int \frac{dx_A}{-r_A}$

From plot it is clear that volume of ideal CSTR (area) is higher than of the ideal PFR. For positive order reactions PFR is always preferred over CSTR

18.Solution:- (a)

Mole balance

Input-Output-disappearance = Accumulation

At steady state,

$(QC_{A0} + RQC_A) - (RQ + Q)C_A = kC_A V$

$$\Rightarrow QC_{A0} - QC_A = kC_A V$$

$$\Rightarrow C_{A0} - C_A = kC_A \tau$$

$$\tau = \frac{C_{A0} - C_A}{kC_{A0}(1 - X_A)}$$

$$\tau = \frac{X_A}{k(1 - X_A)} \Rightarrow \tau k = \frac{X_A}{1 - X_A}$$

$$X_A = \frac{\tau k}{1 + \tau k}$$

So , conversion X_A is independent of Recycle ratio R

So final conversion =50%

19. Solution

For reaction given, rate equation can be representing as, $-r_A = k_1 C_A - k_2 C_B$

For MFR, $\tau_m = \frac{C_{A_o} \cdot X_A}{(-r_A)} = \frac{C_{A_o} \cdot X_A}{k_1 C_A - k_2 C_B}$

$C_A = C_{A_0}(1 - X_A)$ *and* $C_B = C_{A_o}.X_A$

So , $\tau_m = \frac{X_A}{k_1(1 - X_A) - k_2 X_A}$

So, for case – I

$$1 = \frac{0.2}{k_1(1 - 0.2) - k_2(0.2)} \Rightarrow 4k_1 - k_2 = 1 \qquad \text{(I)}$$

For case –I

$\tau_m = 1\text{sec} \quad \Rightarrow \quad C_A = 8\ \text{mol/l}$

$X_A = 1 - \frac{8}{10} = 0.2$

For case –II

$\tau_m = 5\text{sec} \quad \Rightarrow \quad C_A = 5\ \text{mol/l}$

$X_A = 1 - \frac{5}{10} = 0.5$

For case – II

$$5 = \frac{0.5}{k_1(1 - 0.5) - k_2(0.5)} \Rightarrow k_1 - k_2 = 0.2 \qquad \text{(II)}$$

On solving equation (I) and (II)

$k_1 = 0.2667\ \text{sec}^{-1}$

20. Solution: 0.80

Design equation for CSTR is

$$\tau = \frac{C_{A0} - C_A}{(-r_A)} = \frac{V}{V_0} = \frac{C_{A0} - C_A}{0.005C_A^2}$$

Given: $V = 2m^3$, $v_0 = 0.5m^3/hr$

$C_{A0} = 1000\ \text{mol/m}^3$

$$\tau = \frac{C_{A0} X_A}{0.005 \times C_A^{\alpha}(1 - X_A)^2}$$

$$= \frac{X_A}{0.005 \times C_{A0}(1 - X_A)^2}$$

$$\frac{V}{v_0} = \frac{2}{0.5} = \frac{X_A}{0.005 \times 1000 \times (1 - X_A)^2}$$

$$(1 - X_2)^2 = 0.05X_A,$$

$$1 - 2X_A + X_A^2 = 0.05X_A$$

$$X_A^2 - 2.05X_A + 1 = 0$$

$$X_A = 0.80$$

21.Solution: 50%

$$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{kC_A C_B}$$

$$\frac{2}{10 \times 2} = \int_0^{x_A} \frac{dx_A}{2.5C_{A0}(1 - x_A)(C_{A0} - C_{A0}x_A)}$$

$$\frac{1}{10} = \int_0^{x_A} \frac{dx_A}{2.5(2)(1 - x_A)2(1 - x_A)}$$

$$\frac{1}{10} = \frac{1}{10}\int_0^{x_A} \frac{dx_A}{(1 - x_A)^2}$$

$$1 = \frac{1}{1 - X_A}\Bigg]_0^{X_A}$$

$$1 = \frac{1}{1 - X_A} - 1$$

$$\frac{1}{1 - X_A} = 2 \Rightarrow 1 - X_A = \frac{1}{2}$$

$$X_A = \frac{1}{2} = 0.5 = 50\%$$

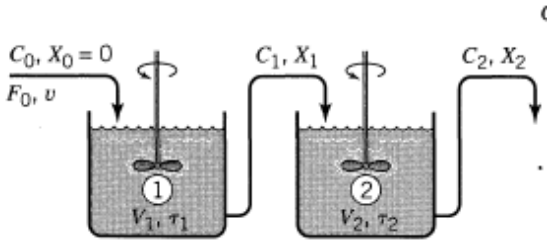
3 DESIGN OF MULTIPLE REACTOR SYSTEM

In this chapter we will deal with systems where there is more than one type of reactors. Reactors can be connected in series or parallel and the reactors can be of same type or different type. For simplicity we will stick to constant volume reaction systems only. So we have the following combinations

- MFRs in series
- PFRs in series
- MFR & PFR in series
- MFR in parallel
- PFR in parallel

The rate law is independent of type and size of reactor, so order and rate constant will not change from one reactor to other.

3.1 MFRs in series



For the first MFR

$$\tau_1 = \frac{C_{Ao} - C_{A1}}{(-r_A)_1}$$

For the second MFR

$$\tau_2 = \frac{C_{A1} - C_{A2}}{(-r_A)_2}$$

The rates are always calculated at the exit concentration of the respective reactors. We can also write the above relations in terms of conversion. We will define conversion with respect to the inlet to the first reactor, therefore all the conversions are with respect to C_{Ao}.

$$C_{A1} = C_{Ao}(1 - X_{A1}) \;\&\; \tau_1 = \frac{C_{Ao} X_{A1}}{-r_{A1}}$$

$$C_{A2} = C_{Ao}(1 - X_{A2}) \;\&\; \tau_2 = \frac{C_{Ao}(X_{A1} - X_{A2})}{-r_{A2}}$$

3.1.1 FIRST ORDER REACTION (CVRS) IN A SERIES OF MFRs

Assuming that the reactors are at different temperatures T_1, T_2 .....and of different volume V_1, V_2..... Hence for a first order reaction

$$\tau_1 = \frac{C_{Ao} - C_{A1}}{k_1 C_{A1}}; C_{A1} = \frac{C_{Ao}}{1 + k_1\tau_1}$$

$$\tau_2 = \frac{C_{A1} - C_{A2}}{k_2 C_{A2}}; C_{A2} = \frac{C_{A1}}{1 + k_2\tau_2} = \frac{C_{Ao}}{(1 + k_1\tau_1)(1 + k_2\tau_2)}$$

$$\therefore C_{AN} = \frac{C_{Ao}}{(1 + k_1\tau_1)(1 + k_2\tau_2).....(1 + k_N\tau_N)}$$

$$X_{AN} = 1 - \frac{1}{(1 + k_1\tau_1)(1 + k_2\tau_2).....(1 + k_N\tau_N)}$$

If temperatures of all the tanks and volume of all the tanks are same, then the expression simplifies to

$$C_{AN} = \frac{C_{Ao}}{(1+k\tau_i)^N}$$

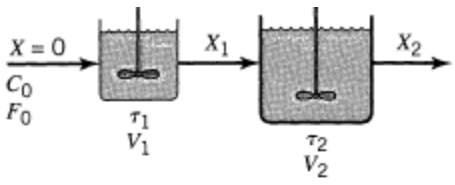
$$X_{AN} = 1 - \frac{1}{(1+k\tau_i)^N}$$

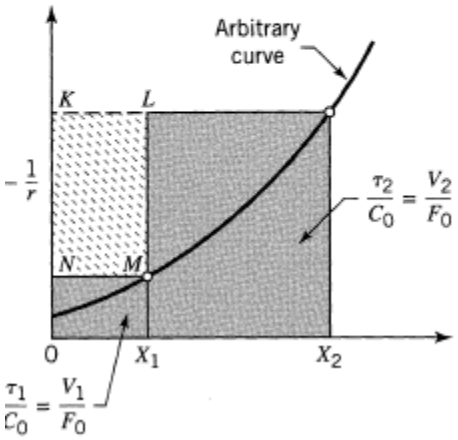
Where τ_i is the space time of individual tank.

3.1.2 SELECTING BEST ARRANGEMENT OF MFRs IN SERIES

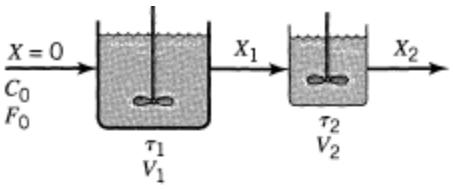
Suppose two MFRs of unequal volumes are connected in series. The conversion to obtained from the combination is fixed i.e., X_2 is fixed. The best arrangement is that which minimizes the total reactor volume for the given conversion.

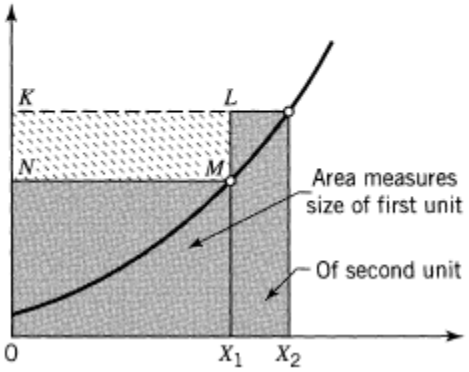
The question is what should be value of intermediate conversion X_1 to minimize the total volume.





If we place the bigger MFR before the smaller MFR, then the total volume is given by the shaded area.



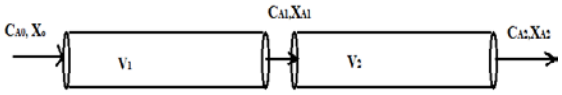


The shaded area will be minimum if the area KLMN is maximum. Since point X_1 is not fixed, the area of KLMN is not fixed and we want to maximize this area. The area of KLMN will be maximum if the diagonal of the rectangle is parallel to the tangent to the curve at X_1. So it suggests that best combination of reactors depends upon the kinetics and hence the order of the reaction. We can make following conclusions

- For first order reaction, the two MFRs should be of equal volume.
- For n>1 smaller MFR should be followed by bigger MFR. So first MFR should be smaller while the second should be bigger
- For n<1, bigger MFR should be followed by smaller MFR.

3.1.3 PFRs IN SERIES

When PFRs are connected in series, then the combination of reactor behaves as a single PFR of Total volume V obtained by adding the individual volumes of the PFRs.



The above combination can be treated as a single PFR of volume V_1+V_2 and space time $\tau_1+\tau_2$.

3.1.4 DIFFERENT TYPES OF REACTORS IN SERIES

There are cases when PFR & CSTR are connected in series. The question arises that which combination is better. The combination which provides maximum conversion for a given total volume or the combination which has a minimum total volume required for a given conversion becomes the preferred choice of rectors. The results can be summarized as

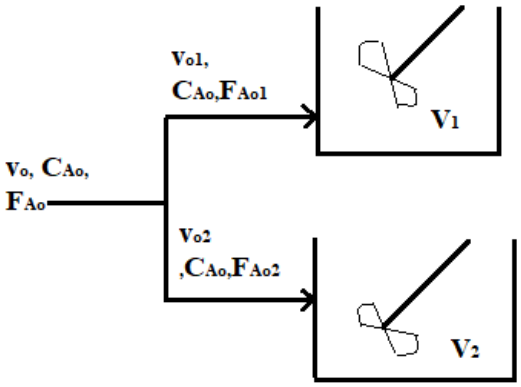
Before understanding the best arrangement, let us understand the extent of mixing. We know that in an ideal PFR the extent of mixing is zero. So whatever is the size of PFR, smaller or bigger, the extent of mixing remains zero. But in case of MFRs, the bigger MFR has greater extent of mixing and as the size of MFR increases the extent of mixing increases.

- For reaction order greater than 1 i.e., n>1 late mixing is preferred. The combination in which extent of mixing increases from first reactor to the last reactor is preferred combination. Hence
  $PFR \rightarrow small\ MFR \rightarrow Large\ MFR$
  Should be the choice.
- When the order of reaction is equal to one, the arrangement of reactors has no effect on conversion. Hence we will obtain same conversions in any arrangement.
- When order is less than one, n<1 then early mixing is preferred. We will prefer that arrangement of reactors where extent of mixing decreases from first reactor to last reactor. Hence
  $\text{large MFR} \rightarrow \text{small MFR} \rightarrow \text{PFR}$

3.2 REACTORS IN PARALLEL

When reactors are connected in parallel, then they are connected such that the residence time in both reactants remains same. By this way we can get the most economical combination.

When connected in parallel, the net volumetric flowrate and net molar flowrate gets divided into different parts (equal to number of reactors), not necessarily in equal parts. However the concentration of any part remains the same. The main stream is divided into different parts such that each divided branch has same residence time inside the reactor. Let us consider the following example of two MFRs connected in parallel



The flowrates will be divided such that

$$\frac{V_1}{F_{Ao1}} = \frac{V_2}{F_{Ao2}}$$

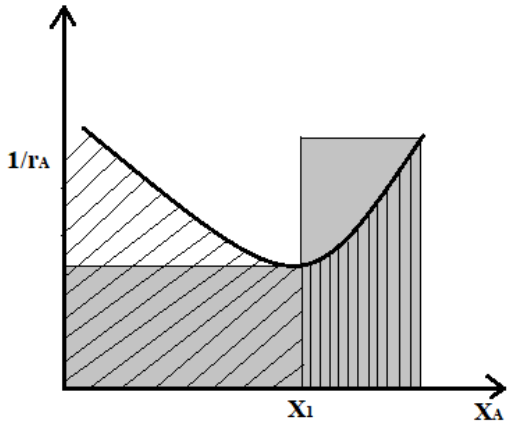
$$\frac{\tau_1}{C_{Ao}} = \frac{\tau_2}{C_{Ao}} or \frac{V_1}{v_{o1}} = \frac{V_2}{v_{o2}}$$

Similarly, when two PFRs are connected in series the flow rates will be divided so that space time in both the branches remains same.

3.3 BEST REACTOR ARRANGEMENT

For a given $\frac{1}{-r_A} vs\, X_A$ curve, the best reactor arrangement can be found by minimizing the total reactor volume. The change in the type of reactor will take place at that point of conversion where the curve changes its nature.

In the following figure, it is clear that from 0 to X_1 CSTR requires less volume, while from X_1 to final conversion PFR requires less volume. So the best combination will be a CSTR followed by a PFR.



The plot can also be between $\frac{1}{-r_A} vs\, C_A$.

The same technique can be used to select the best possible arrangement. But as the reaction proceeds, the conversion increases while concentration of reactant decreases. Hence when plotted with concentration, the graph should be observed from right to left.

o

GATE QUESTIONS

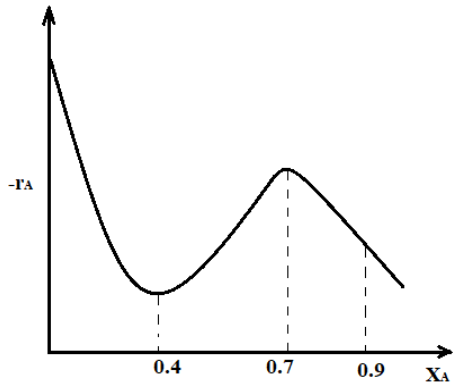
1. The conversion for a first-order liquid-phase reaction $A \rightarrow B$ in a CSTR is 50%. If another CSTR of the same volume is connected in series, then the percentage conversion at the exit of the second reactor will be

(a) 60 (b) 75

(c) 90 (d) 100

(GATE 2001)

2. A liquid phase reaction is to be carried out under isothermal conditions. The reaction as a function of conversion has been determined experimentally and is shown in figure below. What choice of reactor of combination of reactors will require the minimum overall reactor volume, if a conversion of 0.9 is desired?



(a) CSTR followed by a PFR

(b) PFR followed by a CSTR

(c) CSTR followed by a PFR followed by CSTR

(d) PFR followed by a CSTR followed by a PFR

(GATE 2003)

COMMON DATA QUESTIONS

The liquid phase reaction $A \rightarrow$ products is to be carried out at constant temperature in a CSTR+ PFR) is 95%. The CSTR has a volume of 75 L. Pure A is fed to the CSTR, at a concentration C_{A0} =2mol/L and a volumetric flow rate of 4 L/min. The kinetics of the reaction given by

$$-r_A = 0.1C_A^2 . \frac{mol}{L - \min}$$

3. The conversion achieved by the CSTR is

(a) 40% (b) 50%

(c) 60% (d) 80%

(GATE 2008)

4. The volume of the PFR required (in litre) is

(a) 380 (b) 350

(c) 75 (d) 35

(GATE 2008)

COMMON DATA QUESTION

The liquid-phase reaction $A \rightarrow B + C$ is conducted isothermally at 50 ^oC in a Continuous stirred tank reactor (CSTR). The inlet concentration of A is 8.0 g-mol/L. At a space time of 5 min, the concentration of A at the exit of CSTR is 4.0 g-mol/L. The kinetics of the reaction is $-r_A = kC_A^{0.5} \frac{g - mol}{L - \min}$.. A plug flow reactor of the same volume is added in series after the existing CSTR.

5. The rate constant (k) for this reaction at 50 ^{o}C is

(a) $0.2\left(\frac{g-mol}{L}\right)^{0.5} \min^{-1}$

(b) $0.2\left(\frac{L}{g-mol}\right)^{0.5} \min^{-1}$

(c) $0.4\left(\frac{g-mol}{L}\right)^{0.5} \min^{-1}$

(d) $0.4\left(\frac{L}{g-mol}\right)^{0.5} \min^{-1}$

(GATE 2009)

6. The concentration of A (in g-mol/L) at the exit of the plug flow reactor is

(a) 0.5 (b) 1.0

(c) 2.0 (d) 2.5

(GATE 2009)

COMMON DATA QUESTION

A liquid phase reaction $A \rightarrow B$ is conducted isothermally in a CSTR having a residence time of 2 s. The inlet concentration of species A is 2 mol/L , and the outlet concentration is 1 mol/L. The rate law for the reaction is $-r_A = \frac{kC_A}{K + C_A}$ where, k=5mol/L-s.

7. The value of K in mol/L is

(a) 11 (b) 9

(c) 5 (d) 2

(GATE 2010)

8. If the same reaction is conducted in a series of two CSTR with residence times 1s and 0.2s, then the inlet concentration of A in mol/L, required to attain an outlet concentration of A in mol/L, is

(a) 2.64 (b) 2.00

(c) 1.64 (d) 0.54

(GATE 2010)

COMMON DATA QUESTION

In an aqueous solution, reaction $P \rightarrow Q$ occurs under isothermal conditions following first order kinetics. The feed rate is $500\,cm^3/\min$ and concentration of P in the feed is $1.5\times10^{-3}\,mol/cm^3$. the reaction is carried out in a 5 L CSTR. At steady, 60% conversion is observed.

9. The rate constant (in $\min^{-1}$) is

(a) 0.06 (b) 0.15

(c) 0.21 (d) 0.28

(GATE 2011)

10. The 5L CSTR is replaced by five CSTRs in series. If the capacity of each new CSTR is 1 L, then the overall conversion (in percentage) is

(a) 65 (b) 67

(c) 73 (d) 81

(GATE 2011)

COMMON DATA QUESTION

The first order liquid phase reaction $A \rightarrow P$ is conducted isothermally in a plug flow reactor of 5 L volume. The inlet volumetric flow rate is 1 L/min and the inlet concentration of A is 2 mol/L

11. If the exit concentration of A is 0.5mol/L, then the rate constant (in $\min^{-1}$) is

(a) 0.06 (b) 0.28

(c) 0.42 (d) 0.64

(GATE 2012)

12. The plug flow reactor is replaced by 3 mixed flow reactors in series, of 2.0L volume. The exact conversion of A (in %) is

(a) 35.9 (b) 52.5

(c) 73.7 (d) 94.8

(GATE 2012)

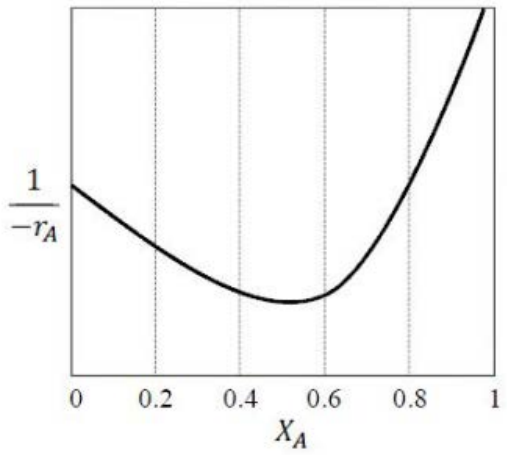
13. A first order liquid phase reaction is carried out isothermally at a steady state in a CSTR and 90% conversion is attained. With the same inlet conditions and for the same overall conversion, if the CSTR is replaced by two smaller and identical isothermal CSTR in series, the% reduction in total volume, to the nearest integer is

(a) 30% (b) 45%

(c) 52% (d) 40%

(GATE 2013)

14. The following reaction rate curve is shown for a reaction $A \rightarrow P$. Here $(-r_A)$ and X_A represents reaction rate and conversion, respectively. The feed is pure A and 90% conversion is desired.



Which amongst the following reactor configurations gives the lowest total volume of the reactor (S)?

(a) CSTR followed by PFR

(b)Two CSTR in series

(c) PFR followed by CSTR

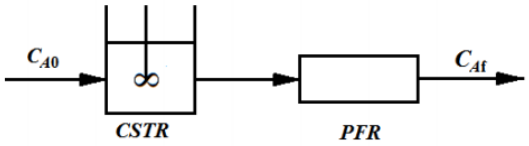
(d) A single PFR

(GATE 2017)

15. A set of standard stainless steel pipes, each of internal diameter 26.65 mm and 6000 mm length, is used to make a plug flow reactor by joining them in series to carry out degradation of polyethylene. Seven such pipes are required to obtain a conversion of 66% at 450 K. The minimum number of standard 8000 mm long pipes of the same internal diameter to be procured for obtaining at least 66% conversion under the same reaction conditions is _____

(GATE 2018)

16. A CSTR and a PFR of equal volume are connected in series as shown below to carry out a first-order, isothermal, liquid phase reaction $A \rightarrow P$



The rate constant is $0.2s^{-1}$.the space-time is 5 s for both the reactors. The overall fractional conversion of A is _____ (rounded off to third decimal place)

(GATE 2018)

ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(B)	(D)	(C)	(B)	(C)	(B)	(B)	(C)	(B)	(C)
11	12	13	14	15	16				
(B)	(C)	(C)	(A)	(6)	(0.816)				

EXPLANATIONS

1.Answer:- (b)

For a CSTR,

$$\frac{\tau}{C_A} = \frac{X_A}{-r_A}$$

$$\frac{\tau}{C_{A_0}} = \frac{X_A}{KC_{A_0}(1-X_A)}$$

For first order reaction,

$$k\tau = \frac{X_A}{1-X_A}$$

Given,

$$X_A = 0.5$$

$$\therefore K\tau = \frac{0.5}{1-0.5}$$

$$K\tau = 1$$

Now, for two tanks of same volume in series,

$$\frac{K\tau}{N} = (1-X_A)^{-1/2} - 1$$

Putting values,

$$\frac{2}{2} = (1-X_A)^{-1/2} - 1$$

$$K\tau = 2K\tau_i = 2\times 1)$$

$$(1-X_A)^{-1/2} = 2$$

$$1-X_A = \frac{1}{4}$$

$$X_A = \frac{3}{4} = 0.75$$

Overall conversion =75%

2.Answer:- (d)

$$0 < X_A < 0.4$$

Initially the rate of reaction is maximum and rate decreases with increase in conversion or decrease in concentration of reactant i.e. reaction order is positive in this region. For the positive order reactions PFR is best.

$$0.4 < X_A < 0.7$$

After 0.4 conversion, the rate increases with increase in conversion which shows a change in reactor type. This indicates reaction order is negative in this region. CSTR should be selected for this region.

$$X_A > 0.4$$

Then after 0.7 conversion, rate again decreases with increase in conversion which again shows a change in reactor type i.e. reaction order is positive in this region. For the positive order reaction PFR is best.

Thus for minimum overall reactor volume, PFR followed by a PFR is correct option.

3.Answer:(c)

Given, $C_{A_0} = 2mol/L, V_0 = 4L/\min$

$V = 75L$ and $-r_A = 0.1C_A^2$

For CSTR, $\frac{V}{F_{A_0}} = \frac{X_A}{(-r_A)}$

$$\frac{V}{V_0 C_{A_0}} = \frac{X_A}{0.1C_A^2}$$

$$\frac{75}{4\times 2} = \frac{X_A}{0.1C_A^2(1-X_A)^2}$$

$$\frac{75}{8} = \frac{X_A}{0.1\times 4(1-X_A)^2}$$

$$X_A^2 - 2.27X_A + 1 = 0$$

$$X_A = 1.67 or 0.6$$

Since, conversion can never be greater than 1, therefore X_A=0.6 or 60%.

4. Answer: (b)

Here,

$$\therefore C_A = C_{A_0}(1-X_A)$$

$$= 2(1-0.6) = 0.8 \text{ mol/L}$$

Given, overall conversion of A by CSTR+PFR system is 95%.

Thus, $C_A = C_{A_0}(1-0.95)$

$$= 2(1-0.95) = 0.1 \text{ mol/L}$$

Now, for PFR, $\frac{V}{F} = \int \frac{dX_A}{(-r_A)}$

$$\frac{V}{V_0 C_{A_0}} = \int_{0.6}^{0.875} \frac{dX_A}{0.1C_{A_0}^2(1-X_A)^2}$$ V=350 L

$$\frac{V\times 0.1\times C_{A_0}}{V_0} = \left[\frac{1}{1-X_A}\right]_{0.6}^{0.95}$$

5.Answer: (c)

For a CSTR,

$$\frac{V}{F_{A_0}} = \frac{X_A}{(-r_A)} = \frac{\tau}{C_{A_0}}$$

$$(-r_A) = \frac{C_{A_0}X_A}{\tau} = \frac{C_{A_0}-C_A}{\tau}$$

$$or \quad kC_A^{0.5} = \frac{C_{A_0}-C_A}{\tau}$$

$$\therefore k\times\sqrt{4} = \frac{8-4}{5}$$

$$k = 0.4\left(\frac{g-mol}{L}\right)^{0.5} \min^{-1}$$

6.Answer:(b)

C_{A_2} = ?

For PFR

$$\tau = \int_{C_{A_1}}^{C_{A_2}} \frac{dC_A}{(-r_A)}$$

$$\tau = -\int_{C_{A_1}}^{C_{A_2}} \frac{dC_A}{kC_A^{0.5}} = \frac{1}{0.5k}\left(\sqrt{C_{A_1}} - \sqrt{C_{A_2}}\right)$$

For same volume of PFR and MFR, $\tau_{PFR} = \tau_{MFR}$

$$\therefore 5 = \frac{\left(\sqrt{4}-\sqrt{C_{A_2}}\right)}{0.5\times 0.4}$$

$$C_{A_2} = 1g-mol/L$$

7.Answer:(b)

For CSTR,

$$\frac{V}{F_{A_0}}=\frac{X_A}{(-r_A)}=\frac{\tau}{C_{A_0}}$$

Given, $\tau=2s, C_{A_0}=2mol/L$

$$C_A=1mol/L$$

$$\therefore X_A=1-\frac{C_A}{C_{A_0}}=\frac{1}{2}\Rightarrow(-r_A)=\frac{X_A C_{A_0}}{\tau}$$

$$\frac{kC_A}{k+C_A}=\frac{X_A C_{A_0}}{\tau}$$

$$\frac{5\times1}{K+1}=\frac{\frac{1}{2}\times2}{2}$$

$$\frac{5}{K+1}=\frac{1}{2}\Rightarrow K=9mol/L$$

8.Answer:(c)

For CSTR, we have

$$\frac{X_A}{(-r_A)}=\frac{\tau}{C_{A_0}}$$

Or $(-r_A)=\frac{C_{A_0}X_A}{\tau}=\frac{C_{A_0}-C_A}{\tau}$

Now, for 2nd reactor

$\tau_2=0.2, C_{A_1}=?, C_{A_2}1mol/L$

Also $(-r_A)=\frac{kC}{k+C_A}$

Where, k=5 and K=9

$$\therefore\frac{5C_{A_2}}{9+C_{A_2}}=\frac{C_{A_1}-C_{A_2}}{\tau_2}\,or\,\frac{5\times1}{9+1}=\frac{C_{A_1}-1}{0.2}$$

$$C_{A_1}=1.1$$

Now, for 1st reactor $\frac{5C_{A_1}}{9+C_{A_1}}=\frac{C_{A_0}-C_{A_1}}{\tau_1}$

$$\frac{5\times1.1}{9+1.1}=\frac{C_{A_0}-1.1}{1}$$

$$C_{A_0}=1.64mol/L$$

9.Answer:(b) Given $\upsilon_0=500cm^3/\min$

$$C_{A_0}=1.5\times10^{-4}mol/cm^3$$

V= 5L = 5000cm^3 , X_A=0.6

For a CSTR,

$$\frac{V}{F_{A_0}}=\frac{X_A}{-r_A}$$

Or $\frac{V}{\upsilon_0 C_{A_0}}=\frac{X_A}{KC_{A_0}(1-X_A)}$,

First order kinetics,

$$k=\frac{\upsilon_0 X_A}{V(1-X_A)}$$

Putting values,

$$K=\frac{500\times0.6}{5000\times(1-0.6)}$$

$$K=.15\min^{-1}$$

10.Answer:(c)

For each CSTR,

$$\tau_1=\frac{V}{\upsilon_0}=\frac{1000}{500}$$

$$\tau_1=2\min$$

Total residence time

$$\tau=N\tau_1=5\times2$$

$$\tau=10\min$$

For N CSTR in series,

$$1-X_{A_5}=\frac{1}{(1+k\tau_1)^5}$$

$$1-X_{A_5}=\frac{1}{(1+0.15\times 2)^5}$$

$$X_{A_5}=0.73$$

11.Answer:(b)

$A\rightarrow P$

For 1st order reaction in PFR,

$$\frac{V}{F_{A_0}}=\int\frac{dx}{-r_A}$$

$$\frac{V}{F_{A0}}=\int_0^{x_A}\frac{dx_A}{kC_{A0}(1-x_A)}$$

or $\frac{V}{F_{A0}}=\frac{1}{kC_{A0}}.In(1-x_A)...(I)$

Here, V=5 L, C_{A0}=2mol/L, v_o=1L/min

$$F_{A0}=C_{A0}.v_0=2mol/\min$$

$$C_A=0.5mol/L$$

Since, $C_A=C_{A0}(1-x_A)$

$0.5=2(1-x_A)$

Putting values in Eq. (i),

$$\frac{5}{2}-\frac{1}{k\times 2}\log_e(0.25)$$

$$\Rightarrow k\approx 0.28\min^{-1}$$

12.Answer:(c)

For N MFR in series, $\frac{C_{AN}}{C_{A0}}=\frac{1}{(1+k\tau_i)^N}$

Or $1-x_A=\frac{1}{(1+k\tau_i)^N}$

Here, $\tau_i=\frac{2}{1}=2\min, N=3$

Putting values,

$$1-X_A=\frac{1}{(1+0.28\times 2)^3}$$

$$X_A=0.737=73.7\%$$

13.Answer:(c)

For (Mixed flow reactor) MFR,

$$k\tau_1=\frac{C_{A0}-C_{A1}}{C_{A1}}$$

$$=\frac{C_{A0}}{C_{A1}}-1$$

$$\frac{C_{A0}}{C_{A1}}=1+k\tau_1 \_\_\_\_(I)$$

Similarly, for 2^{nd} MFR

$$\frac{C_{A1}}{C_{A2}}=1+k\tau_2 \_\_\_\_(II)$$

By Eqs (I) and (II) $\frac{C_{A0}}{C_{A2}}=(1+K\tau_1)(1+K\tau_2)$

But $\frac{C_{A_2}}{C_{A_0}}=1-X_A=1-0.9=0.1$

And $\tau_1=\tau_2$ for identical reactors,

$$10=(1-K\tau_1)^2$$

$$1+K\tau_1=3.16$$

$$K\tau_1=2.16$$

% Reduction in reactor volume

$$=\frac{V-(V_1+V_2)}{V}\times 100$$

$$=\frac{V-2V_1}{v}\times 100=\frac{k\tau-2k\tau_1}{k\tau}\times 100$$

$$=\frac{9-2\times 2.16}{9}\times 100=52\%$$

14.Answer:(a)

15.Answer: (6)

$$7 \text{ pipe volume } = 7 \times 6 \times \frac{\pi D^2}{4}$$

To have same volume,

The no. of pipes 8m required = $\frac{7 \times 6 \times \frac{\pi D^2}{4}}{8 \times \frac{\pi D^2 4}{4}} = 5.25 = 6$

16.Answer :- 0.816

$$T = \frac{C_{A0} - C_{A1}}{KC_{A1}}$$

$$5 = \frac{C_{A0} - C_{A1}}{0.2C_{A1}}$$

$$C_{A0} = C_{A1} + C_{A1}$$

$$C_{A0} = \frac{1}{2} C_{A0} C_{A0}(1 - xA_1) = \frac{1}{2} C_{A0}$$

$$C_{A1} = 0.5$$

$$\frac{T}{C_{A0}} = \int_{x_{A1}}^{x_{A2}} \frac{dX_A}{0.5C_{A0}(1 - x_A)}$$

$$5 = \int_{0.5}^{x_{A2}} \frac{dX_A}{0.2(1 - X_A)}$$

$$1 = -\ln\left[1 - X_A\right]_{0.5}^{x_{A2}}$$

$$1 = \ln(0.5) - ln(1 - x_{A2})$$

$$1 - X_{A2} = 0.18$$

$$X_{A2} = 0.816 = 81.6\%$$

4 MULTIPLE REACTIONS

Till now we were dealing with single reactions where only one rate law exists. Those reactions where more than one rate law exists are called multiple reactions.

Series reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2}$$

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A$$

$$r_B = \frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$r_C = \frac{dC_C}{dt} = k_2 C_B$$

And parallel reactions

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

$$r_R = k_1 C_A$$

$$r_S = k_2 C_A$$

$$(-r_A) = k_1 C_A + k_2 C_A$$

And various other combination of series and parallel reactions are considered as multiple reactions. We will only discuss simple series and parallel reactions. The kinetics of series and parallel reactions are already discussed in chapter 1.

4.1 SELECTIVITY

Let us consider a parallel reaction where R is the desired product and S is the undesired product.

$$A \xrightarrow{k_1} R; r_R = k_1 C_A^{n_1}$$

$$A \xrightarrow{k_2} S; r_S = k_2 C_A^{n_2}$$

We define instantaneous selectivity of R w.r.t S as

$$S = \frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} C_A^{n_1 - n_2}$$

- This expression of instantaneous selectivity remains same for CSTR as well as PFR.
- We can also define overall selectivity as

$$\bar{S} = \frac{\text{total moles of R formed}}{\text{total moles of S formed}}$$

4.1.1 MAXIMIZING SELECTIVITY

Since selectivity is the ratio of moles of desired product formed to undesired product formed, therefore we always want to maximize selectivity. The expression for selectivity contains two terms

$\frac{k_1}{k_2}$ which is temperature dependent and

$C_A^{n_1 - n_2}$ which is concentration dependent

We will analyse selectivity by keeping one factor (out of temperature and concentration) constant and varying the other factor.

4.1.2 EFFECT OF CONCENTRATION ON SELECTIVITY

The concentration dependent term in the definition of selectivity is raised to power n_1-n_2. Hence, we have following cases

CASE I: n_1-n_2 is positive

For maximizing selectivity, the concentration inside the reactor has to be as high as possible. We know that in a CSTR, there is a sudden decrease in concentration and it remains at the lowest value throughout the reactor. While in PFR or bath reactors there is a progressive decrease in concentration and concentrations are at higher values in these reactors. So for this case PFR or batch reactors should be preferred.

CASE II: n_1-n_2 is negative

Because concentration is raised to negative power, hence to maximize selectivity concentration within the reactor should be kept as low as possible. Therefore, CSTR should be preferred.

CASE III: n_1=n_2

In this case choice of reactors has no effect on selectivity of desired product

- We can conclude from above discussion that if the order of desired reaction is greater than the order of undesired reaction, PFR or batch reactor should be preferred and vice-versa.
- For reactions in parallel, the concentration level of reactants is the **key** to proper control of product distribution. A high reactant concentration favours the reaction of higher order, a low concentration favours the reaction of lower order, while the concentration level has no effect on the product distribution for reactions of the same order.

The reactions can also be of type

$$A + B \xrightarrow{k_1} R; r_R = k_1 C_A^{n_1} C_B^{m_1}$$
$$A + B \xrightarrow{k_2} S; r_S = k_1 C_A^{n_2} C_B^{m_2}$$

Here selectivity can be defined in the similar way as

$$S = \frac{k_1}{k_2} C_A^{n_1 - n_2} C_B^{m_1 - m_2}$$

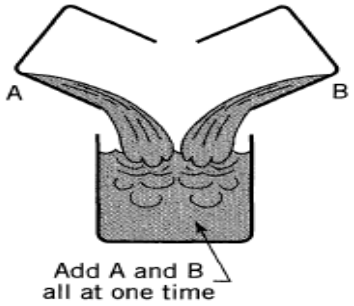
Let us consider a case where $n_1 > n_2 \,\&\, m_1 > m_2$. Now to keep selectivity maximum, both C_A and C_B should be kept high.

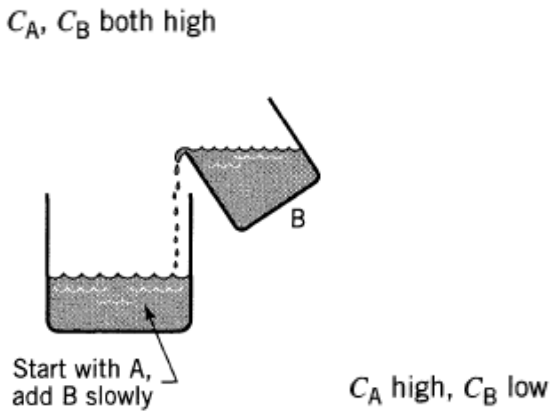
When $n_1 > n_2 \,\&\, m_1 < m_2$, C_A should be kept high and C_B should be kept low. This can be achieved by starting with A adding B slowly to it.

Similarly, when $n_1 < n_2 \,\&\, m_1 > m_2$ C_A should be kept low while C_B should be kept high. This can be achieved by starting with B and adding A slowly to it.

So the product distribution in parallel reactions can be controlled by using the proper contacting pattern for the reacting fluids. This proper contacting pattern can be achieved in a batch or continuous reactor as shown in the figure.

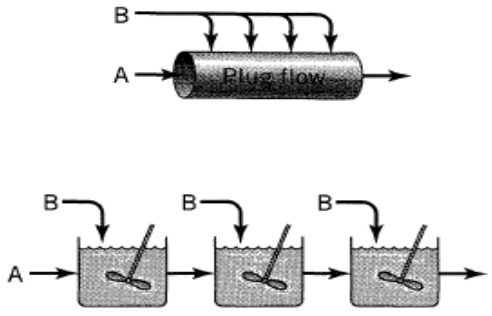
For batch process,





These contacting patterns can also be achieved in continuous reactors. The reactant whose concentration has to be kept high should be added to a PFR and the reactant whose concentration is to be kept low should be added slowly throughout the PFR.

C_A high C_B low



4.1.3 EFFECT OF TEMPERATURE ON SELECTIVITY

The term $\frac{k_1}{k_2}$ also affects selectivity and depends upon conditions of temperature inside the reactor. We know that as temperature increases, the rate constant increases but this increase takes place for both the reactions. So we have the following cases

Case I: If $E_{a1} > E_{a2}$, activation energy of desired reaction is more than the activation energy of undesired reaction.

For this case with increase in temperature the rate constant of desired reaction will increase more than that of undesired reaction. Hence to increase the selectivity temperature should be high.

Case II: If $E_{a1} < E_{a2}$, activation energy of desired reaction is less than the activation energy of undesired reaction. If temperature is increased, then the rate of undesired reaction will increase to a greater extent. Hence to maximize selectivity temperature should be as low as possible.

4.2 YIELD OF A PARALLEL REACTION

Yield is defined to give quantitative treatment to product distribution in a parallel reaction. It can be used to find how many moles of desired and undesired product has been formed. Considering the simple parallel reaction

$$A \xrightarrow{k_1} R; r_R = k_1 C_A^{n_1}$$
$$A \xrightarrow{k_2} S; r_S = k_2 C_A^{n_2}$$

4.2.1 FRACTIONAL YIELD

Fractional yield is defined within the reactor and its expression is same for both PFR and CSTR. Fractional yield is defined as

$$\phi_{\frac{R}{A}} = \frac{r_R}{-r_A} = \frac{dC_R}{dC_R + dC_S} = \frac{k_1 C_A^{n_1}}{k_1 C_A^{n_1} + k_2 C_A^{n_2}}$$
$$\phi_{\frac{S}{A}} = \frac{r_S}{-r_A} = \frac{dC_S}{dC_R + dC_S} = \frac{k_2 C_A^{n_2}}{k_1 C_A^{n_1} + k_2 C_A^{n_2}}$$

Note that $-r_A = r_R + r_S$ is valid only for the above reaction. For different stoichiometry proper relation has to be derived.

Overall yield can also be defined as

$$\Phi_{\frac{R}{A}} = \frac{moles\ of\ R\ formed}{moles\ of\ A reacted} = \frac{N_R - N_{Ro}}{N_{Ao} - N_A}$$

$$\Phi_{\frac{S}{A}} = \frac{moles\ of\ S\ formed}{moles\ of\ A reacted} = \frac{N_S - N_{So}}{N_{Ao} - N_A}$$

For constant volume reaction system

$$\Phi_{\frac{R}{A}} = \frac{moles\ of\ R\ formed}{moles\ of\ A reacted} = \frac{C_R - C_{Ro}}{C_{Ao} - C_A}$$

$$\Phi_{\frac{S}{A}} = \frac{moles\ of\ S\ formed}{moles\ of\ A reacted} = \frac{C_S - C_{So}}{C_{Ao} - C_A}$$

- Overall yield for reactors can be found by taking average of fractional yield. $\Phi = \bar{\phi}$

4.2.2 OVERALL YIELD FOR A MFR

In a MFR there is a sudden drop in concentration, and there is only one value of concentration throughout the MFR. Therefore only one value of fractional yield exists inside the reactor.

This is the value of fractional yield which is calculated at the exit concentration of the MFR. Hence the average of the fractional yield is equal to this value.

$$\Phi_{MFR} = \bar{\phi}_{\frac{R}{A}} = \phi_{\frac{R}{A}}\ at\ exit\ concentration$$

$$= \frac{k_1 C_{Af}^{n_1}}{k_1 C_{Af}^{n_1} + k_2 C_{Af}^{n_2}}$$

Therefore, total moles of R formed in a MFR is given by

$$N_R = N_{Ro} + \Phi_{\frac{R}{A}|MFR}(N_{Ao} - N_A)$$

$$N_S = N_{So} + \Phi_{\frac{S}{A}|MFR}(N_{Ao} - N_A)$$

For CVRS system

$$C_R = C_{Ro} + \Phi_{\frac{R}{A}|MFR}(C_{Ao} - C_A)$$

$$C_S = C_{So} + \Phi_{\frac{S}{A}|MFR}(C_{Ao} - C_A)$$

4.2.3 OVERALL YIELD FOR PFR

In a PFR there is a gradual decrease in concentration, due to which there exist different values of concentration and hence different values of fractional yield inside PFR. Overall yield for a PFR can be calculated by taking average of these different fractional yields.

$$\Phi_{\frac{R}{A}}|_{PFR} = \bar{\phi}_{\frac{R}{A}} = \frac{\int_{C_{Ao}}^{C_{Af}} \phi_{\frac{R}{A}} dC_A}{\int_{C_{Ao}}^{C_{Af}} dC_A} = \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \phi_{\frac{R}{A}} dC_A$$

The amount of products formed in PFR can be calculated as

$$N_R = N_{Ro} + \Phi_{\frac{R}{A}|PFR}(N_{Ao} - N_A)$$

$$N_S = N_{So} + \Phi_{\frac{S}{A}|PFR}(N_{Ao} - N_A)$$

For CVRS system

$$C_R = C_{Ro} + \Phi_{\frac{R}{A}|PFR}(C_{Ao} - C_A)$$

$$C_S = C_{So} + \Phi_{\frac{S}{A}|PFR}(C_{Ao} - C_A)$$

$$C_R = C_{Ro} - \int_{C_{Ao}}^{C_{Af}} \phi_{\frac{R}{A}} dC_A$$

$$C_S = C_{So} - \int_{C_{Ao}}^{C_{Af}} \phi_{\frac{S}{A}} dC_A$$

- Note that $\Phi_{\frac{R}{A}} = 1 - \Phi_{\frac{S}{A}}$. This relation is valid only for the given stoichiometry.

4.3 OPTIMUM τ FOR A SERIES REACTION IN A MFR

The kinetic equations for series and parallel reactions developed earlier are only valid for batch reactor and constant volume plug flow reactors. However, if series or parallel reaction takes place in a MFR, the equation should be obtained by writing material balance on the reactor.

For the MFR , material balance gives

In – out – disappearance by reaction = 0

Writing the equation for reactant A gives

$$F_{Ao} - F_A - (-r_A)V = 0$$
$$vC_{Ao} - vC_A - k_1 C_A V = 0$$
$$Considering \frac{V}{v} = \tau_M$$
$$\frac{C_A}{C_{Ao}} = \frac{1}{1 + k_1 \tau_M}$$

Writing the balance for product R

$$-r_A = k_1 C_A$$
$$r_R = k_1 C_A - k_2 C_R$$

We know that

$$C_A = \frac{C_{AO}}{1 + k_1 \tau_m}$$

Material balance on R

Input + Generation of R = Output

$$(r_R)V = vC_R$$
$$(k_1 C_A - k_2 C_R)V = vC_R$$
$$k_1 C_A \tau_m - k_2 C_R \tau_m = C_R \qquad Q \frac{V}{v} = \tau_m$$
$$(1 + k_2 \tau_m) C_R = k_1 C_A \tau_m$$
$$C_R = \frac{k_1 C_A \tau_m}{(1 + k_2 \tau_m)}$$
$$C_R = \frac{k_1 C_{A0} \tau_m}{(1 + k_1 \tau_m (1 + k_2 \tau_m)}$$

to maximize R,

$$\frac{dC_R}{d\tau_m} = 0$$

we obtain,

$$\boxed{\tau_{m\max} = \frac{1}{\sqrt{k_1 . k_2}}}$$

$$\boxed{\frac{C_{R\max}}{C_{Ao}} = \frac{1}{\left[\left(\frac{k_2}{k_1}\right)^{1/2} + 1\right]^2}}$$

GATE QUESTIONS

COMMON DATA QUESTION

The following gas phase reactions are carried out isothermally in a CSTR

$A \rightarrow 2R; r_1 = k_1 p_A; k_1 = 20 mol/(s - m^3 - bar)$

$A \rightarrow 3S; r_2 = k_2 p_A; k_2 = 40 mol/(s - m^3 - bar)$

Total pressure =1 bar, $F_{A0} = 1\ mol/s$; feed is pure A

1. What is the maximum possible value of F_R (mol/s)?

(a) 1/3 (b) 1/2

(c) 2/3 (d) 2

(GATE 2003)

2.The volume of a CSTR required for a fractional conversion of A equal to 0.3 due to the first reaction is

(a) 0.011 (b) 0.021

(c) 0.275 (d) 0.375

(GATE 2003)

3. Pick the wrong design guideline for a reactor in which the reaction $A \rightarrow R$ (desired) and $A \rightarrow S$ (undesired) are to take place. The ratio of the reaction rate is $\frac{r_R}{r_S} = \left(\frac{k_1}{k_2}\right) C_A^{a-b}$

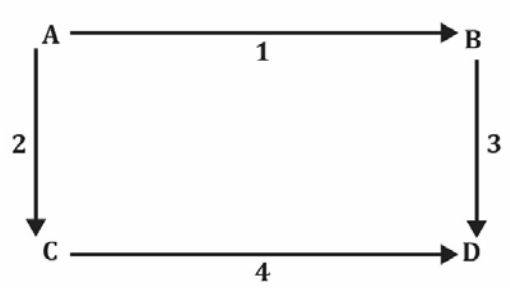
(a) Use high pressure and eliminate inert when a>b

(b) Avoid recycle when a>b

(c)Use batch reactor or plug flow reactor when a>b

(d) Use CSTR with a high conversion when a>b **(GATE 2004)**

4. Consider the following elementary reaction network



The activation energies for the individual reactions are

E_1 =100kJ/mol, E_2 =150kJ/mol,

E_3 =100kJ/mol, and E_4 =200kJ/mol.

If the feed is pure A and the desired product is C, then the desired temperature profile in a plug flow reactor in the direction of flow should be

(a) Constant at low temperature

(b) Constant at high temperature

(c) Increasing

(d) Decreasing

(GATE 2006)

COMMON DATA QUESTION

The following liquid phase reaction is taking place in an isothermal batch reactor.

$A \xrightarrow{k_1 \text{ (first order)}} B \xrightarrow{k_2 \text{ (zero order)}} C$

Feed concentration =1mol/L

5. The time at which the concentration of B will reach its maximum value is given by

(a) $t=\frac{1}{k_1}In\left(\frac{k_1}{k_2}\right)$ (b) $t=\frac{1}{k_2-k_1}In\left(\frac{k_2}{k_1}\right)$

(c) $t=\frac{1}{k_2}In\left(\frac{k_2}{k_1}\right)$ (d) $t=\frac{1}{k_2}In\left(\frac{k_1}{k_2}\right)$

(GATE 2007)

6. The time at which the concentration of B will become zero is given by the following equation

(a) $1-e^{-k_1t}=k_2t$ (b) t = infinite

(c) $t=\frac{1}{k_2}$ (d) $t=\frac{1}{k_1}$

(GATE 2007)

7. The following liquid phase reaction is taking place in an isothermal CSTR

$$A\xrightarrow{k_1}B\xrightarrow{k_2}C$$

$$2A\xrightarrow{k_3}D$$

Reaction mechanism is same as the stoichiometry given above. Given,

k_1=1 min^{-1};k_2=1 min^{-1};k_3=0.5 L/mol-min;
C_{A0}=10 mol/L

C_{B0}=0 mol/L and C_B=1 mol/L, the solution for F/V (flow rate/reactor volume in min^{-1}) yields.

(a) 6.7 (b) 6 and 0.5

(c) 2 and 4/3 (d) 8

(GATE 2007)

8. Determine the level of C_{A0} (high , low, intermediate), temperature profile (high, low, increasing, decreasing), which will favour the formation of the desired product indicated in the reaction scheme given below

$$A\xrightarrow{1}R\xrightarrow{3}S(\text{Desired})$$

$$A\xrightarrow{2}U$$

n_1	E_1	n_2	E_2	n_3	E_3
2	25	1	35	3	45

(a) High C_{A0} , increasing t, plug flow reactor

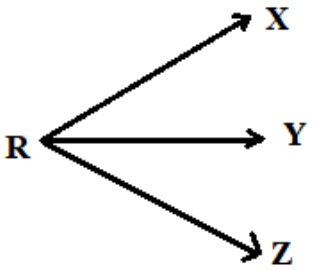
(b) Low C_{A0} increasing t, plug flow reactor

(c) High C_{A0} decreasing t, mixed flow reactor

(d) High C_{A0} decreasing t, plug flow reactor

(GATE 2007)

9. Reactant R forms three products X, Y and Z irreversibly, as shown below



The reaction rates are given by $r_X=C_{R,}r_Y=k_yC_R^{1.5}$ and $r_z=k_zC_R$. the activation energies for formation of X. Y and Z are 40, 40 and 5 kJ/mol respectively. The pre-exponential factors for all reactions are nearly same. The desired conditions for maximizing the yield of X are

(a) high temperature, high concentration of R

(b) low temperature, low concentration of R

(c) low temperature, high concentration of R

(d) high temperature, low concentration of R **(GATE 2011)**

10. Consider the reaction scheme shown below: $A \rightarrow B \rightarrow C$

Both the reactions are of first-order. The activation energies for k_1 and k_2 are 80 and 20 kJ/mol respectively. To maximize the yield of B, it is preferable to use

(a) CSTR and high temperature

(b) PFR and high temperature

(c) CSTR and low temperature

(d) PFR and low temperature

(GATE 2012)

COMMON DATA QUESTION

Liquid reactant A decomposes as follows

$A \rightarrow R,\ r_R = k_1 C_A^2$ $\quad k_1$=0.5 m^3/mol-s

$A \rightarrow S,\ r_s = k_2 C_A$ $\quad k_2 = 1\ s^{-1}$

An aqueous feed of composition $C_{A0} = 30 mol/m^3, C_{R0} = 2 mol/m^3$. $C_{s0} = 1 mol/m^3$

enters a CSTR in which the above reaction occur. Assume isothermal and steady state conditions.

11. If the conversion of A is 80% the concentration of R in the exit stream in mol/m^3, to the nearest integer, is

(a) $40 mol/m^3$ (b) $50 mol/m^3$

(c) $30 mol/m^3$ (d) $20 mol/m^3$

(GATE 2013)

12. What is the % conversion of A, to the nearest integer, so that the concentration of S in the exit stream is 11.8 mol/m^3?

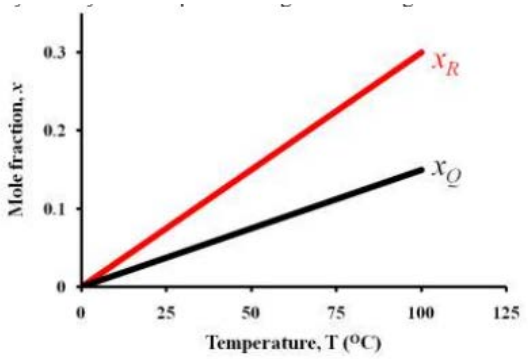
(a) 90% (b) 40%

(c) 60% (d) 50%

(GATE 2013)

13. In a laboratory batch setup, reaction of P over a catalyst was studied at various temperatures. The reactions occurring are $P \rightarrow 2Q; P \rightarrow R$

At the end of one hour of operation, the batch contains X_P, X_Q and X_R mole fraction of P, Q and R components, respectively. The mole fractions of product components $(X_Q$ and $X_R)$ were found to vary linearly temperature as given in the figure.



If the yield of Q based on reactant P consumed (Y_Q) at 25^0C was found to be0.40,then the value of Y_Q at $60^0 C$ is _____(rounded off to second decimal place). **(GATE 2018)**

ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(C)	(B)	(D)	(D)	(A)	(A)	(B)	(A)	(D)	(B)
11	12	13							
(D)	(A)	(0.4)							

EXPLANATIONS

1.Answer:(c)

$A \to 2R, r_1 = k_1 p_A, k_1 = 20 mol/s-m^3-bar$

$A \to 3S, r_2 = k_2 p_A,\ k_2 = 40 mol/s-m^3-bar$

Total rate of reaction for A,

$(-r_A) = r_1 + r_2 = (k_1 + k_2) p_A$

$\therefore \dfrac{r_1}{(-r_A)} = \dfrac{k_1}{k_1 + k_2} = \dfrac{20}{20+40}$

$\dfrac{r_1}{(-r_A)} = \dfrac{1}{3}$

For 1 mol of A disappearing in $A \to 2R$, 2 mol of R produced.

$\therefore$ Maximum possible value of $F_R = \dfrac{1}{3} \times 2 = \dfrac{2}{3}$

2.Answer:(b)

For CSTR, $\dfrac{V}{F_{A_o}} = \dfrac{X_A}{(-r_A)}$

Here, X_A=0.3, F_{Ao}=1 mol/s

But this conversion is only due to first reaction. According to the previous relation twice of this will react through the second reaction Hence the conversion of A is 0.9

$\dfrac{V}{F_{A_o}} = \dfrac{X_A}{(-r_A)}$

$\dfrac{V}{F_{A_o}} = \dfrac{X_A}{k_1 p_{A_o}(1 - X_A)} \left(\begin{matrix} p_{A_o} = 1, \\ \text{Pure Feed} \end{matrix} \right)$

$\dfrac{V}{1} = \dfrac{0.3}{20(1-0.3)}$

$V = 0.021\ m^3$

3.Answer: (d)

$A \to S(Undesired)$ $\qquad$ $A \to R(Desired)$

Given, $\dfrac{r_R}{r_s} = \left(\dfrac{k_1}{k_2} \right) C_A^{a-b}$

a>b; PFR should be used CSTR is wrong to use when a>b. If R desired product

4.Answer:(d)

Given,

$E_1 = 100 kJ/mol, E_2 = 100 kJ/mol,$

$E_3 = 100 kJ/mol, E_4 = 100 kJ/mol,$

When the feed is pure A, higher temperature of the reactor will favor reaction 2 because $E_2 > E_1$. after substantial amount of C is formed, we don't want reaction 4 to take place. Since E_4 is largest, lower temperature will be desired so as to lower the formation D from reaction 4.

Thus, decreasing temperature profile is correct answer.

5.Answer: (a)

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Given,

$C_{A_0} = 1 mol/L$

For 1st order reaction,

$$\frac{dC_A}{dt} = -k_1 C_A$$

Or $$\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A} = -k_1 \int_0^t dt$$

$$ln(C_A / C_{A_0}) = -k_1 t$$

$$C_A = C_{A_0} e^{-k_1 t} \quad (as\ C_{A_0} = 1)$$

$$C_A = e^{-k_1 t} ...(1)$$

Now, for B,

$$\frac{dC_B}{dt} = k_1 C_A - k_2$$

$$= k_1 e^{-k_1 t} - k_2 ...(2)$$

For maximum value of concentration of B,

$$\frac{dC_B}{dt} = 0$$

$$k_1 e^{-k_1 t} - k_2 = 0$$

$$e^{-k_1 t} = \frac{k_2}{k_1}$$

$$\ln e^{-k_1 t} = \ln(k_2 / k_2)$$

$$t = \frac{1}{k_1} ln\left(\frac{k_1}{k_2}\right)$$

6.Answer:- (a)

Form Eq. (2),

$$\frac{dC_B}{dt} = k_1 e^{-k_1 t} - k_2$$

$$\int dC_B = \int (k_1 e^{-k_1 t} - k_2) dt + C$$

$$C_B = -e^{-k_1 t} - k_2 t + C ...(3)$$

At t=0, C_B =0 (as there is no B in the feed)

$$\therefore 0 = -1 - 0 + C$$

$$C = 1$$

From Eq. (3) ,

$$C_B = 1 - k_2 t - e^{-k_1 t}$$

Now, for $C_B = 0, t = ?$

$$\therefore 0 = 1 - k_2 t - e^{-k_1 t} \quad \text{or} \quad 1 - e^{-k_1 t} = k_2 t$$

7.Answer: (b)

Given,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$2A \xrightarrow{k_3} D$$

$$-r_A = k_1 C_A + 2k_3 C_A^2$$

$$-r_B = k_1 C_A + k_2 C_B$$

$$r_C = k_2 C_B$$

$$r_D = k_3 C_A$$

Also given, $k_1 = 1 min^{-1}$, $k_2 = 1 min^{-1}$,

$$k_3 = 0.5 \frac{L}{mol - \min}$$

$$C_{A_0} = 10 mol/L, C_{B_0} = 0, C_B = 1 mol/L$$

$$\frac{F}{V} = ?$$

Applying material balance for A for CSTR,

$$FC_{A_0} = FC_A + (-(r_A))V$$

(Here, F is volumetric flow rate in L/min)

Or $$F \times 10 = FC_A(k_1 C_A + k_2 C_A^2)V$$

$$\frac{F}{V} = \frac{k_1 C_A + k_2 C_A^2}{10 - C_A}$$

$$= \frac{C_A + 0.5C_A^2}{10 - C_A} \ldots (1)$$

Applying material balance B,

$$FC_{B_0} = FC_B + (-r_B)V$$
$$0 = F \times 1 + (1 \times 1 - 1 \times C_A)V$$
$$\frac{F}{V} = C_A - 1 \ldots (2)$$

From Eqs. (1) and (2),

$$C_A + 0.5C_A^2 = (10 - C_A)(C_A - 1)$$
$$1.5C_A^2 - 10C_A + 10 = 0$$
$$C_A = 5.44 \text{ and } 1.23$$
$$\frac{F}{V} = 4.44 \text{ and } 0.23$$

The closest answer is 6 and 0.5.

8.Answer: (a)

$$A \xrightarrow{1} R \xrightarrow{3} S(desired)$$
$$A \xrightarrow{2} U$$

As can be seen from the data, the activation energy is highest for desired product reaction. Thus, increasing temperature will favour this desired reaction. And for the same volume of PFR and MFR,PFR is chosen for higher conversion rate. At last, higher initial concentration of A will give higher rate of reaction resulting in more desired product information.

Thus, high C_{A_0}, increasing T, plug flow reactor is correct answer.

9.Answer: (d)

$$k = Ae^{-E/RT}$$
$$k_X = k_Y = Ae^{-40/RT} \text{ and } k_Z = Ae^{-5/RT}$$

At high temperature, $k_X > k_Z$

At high concentration, $r_Y > r_x$

Thus, for maximizing the yield of X, the desired conditions are high temperature and low concentration of R

10.Answer:(b)

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Since, $k = Ae^{-E/RT}$

The activation energy for k_1 (80kJ/mol) is higher than for k_2 (20kJ/mol). Thus, higher temperature is preferable to maximize the yield of B. Also, Plug Flow Reactor (PFR) should be used for better conversion rate.

11.Answer:(d)

Given,

$$C_{A0} = 30 mol/m^3$$
$$C_{R0} = 2 mol/m^3$$
$$X_A = 0.8$$
$$\therefore C_A = C_{A0}(1 - X_A)$$
$$= 30(1 - 0.8) = 6 mol/m^3$$

Applying material balance for A,

$$vC_{A0} = vC_A + (-r_A)V$$
$$vC_{A0} = vC_A + (k_1C_A^2 + k_2C_A)v$$
$$v(C_{A0} - C_A) = (k_1C_A^2 + k_2C_S)v$$
$$v(30 - 6) = (0.5 \times 6 \times 6 + 1 \times 6)v$$
$$\frac{V}{v} = \tau = 1s$$

Applying material balance for R,

$$vC_{R0} = vC_R - r_R.v$$
$$C_{R0} = C_R - k_1 C_A^2 \tau$$
$$C_R = C_{R0} + k_1 C_A^2 \tau$$
$$C_R = 2 + 0.5 \times 6 \times 6 \times 1$$
$$C_R = 20 mol/m^3$$

12.Answer: (a)

Applying material balance for S,

$$vC_{so} = vC_s(-r_s)v$$
$$C_{so} = C_s - k_2 C_{A\tau}$$
$$1 = 11.8 - 1 \times C_{A\tau}$$
$$C_{A\tau} = 10.8$$

Now, applying material balance for A,

$$vC_{A0} = vC_A + (-r_A)V$$

Or $C_{A0} = C_A + (k_1 C_A^2 + k_2 C_A)\tau$

Or $C_{A0} = C_A + (0.5C_A + 1)C_A\tau$

$$30 = C_A + (0.5C_A + 1) \times 10.8 = C_A = 3$$

% conversion of A,

$$X_A = 1 - \frac{C_A}{C_{A0}} = 1 - \frac{3}{30} = 0.9 = 90\%$$

13.Answer: 0.4(independent of temp)

5 NON-ISOTHERMAL REACTORS

5.1 THE ENERGY BALANCE EQUATION

So far we were only dealing with isothermal reactors, temperature was not changing. Hence there was no need to write energy balance for those reactors. In non-isothermal reactors, the temperature is not constant and hence along with material balance equations, energy balance equation is also required.

- These non-isothermal reactors are ideal reactors and therefore the design equations developed in the previous chapters are valid here.
- In batch reactors, the temperature changes with time.
- In PFR the temperature changes along the length of the reactor with increase in conversion.
- In MFR, there is sudden change in temperature just like sudden change in conversion and concentration. The entire MFR is at the same temperature. However, this temperature is different from the inlet temperature.
- Note that the energy balance equation for any reactor remains same.

The general equation of energy balance at steady state is

$$\Delta H = Q_{external}$$

$$\Delta H_{product} - \Delta H_{reactant} + \Delta H^{o}_{rxn}(F_{Ao}X_A) = Q_{external}$$

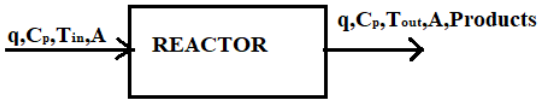
The above equation is written for a continuous steady state reactor. Enthalpy of products and reactants are calculated with respect to a reference temperature. This reference temperature should be same as the temperature at which enthalpy of reaction is known.

If energy balance equation has to be written for a batch reactor, then energy accumulation term should also be there.

(ENERGY OUT-ENERGY IN+ $\Delta H_{rxn}N_{Ao}X_A$) =(FINAL ENERGY OF SYSTEM-INITIAL ENERGY OF SYSTEM)

- The energy balance equation can be written on the basis of mass or on the basis of moles. Before writing the energy balance we should check the units of specific heat. If specific has the units of mass then energy balance should be written on mass basis and if specific heat has the units of moles then energy balance should be written on the basis of moles.

5.1.1 ENERGY BALANCE ON THE BASIS OF MASS



Consider the above reactor where q denotes volumetric flow rate of the

streams, C_P denotes the specific heat of the streams which is assumed to be constant with temperature. During a chemical reaction the total mass remains same. Hence assuming density of the mixture to remain constant we can write the following energy balance equation at steady state on the basis of mass

$$\Delta H_{products} - \Delta H_{reactants} + \Delta H_{rxn} F_{Ao} X_A = Q_{ext}$$

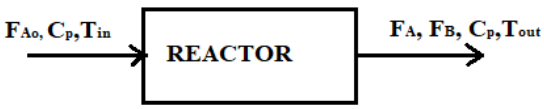
$$\rho \dot{q} C_P (T_{out} - T_{ref}) - \rho \dot{q} C_P (T_{in} - T_{ref})$$

$$+\Delta H_{rxn} (\dot{q} C_{Ao} X_A) = Q_{ext}$$

Q_{ext} should be written according to the convention that heat added to the system is positive while heat withdrawn from the system is negative. The enthalpy of reaction should be calculated at the same reference temperature. The enthalpy of reaction should be used along with its sign depending on whether the reaction is endothermic or exothermic.

5.1.2 ENERGY BALANCE ON THE BASIS OF MOLES

When balance is written on the basis of moles, we should be careful about each and every component separately in the reactant and product stream. Consider a reaction $A \rightarrow B$ and assume that $C_{PA} = C_{PB} = C_P$. Assuming that reactant A is not converted completely we can write the following energy balance equation.



$$(F_A C_P + F_B C_P)(T_{out} - T_{ref}) - F_{Ao} C_P (T_{in} - T_{ref})$$

$$+\Delta H_{rxn} F_{Ao} X_A = Q_{ext}$$

Substituting

$$F_A = F_{Ao}(1 - X_A)$$

$$F_B = F_{Ao} X_A$$

we get

$$X_A = \frac{C_P (T_{out} - T_{ref})}{-\Delta H_{rxn}}$$

Note that the above relation is not universal. It is only valid for the given reaction & adiabatic reactors and for the above assumption. For any other reaction, each component should be considered separately with its individual specific heat.

5.2 ADIABATIC REACTORS

For adiabatic reactors there is no heat interaction between the system and the surroundings and hence $Q_{ext} = 0$. By using energy balance we can conclude

- If the reaction is endothermic and takes place in adiabatic reactors, then the exit temperature should be lower than the inlet temperature.
- If the reaction is exothermic and takes place in a diabetic reactor then the exit temperature must be higher than the inlet temperature.
- The above discussion also suggest that an adiabatic reactor should always be non-isothermal.
- We should note that we cannot maintain temperature profile of our choice in an adiabatic reactor. The temperature profile is fixed in an adiabatic reactor.
- If we want to maintain a desired temperature profile, then heat

must be added or removed and it suggests that reactor cannot be adiabatic.

5.3 EQUILIBRIUM AND ACTUAL CONVERSION OF A REACTION

When a reaction proceeds its conversion always increases and reaches a certain value depending the time in a batch reactor or PFR and volume of MFR. This conversion is called the actual conversion and depends upon the actual conditions (time, volume, length of reactor etc).

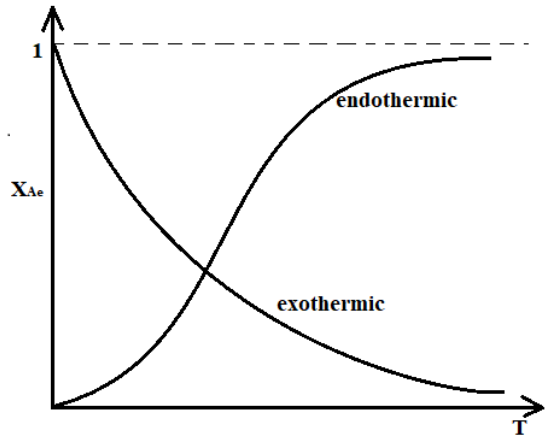
However, what is the maximum conversion that can be attained by a reaction is decided by the thermodynamics and this value is called the equilibrium conversion. We can say that it is the maximum possible value of actual conversion provided sufficient residence time or volume of reactor.

The maximum possible conversion of irreversible reaction is 100%. But for reversible reactions it is less than hundred percent. Note that we always want higher values of equilibrium conversion because if maximum possible conversion is high then only we can achieve higher value of actual conversion.

5.3.1 DEPENDENCY OF EQUILIBRIUM CONSTANT AND EQUILIBRIUM CONVERSION

- Equilibrium constant of a reaction depends only on temperature. It is not affected by pressure or presence or absence of inert.
- For endothermic reactions, with increase in temperature, equilibrium constant increases.
- For exothermic reactions, with increase in temperature, the equilibrium constant decreases.
- The above results can be easily proved by Vant-Hoff's equation.
- The equilibrium conversion of a reversible reaction depends upon temperature, pressure, presence or absence of inert in the system.
- With increase in temperature, the equilibrium conversion increases for endothermic reactions while decreases for exothermic reactions.
- With increase in pressure the equilibrium conversion shifts in that direction where there is a decrease in number of moles of gaseous species and vice-versa.
- Addition of inert to the system has the same effect as that of decreasing the pressure.
- These results can be easily verified by using the Le-Chatelier's principle.

In earlier chapters we were dealing with isothermal reactors and hence the equilibrium conversion was also constant. However, in non-isothermal reactions with increase in conversion the temperature changes due to which the equilibrium conversion also changes. Therefore, designing of non-isothermal reactors are complex.

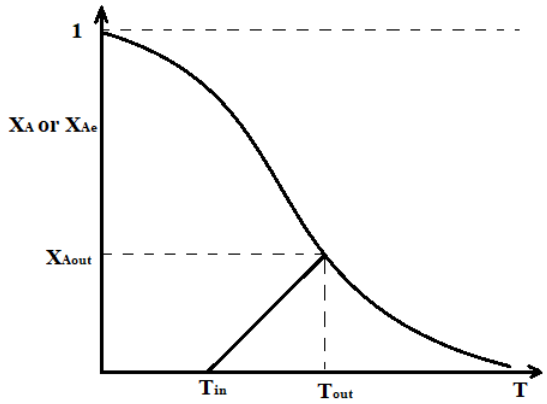


For a reversible reaction we can obtain the expression for the equilibrium conversion by writing the expression of net rate and equating it to zero. At equilibrium the net rate which is forward rate minus the backward rate becomes zero and the conversion at this condition becomes the equilibrium conversion. This value of equilibrium conversion is independent of type of reactor.

- For a reversible reaction, if forward reaction is endo thermic then backward must be exothermic and vice-versa.
- For a reversible reaction, the endothermic path always has a higher activation energy than the exothermic path. The path with higher activation energy is more temperature sensitive.
- Hence for reversible exothermic reaction where backward reaction is endothermic, with increase in temperature both the rate constant increases. However the increase in backward rate constant is more. Hence the ratio $\frac{k_f}{k_b}$ decreases or K_C decreases.

5.4 REVERSIBLE REACTIONS IN ADIABATIC REACTORS

If a reversible exothermic reaction takes place in an adiabatic reactor, then we know that with increase in conversion the temperature of the reaction mixture will increase. With increase in this temperature the equilibrium conversion decreases. There will be a temperature when increasing actual conversion becomes equal to decreasing equilibrium conversion. After this there will be no increase in actual conversion. This can be shown in the following figure



It can be understood from the above figure that if we want to increase the conversion achieved then the inlet temperature must be reduced. Note that above figure is only for reversible exothermic reaction. The straight line in the above figure is obtained from energy balance and has a slope of $\frac{C_P}{-\Delta H_{rxn}}$. For exothermic reactions this slope will be positive. For endothermic reactions, the slope will be negative.

The conversion achieved can also be increased by doing inter-stage cooling.

5.5 OPTIMUM TEMPERATURE PROGRESSION

Now we will talk about those reactors where we can maintain a desired temperature profile. If we want to maintain a temperature profile of our choice then the reactor has to be non-isothermal. Optimum temperature progression means the temperature profile that we want to maintain inside the reactor to minimize the reactor volume. This temperature progression can be a constant temperature or a changing temperature (with time in batch reactors and with length in a PFR)

- For irreversible reactions whether endothermic or exothermic, the rate constant increases with temperature and hence the rate also increases. So for these reactions the reactor should be maintained at maximum possible constant temperature. This maximum temperature is decided by the material of construction.
- For reversible reactions, there are two factors. Rate and equilibrium conversion.
- For reversible endothermic reactions, with increase in temperature the forward rate increases and equilibrium conversion also increases. Hence these reactions should be carried out at maximum possible constant temperature.
- For reversible exothermic reactions, with increase in temperature equilibrium conversion decreases and therefore we should use decreasing temperature profile.

GATE QUESTIONS

1. The reaction $A \rightarrow B$ is conducted in an adiabatic plug flow Reactor (PFR). Pure A at a concentration of 2 k mol/ m^3 is fed to the reactor at the rate of 0.01 m^3 /s and at a temperature of 500 K. If the exit conversion is 20%, then the exit temperature (in Kelvin) is

$\Delta H_2 = -50000 KJ / Kmol, C_{PA}$
$= C_{PB} = 100 KJ / Kmol.K$

(a) 400 (b)500

(c) 600 (d) 1000

(GATE 2001)

2. A batch adiabatic reactor at an initial temperature 373 ^0K is being used for the reaction $A \rightarrow B$. Assume the heat of reaction is -1 kJ/mol at 373 ^0K and the heat capacity of both A and B to be constant and equal to 50 J/mol-K. The temperature rise after a conversion of 0.5 will be

(a) 5 ^0C (b) 10 ^0C

(c) 20 ^0C (d) 100 ^0C

(GATE 2002)

3. An exothermic reaction takes place in an adiabatic reactor. The product temperature_____ the reactor feed temperature.

(a) Is always equal to

(b) is always greater than

(c)is always less than

(d) may be greater or less than

(GATE 2002)

4. A CSTR is to be designed in which an exothermic liquid phase first order reaction of the type $A \rightarrow R$ is taking place. The reactor is to be provided with a jacket in which coolant is flowing. Following data is given

$C_{A0} = 5 kmol / m^3; X_A = 0.5;$ feed temperature = reactor temperature = $40^0 C;$ rate constant at $40^0 C = 1 \min^{-1}; (\Delta H) = -4 kJ / mol;$ $\rho = 1000 kg / m^3;$

C_p = 4 J/g ^{0}C ; q = 10^{-3} m^3/min (ρ and C_p are same for the reactant and product streams).

The amount of heat to be removed is

(a)2/3 kW (b)1 kW

(c) 5/3 kW (d)4 Kw

(GATE 2003)

5. An irreversible aqueous phase reaction $A + B \rightarrow P$ is carried out in an adiabatic mixed flow reactor. A feed containing 4 kmol/ m^3 of each A and B enters the reactor at 8 m^3/h. If the temperature of the exit stream is never to exceed 390 K, what is the maximum feed inlet temperature allowed?

Data : Heat of reaction =-50kJ/mol, density of the reacting mixture =1000 kg/ m^3, specific heat of reacting mixture 2 kJ/kg-K.

The above data can be assumed to be independent of composition and temperature.

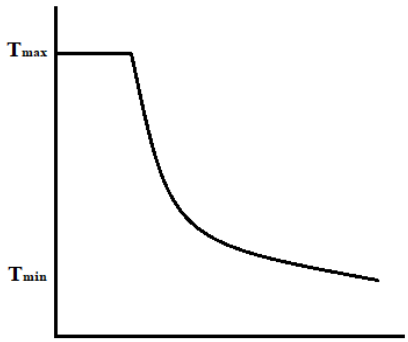
(a) 190 K (b)290 K

(c) 390 K (d)490 K

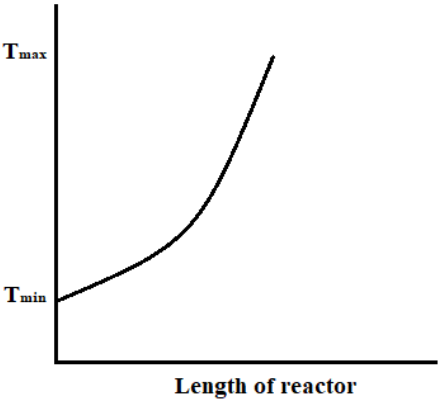
(GATE 2004)

6. Consider a reversible exothermic reaction in a plug flow reactor. The maximum and minimum permissible temperatures are T_{max} and T_{min} respectively. Which of the following temperature (T) profiles will require the shortest residence time to achieve the desired conversion?

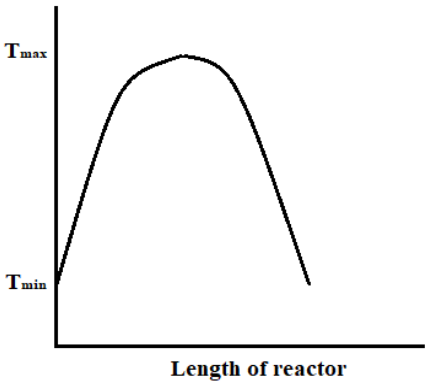
(a)



(b)



(c)



(d)

(GATE 2004)

7.An endothermic aqueous phase first order irreversible reaction is carried out in an adiabatic plug flow reactor. The rate of reaction

(a) is maximum at the inlet of the reactor

(b) goes through a maximum along the length of the reactor

(c) goes through a minimum along the length of the reactor

(d) is maximum at the exit of the reactor

(GATE 2004)

8. The gas phase reaction $A \rightarrow B + C$ is carried out in an ideal PFR achieving 40% conversion of A. The feed has 70 mol% A and 30 mol% inerts. The inlet temperature is 300 K and the outlet temperature is s400 K. The ratio of the outlet to inlet molar concentration of A (assuming ideal gas mixture and uniform pressure) is

(a) 0.60 (b) 0.30

(c) 0.47 (d) 0.35

(GATE 2005)

9. A liquid phase exothermic first order reaction is being conducted in a batch reactor under isothermal conditions by removing heat generated in the reactor

with the help of cooling water. The cooling water flows at a very high rate through a coil immersed in the reactor such that there is negligible rise in its temperature from inlet to outlet of the coil. If the rate constant is given as k, heat of reaction (ΔH), volume of the reactor V, initial concentration as C_{A0}, overall heat transfer coefficient U, heat transfer area of the coil is equal to A, the required, cooling water inlet temperature T_{ci} is given by the following equation

(a) $T_{ci} = T - \dfrac{(-\triangle H)VkC_{A0}}{UA}$

(b) $T_{ci} = T - \dfrac{(-\triangle H)VkC_{A0}e^{-kt}}{UA}$

(c) $T_{ci} = T - \dfrac{(-\triangle H)VkC_{A0}e^{-kt}}{UAt}$

(d) $T_{ci} = T - \dfrac{(-\triangle H)VkC_{A0}}{UAt}$

(GATE 2007)

10. The homogeneous reaction $A + B \rightarrow C$ is conducted in an adiabatic CSTR at 800K so as to achieve a 30% conversion of A. The relevant specific heats and enthalpy change of reaction are given by $C_{p,B} = 100J(mol-K), C_{p,C} = 150J/mol\,\text{K}$

$C_{p,A} = 50J(mol-K), \Delta H^{rxn} = -100kJ/mol$

If the feed , a mixture of A and B, is available at 550 ^oK, the mole fraction of A in the feed that is consistent with the above data is

(a) 5/7 (b) 1/4

(c) ½ (d) 2/7

(GATE 2008)

11. The liquid-phase reaction $A \rightarrow B$ is conducted in an adiabatic plug flow reactor.

Data:

Inlet concentration of A =4.0 $kmol/m^3$

Density of reaction mixture (independent of temperature) = 1200 kg/m^3

Average heat capacity of feed stream (independent of temperature) =2000J/kg-K

Heat of reaction (independent of temperature) =-120kJ/mol of A reacting

If the maximum allowable temperature in the reactor is 800 ^oK, then the feed temperature (in ^oK) should not exceed ?

(a) 400 (b) 500

(c) 600 (d) 700

(GATE 2009)

12. For an exothermic reversible reaction, which one of the following correctly describes the dependence of the equilibrium constant (K) with temperature (T) and pressure (P)?

(a) K is independent of T and P

(b) K is increases with an increase in T and P

(c) K is increases with T and decreases with P

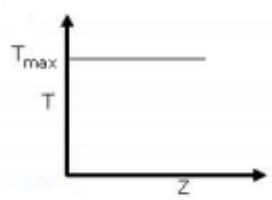
(d) K decreases with an increase T and is independent of P

(GATE 2012)

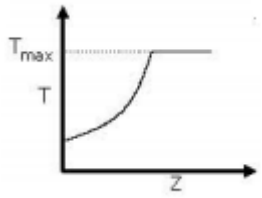
13. The elementary reversible exothermic gas-phase reaction $A + 3B \rightleftharpoons 2C$ is to be conducted in a non-isothermal, non-adiabatic plug flow

reactor. The maximum allowable reactor temperature is T_{max}. To minimize the total reactor volume, the variation of temperature (T) with axial distance from inlet(Z) will be

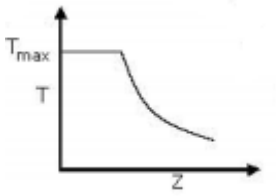
(a)



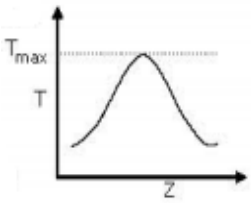
(b)



(c)



(d)



(GATE 2012)

14. Determine the correctness of the following Assertion $[a]$ and Reason $[r]$.

Assertion: significant combustion of coke takes only if it is heated at higher temperature in presence of air

Reason: $C + O_2 \rightarrow CO_2$ is an exothermic reaction.

(a) Both $[a]$ and $[r]$ are true and $[r]$ is the correct reason for $[a]$

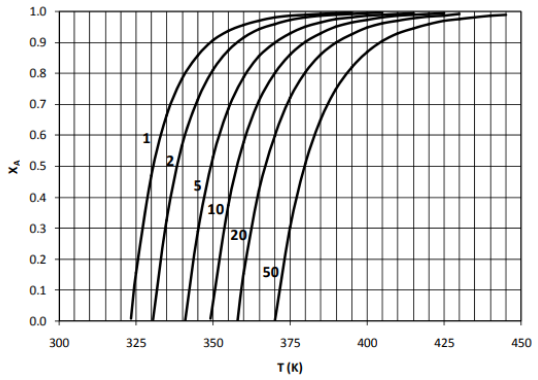
(b) Both $[a]$ and $[r]$ are true and $[r]$ is not the correct reason for $[a]$

(c) $[a]$ is correct but $[r]$ is false

(d) Both $[a]$ and $[r]$ are false

(GATE 2014)

15. A liquid phase irreversible reaction $A \rightarrow B$ is carried out in an adiabatic CSTR operating under steady state conditions. The reaction is elementary and follows the first order law. For this reaction, the figure below shows the conversion (X_A) of A as a function of temperature (T) for different values of the rate of reaction $(-r_A$ in $molm^{-3}s^{-1})$ denoted by the numbers to the left of each curve. This figure can be used to determine the rate of the reaction at a particular temperature, for a given conversion of A.



The inlet stream does not contain B and the concentration of A in the inlet stream is 5 mol/m^3. The molar feed rare of A is 100 mol/s. A steady state energy balance for this CSTR results in the following relation: $T = 350 + 25X_A$ where T is the temperature (in K) of the exit stream and X_A is the conversion of A in the CSTR. For an exit conversion of 80% of A. The volume (in m^3, rounded off to the first decimal place) of CSTR required is ____

(GATE 2016)

ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(C)	(B)	(B)	(C)	(B)	(B)	(A)	(D)	(B)	(A)
11	12	13	14	15					
(C)	(A)	(B)	(B)	(8)					

EXPLANATIONS

1.Answer:(c)

Given $C_{A_0} = 2kmol/m^3, v_0 = 0.01m^3/s$

$T_1 = 500\ \text{K}, X_A = 0.2$
$C_{PA} = C_{PB} = 100kJ/mol-K$
$\Delta H = 50000\ kJ/kmol\ of\ reacted$

Applying energy balance,
$(V_0 C_{A0} C_{PB} T_2) - (V_0 C_{A0} C_{PA} T_1) +$
$(\Delta H \times V_0 \times C_{A0} X_A) = 0$
$C_{PB} T_2 - C_{PA} T_1 = \Delta H . X_A$

Putting values,
$100T_2 - 100 \times 500 = 50000 \times 0.2$

$T_2 = 600$

2.Answer:(b)

Given,

$A \rightarrow B$

$C_{pA} = C_{pB} 50\ j/mol-K$
$-\Delta H = -1kj/mol = -1000\ j/mol$
$X_A = 0.5$
$((\Delta T)C_p = \Delta H_\tau \times X_A)$
$(\Delta T)50 = 1000 \times 0.5$
$\Delta T = 10^0 C$

3. Answer:(b)

For exothermic reaction in adiabatic reactor, product temperature is always greater than feed temperature.

4.Answer:(c)

Given $C_{A_0} = 5kmol/m^3, X_A = 0.5$

$T = 40^o C, k = 1\text{min}^{-1}$
$(\Delta H) = -40kj/mol, \rho = 1000kg/m^3$
$C_p = 4kj/kg-K, q = 10m^{-3}/m^3\ \text{min} = V_o$

Amount of heat removed
$= V_o C_{A_0}(1 - X_A) \times \Delta H$

$= \frac{10^{-3}}{60}\frac{m^3}{s} \times 5 \times 10^3 \frac{mol}{m^3} \times 0.5 \times 40 \frac{kj}{mol}$
$= \frac{5}{3}\frac{kj}{s} = \frac{5}{3}kW$

5.Answer:-(b)

Given, $C_{A_0} = 4kmol/m^3 = 400mol/m^3$

$V_o = 8m^3/h$

$(-\Delta H) = 50kj/mol, \rho = 1000kg/m^3,$
$C_p = 2kj/kg-K$

Applying energy balance for maximum heat generated or all A reacted,

$8m^3/h \times 1000kg/m^3 \times 2kj/kg-K \times \Delta T_{\max}$
$= 8m^3/h \times 4000mol/m^3 \times 50kj/mol$

Or $\Delta T_{\max} = 100$

Or $390 - \Delta T_{inlet} = 100$

$T_{inlet} = 290K$

6.Answer:(b)

Given reversible exothermic reaction in a PFR.

$A \rightleftharpoons B$

Option (a) Maximum temperature is being maintained throughout the reactor. When the product concentration increased, rate of backward reaction also increases due to higher T. Thus, overall rate of reaction decreases. It is not a desirable case.

Option (b) Initial higher temperature gives higher rate of forward reaction and decrease in temperature with length of the reactor will not increase the backward rate of reaction. The residence time will be shortest.

Option (c) and (d) Initial lower temperature will give lower rate of forward reaction and with increase in temperature and product concentration, the backward rate of reaction increases resulting in decrease in overall reaction rate.

Thus, (b) is correct answer.

7.Answer :(a)

For adiabatic PFR, an endothermic 1^{st} order aqueous phase reaction would maximum rate of reaction at the inlet of the reactor because the temperature is maximum at the inlet and temperature decreases along the reactor due to endothermic reaction.

8.Answer:(d)

A	$\rightarrow$	B	+	C	inert
Initial moles 70		0		0	30
After 100% 0		70		70	30

$$\varepsilon_A = \frac{170-100}{100}$$

$$= 0.7$$

$$C_A = C_{Ao}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)$$

$$C_A = 0.47C_{Ao} \quad @300k$$

But the outlet gas is at 400k

$$C_{A@400k} = C_A \times \frac{300}{400}$$

$$= 0.47C_{Ao} \times 3/4$$

$$= 0.35C_{Ao}$$

$$\frac{C_{A@400k}}{C_{Ao}} = 0.35$$

Ratio of outlet to inlet molar concentration of $A = \frac{0.33}{0.7} = 0.47$

9.Answer:(b)

For batch reactor , applying the material balance,

Input = Output +Reaction + Accumulation

$$0 = 0 + (-r_A)V + \frac{dN}{dt}$$

Or $$\frac{dN_A}{dt} = -(-r_A)V$$

Or $$\frac{dC_A}{dt} = -kC_A$$ (first order reaction)

$$\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A} = -k\int_0^t dt$$ or

$$C_A = C_{A_0}e^{-kt} \ldots(1)$$

Now, Heat generated = Heat removed

$$(-r_A)V(-\Delta H) = UA(T - T_0)$$

$kC_A V(-\Delta H) = UA(T - T_0)$

Or $\frac{kV}{UA}.C_{A0}e^{-kt}(-\Delta H) = (T - T_0)$

Or $T_{ci} = T - \frac{(-\Delta H)kVC_{A_0}e^{-kt}}{UA}$

10.Answer:(a)

$$A + B \rightarrow C$$

Initial moles $n_A \quad n_B \quad 0$

Moles after 30% conversion $n_A - 0.3n_A$

$n_B - 0.3n_A \qquad 0.3n_A$

Applying the energy balance for the adiabatic CSTR,

Input = Output +generation

$\sum n_{in}C_p\Delta T_1 = \sum n_{out}C_p\Delta T_0 + \Delta H^{r\times n}\varepsilon$

$\varepsilon = \frac{n_A - (n_A - 0.3n_A)}{1} = 0.3n_A = no$. Of moles of A reacted

Thus, putting values

$n_A \times 100 \times (550 - T\gamma) + n_B \times 50 \times (550 - T\gamma) =$
$0.7n_A \times 100 \times (800 - T\gamma) + (n_B - 0.3n_A) \times 50 \times (800 - T\gamma)$
$+0.3n_A \times 150 \times 800 - 0.3n_A \times 100 \times 10^3$

(since, $\Delta H^{rxn} = -100 \times 10^3 J/mol$)

Or $5000n_A = 12500n_B$

Or $n_A = \frac{5}{2}n_B$

Thus, the mole-fraction of A in the feed $= \frac{n_A}{n_A + n_B} = \frac{5}{7}$

11.Answer:(c)

$A \rightarrow B$

Given $C_{A_0} = 4kmol/m^3$

$\rho = 1200kg/m^3$
$C_P = 2000J/kg - K$

$\Delta H_x = -120kJ/mol$ of A reacting

Input-Output + Generation = Accumulation

$\rho.V_0.C_P T_1 - \rho V_0 C_P T_2 + V_0 C_{A_0}.\Delta H_x = 0$

$1200 \times V_0 \times 2000(T_1 - T_2) + V_0 \times 4 \times 120 \times 10^6 = 0$

Units $\frac{kg}{m^3} \times \frac{m^3}{s} \times \frac{J}{kg - K} \times K$

$\frac{m^3}{s} \times \frac{kmol}{m^3} \times \frac{kj}{mol} \times 10^6 \frac{mol}{kmol} \times \frac{J}{kJ}$

$24 \times 10^5 (T_1 - T_2) + 480 \times 10^6 = 0$
$T_1 - T_2 = -200$
$T_2 = -200 + 800$
$T_2 = 600$

12.Answer:(b)

For change in temperature and pressure, the equilibrium shift to minimize the effect as per Le's chatlier principal. But equilibrium constant is independent of T and P.

13.Answer:(c)

14.Answer:(b)

Both [a] and [r] are true but [r] is not correct reason for [a].

15.Answer: (8)

Given conditions

$C_{Ao} = 5mol/m^3$

$F_{Ao} = 100mol/\sec$

Temperature profile is given as $T = 350 + 25X_A$

$X_A = 0.8$

On putting this value we will get T= 370 K

At 370 K the value of $(-r_A)$ corresponding to this value $(-r_A) = 10mol/m^2 - s$

For MFR we know

$$\frac{V}{F_{Ao}} == \frac{X_A}{-r_A}; V = F_{Ao}\frac{X_A}{(-r_A)} = \frac{100 \times 0.8}{10}$$

$V = 8\ \mathrm{m}^3$

6 NON-IDEAL REACTORS

In this chapter we will learn about non-ideal reactors, that is, reactors that do not follow the models we have developed for ideal CSTRs, PFRs, and PBRs. We describe how to characterize these non-ideal reactors using the residence time distribution function E(t), the mean residence time $\bar{t}$, the cumulative distribution function F(t), and the variance σ^2. The functions E(t) and F(t) will be developed for ideal PFRs, CSTRs. We will then use these ideal curves to help diagnose and troubleshoot bypassing and dead volume in real reactors. We will learn how to use the residence time data and functions to make predictions of conversion and exit concentration. Because the residence time distribution is not unique for a given reaction system, we must use new models if we want to predict the conversion in a non-ideal reactor.

6.1 RESIDENCE TIME DISTRIBUTION

We will consider following examples to understand the need of residence time distribution.

- In a gas-liquid continuous-stirred tank reactor, the gaseous reactant is bubbled into the reactor while the liquid reactant is fed through an inlet tube in the reactor's side. The continuous liquid phase could be regarded as perfectly mixed, and the reaction rate was proportional to the total bubble surface area. The surface area of a particular bubble depended on the time it had spent in the reactor. Because of their different sizes, some gas bubbles escaped from the reactor almost immediately, while others spent so much time in the reactor that they were almost completely consumed. The time the bubble spends in the reactor is termed the bubble residence time.

- When a reactor is packed with catalyst, the reacting fluid usually does not flow through the reactor uniformly. Rather, there may be sections in the packed bed that offer little resistance to flow, and as a result a major portion of the fluid may channel through this pathway. Hence the molecules following this pathway do not spend as much time in the reactor as those flowing through the regions of high resistance to flow. We see that there is a distribution of times that molecules spend in the reactor in contact with the catalyst.

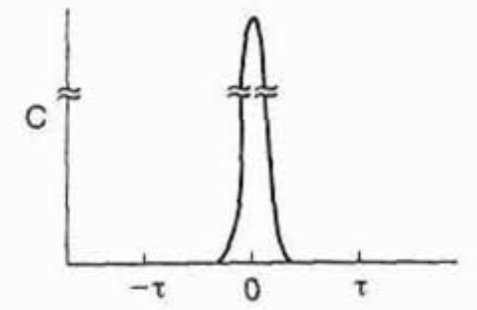
- In many continuous-stirred tank reactors, the inlet and outlet pipes are close together. In one operation it was desired to scale up pilot plant results to a much larger system. It was realized that some short circuiting occurred, so the tanks were modelled as perfectly mixed CSTRs with a bypass stream. In addition to short circuiting, stagnant regions (dead zones) are often encountered. In these regions there is little or no exchange of material with the well-mixed regions and consequently, virtually no reaction occurs in this region.

6.2 RTD EXPERIMENTS

RTD curves can be plotted by doing the tracer experiments. Tracer is an inert substance which is added to the reaction mixture and its concentration is noted in the exit stream with respect to time. A tracer must be non-reactive, should not stick to the reactor walls, should easily mix with the reaction mixture and should be easily detectable. Note that tracer stream are also called stimulus response techniques. Based on methods of addition of tracer we have to types of tracer experiments. The tracer can be injected in the form of a pulse or in the form of a step input.

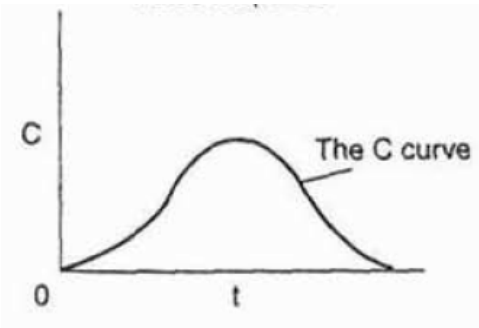
6.3 PULSE RTD EXPERIMENT

In this experiment a fixed amount (moles) of tracer is injected all at once in a very small amount of time. So the input profile is given as



Suddenly the concentration of tracer increases to some value in the reactor and then decreases and after infinite or very long time when the entire tracer comes out of the reactor the concentration of tracer becomes zero inside the reactor.

The curve plotted between concentrations of tracer at the exit of the reactor vs time is known as the **C -CURVE.** A general C-curve for pulse experiment is given by



- The area of C-curve is constant. We know that $\int_0^{N_o} dN = \int_0^{\infty} v_o C(t)dt$ where v_o is the volumetric flow rate of the stream. Hence area of C-curve is $\frac{N_o}{v_o}$

Another important curve for the pulse experiment is the **E-curve. E-curve** is also called **Exit-age distribution** curve or **RTD** curve.

$$\frac{dN}{N_o} = \frac{v_o C(t)dt}{N_o} = \frac{C(t)dt}{N_o / v_o}$$

$$\frac{dN}{N_o} = \frac{C(t)dt}{\int_0^{\infty} C(t)dt} = \frac{C-curve}{Area\ of\ C-curve}$$

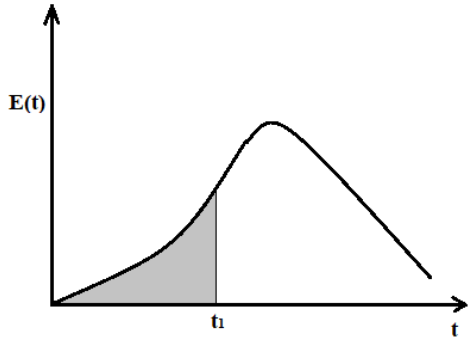
$$E(t)dt = \frac{dN}{N_o} = \frac{C(t)dt}{\int_0^{\infty} C(t)dt} = \frac{C-curve}{Area\ of\ C-curve}$$

$$E-curve = \frac{C-curve}{Area\ of\ C-curve}$$

- It shows that E-curve is proportional to C-curve and hence the shapes of E and C curves are similar.
- E-curve can be obtained from C-curve by dividing the C-curve by its own area.

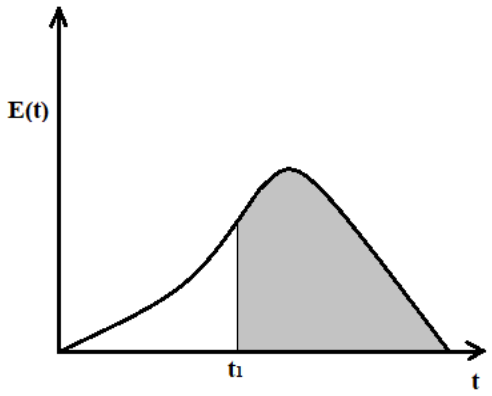
- Since E-curve = $\frac{dN}{N_o}$, it means that a point on the E-curve denotes the fraction of tracer. Hence E(t)dt denotes the fraction of tracer which spends time between t and t+dt inside the reactor.
- The units of E(t) is time^{-1}
- We can conclude that a point on the E-curve denotes the fraction of tracer that spends exactly time t inside the reactor.
- If E-curve is integrated from 0 to t_1, then it shows the fraction of tracer which spends time less than t_1 inside the reactor. This fraction of tracer can also be called as the fraction of tracer younger than t_1

Fraction of tracer younger than t_1 $= \int_0^{t_1} E(t)dt$. This fraction is shown in the shaded area



Fraction of tracer older than t_1 or the fraction of tracer that spends time more than t_1 inside the reactor is given by

$= \int_{t_1}^{\infty} E(t)dt$



- We know that in infinite time all the tracer should come out. Hence the integral of E-curve from zero to infinity should be one. Therefore the area of E-curve is equal to one .
- Since different molecules are spending different times inside the reactor, the average residence time of all the molecules is given by

$$\bar{t} = \frac{\int_0^{\infty} tE(t)dt}{\int_0^{\infty} E(t)dt} \text{ or } \int_0^{\infty} tE(t)dt.$$

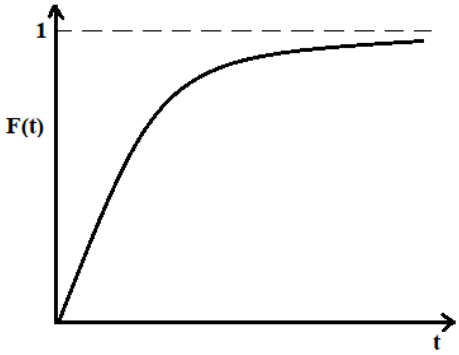
- A vertical line through $\bar{t}$ should divide the area of E-curve into two equal curves.

Another distribution curve is **Cumulative exit age distribution curve** or **F-curve.** The F-curve and the E-curve are as related as $F(t) = \int_0^t E(t)dt$.

It means a point on F-curve gives the same information which is given by the area under the E-curve. Hence a point on the F-curve denotes the fraction of tracer that has spent time less than t inside the reactor. We can write the following relations

$$F(t) = \int_0^t E(t)dt \;\&\; 1 - F(t) = \int_t^{\infty} E(t)dt$$

F-curve has the following nature



6.3.1 MOMENTS OF RTD

Nth Moment of RTD about origin is defined as

$\mu_n = \int_0^\infty t^n E(t)dt$ and nth moment of RTD about its mean is defined as $M_n = \int_0^\infty (t-\bar{t})^n E(t)dt$. Based on this definition, we can define the following:

- moment of RTD about origin $\mu_0 = \int_0^\infty t^0 E(t)dt = \int_0^\infty E(t)dt$ which is equal to area of the E-curve.
- First moment of RTD about origin $\mu_1 = \int_0^\infty tE(t)dt = \bar{t}$ which is equal to the mean residence time.
- The second moment of RTD about its mean is equal to the variance of the RTD and is denoted by σ^2.

  $M_2 = \sigma^2 = \int_0^\infty (t-\bar{t})^2 E(t)dt$

- $\sigma^2 = \int_0^\infty t^2 E(t)dt + \int_0^\infty \bar{t}^2 E(t)dt - \int_0^\infty 2t\bar{t}E(t)dt$

  $\sigma^2 = \mu_2 - \bar{t}^2$

6.3.2 PULSE RTD FOR IDEAL CSTR

The RTD for pulse experiment in an ideal CSTR can be obtained by writing the material balance on the tracer. Since the tracer is injected all at once, the "in" term in the balance becomes zero. However, with time the concentration of tracer changes (decreases) inside the reactor. Therefore, accumulation term should be there. The equation becomes

$in - out = accumulation$

$0 - vC(t) = V\frac{dC(t)}{dt}$

The above differential equation can be solved with condition that at t = 0, C(t)=C$_o$=N$_o$/V, which yields $C(t) = \frac{C_o}{\tau}e^{\frac{-t}{\tau}}$

This is the C-curve of ideal CSTR. The C-curve when divided by its area gives the E-curve $E(t) = \frac{1}{\tau}e^{\frac{-t}{\tau}}$. It shows that the C-curve and the E-curve are exponentially decreasing functions of time for an ideal CSTR.

6.3.3 PULSE RTD FOR IDEAL PFR

In an ideal PFR, there is no axial mixing. The type of input tracer signal that enters the reactor remains as it is at the exit of the reactor. The PFR act as a lag and the output signal is delayed by time which is equal to the space time of the PFR. The pulse input function is also sometimes represented in the form of dirac delta function. Hence output is also a dirac delta function delayed by τ_P.

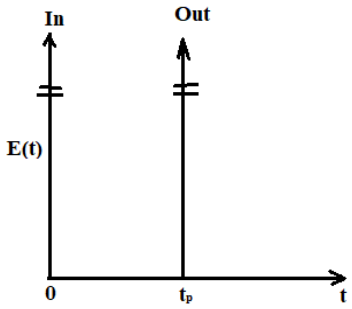
$E(t) = \delta(t-\tau_P)$. The dirac delta function follows these properties

$$\delta(x) = \begin{cases} 0 & \text{when } x \neq 0 \\ \infty & \text{when } x = 0 \end{cases}$$

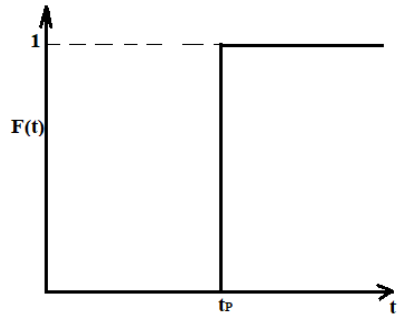
$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1$$

$$\int_{-\infty}^{\infty} g(x)\delta(x-\tau)\, dx = g(\tau)$$

The E-curve for an ideal PFR is shown below



The F-curve for an ideal PFR is also shown below

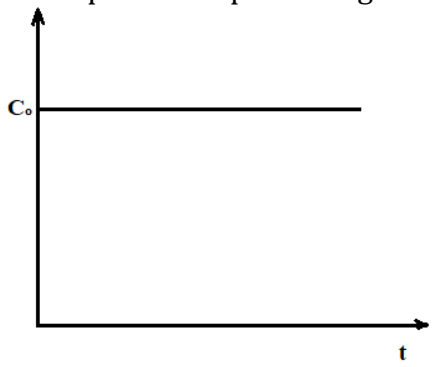


6.4 STEP TRACER EXPERIMENT

In step tracer experiment, tracer is injected continuously at a concentration C_o. The concentration of tracer in the exit stream increases and after some time it becomes equal to the concentration of tracer in the inlet stream after which the experiment can be stopped.

The C-curve of step experiment will be denoted by $C_{step}(t)$. In pulse experiment we divide the C-curve by its area to get E-curve. In step experiment we divide C_{step} curve by C_o and we get the F-curve.

The input tracer profile is given by

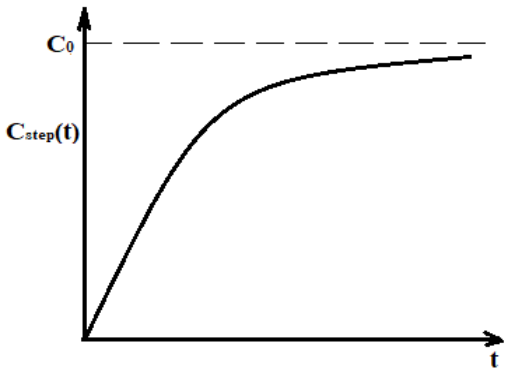


The C_{step} curve for a CSTR can be obtained by writing the material balance on the tracer.

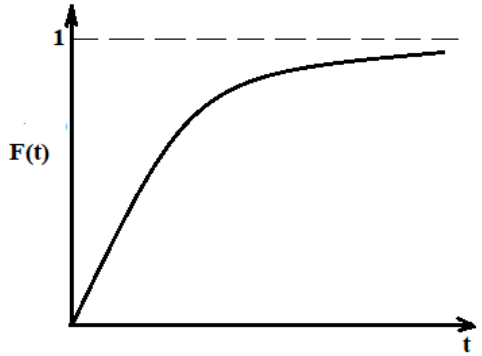
$$vC_o - vC_{step}(t) = V\frac{dC_{step}(t)}{dt}$$

By applying condition that at t=0 , C_{step}=0, we arrive to the following equation

$$C_{step}(t) = C_o(1 - e^{\frac{-t}{\tau_M}})$$



The above curve when divided by C_o generates the F-curve which is same as the curve we obtained for the pulse input.



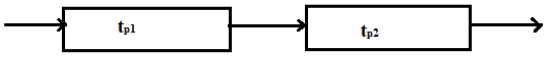
- In an ideal PFR the step signal will be delayed by a time equal to the space time of the PFR. Hence C_{step} curve for a PFR will be a delayed step signal.
- In step experiment, the mean residence time is given by

$$\bar{t} = \frac{\int_0^\infty t dC_{step}}{\int_0^\infty dC_{step}}$$

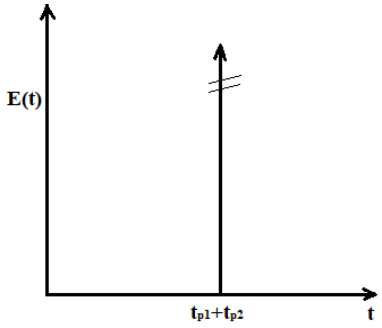
- It is interesting to note that the area with respect to y-axis is $C_o\tau$ and if the area w.r.t y-axis is divided by C_o we get τ which is also equal to mean residence time of the reactor.

6.5 RTD OF REACTORS IN SERIES

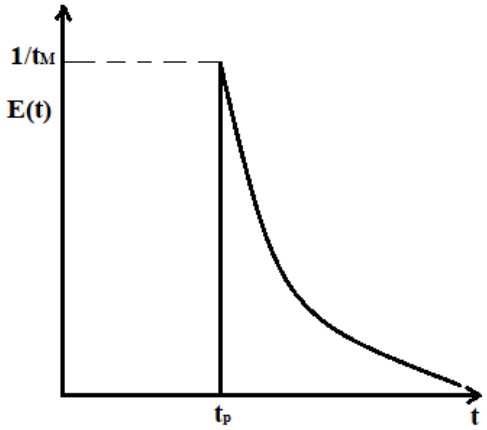
When two ideal PFRs are connected in series, it will act as a single PFR of volume given by adding the individual volumes. Hence the space time of the combination is given by adding the space time of individual reactors.



Please note while plotting the RTD curves for pulse input.



When a PFR is followed by a CSTR, then for a pulse input the RTD curve is given by



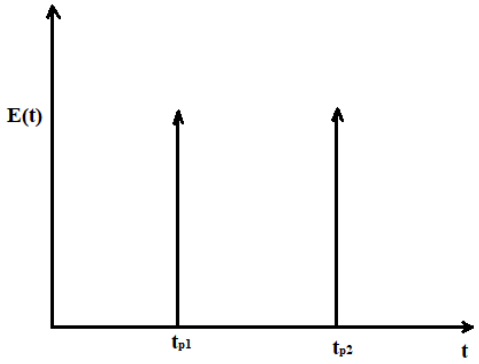
The equation of exponentially decreasing part is given by $\frac{1}{\tau_M} e^{\frac{-(t-\tau_p)}{\tau_M}}$.

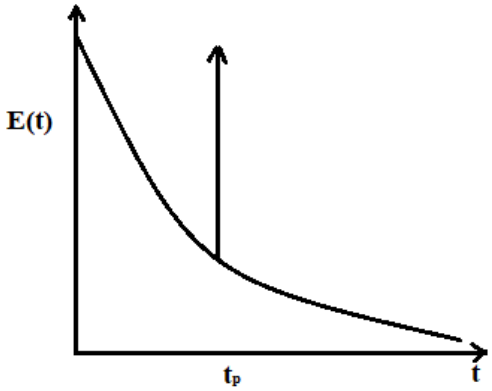
Similar RTD is obtained when CSTR is followed by a PFR.

When MFRs are connected in series, the system behaviour becomes closer to PFR and its RTD also approaches towards PFR.

6.6 RTD OF REACTORS CONNECTED IN PARALLEL

When reactors are connected in parallel, the RTD is obtained by superimposing the RTD of each branch. When two ideal PFRs of different space times are connected in parallel, there will be two pulses in the output as shown. Similarly if a PFR and a CSTR are connected, the RTD will be obtained by superimposing the individual RTDs. Note that the RTD drawn is only for a pulse experiment.





6.7 NON-IDEAL REACTOR MODELS

The tank in series model and dispersion model are the single parameter models. The tank in series model considers a non-ideal reactors as a combination of N tanks (CSTR) in series. The value of N is to be determined. The variance of RTD of ideal PFR is zero while for ideal CSTR is τ^2.

The Dispersion models explains the non-ideality in a tubular reactors. There is no axial dispersion in ideal PFR. Hence dispersion number is zero. While there is infinite mixing in CSTR and hence the dispersion number is infinity. The peclet number can be defined as inverse of dispersion number.

GATE QUESTIONS

1. The mean conversion in the exit stream, for a second order, liquid phase reaction in a non-ideal flow reactor is given by

(a) $\int_0^\infty \frac{k_2 C_{A0} t}{1+k_2 C_{A0} t} E(t)dt$

(b) $\int_0^\infty \frac{1}{1+k_2 C_{A0} t} E(t)dt$

(c) $\int_0^\infty \frac{1}{1+k_2 C_{A0} t}\left[1-E(t)\right]dt$

(d) $\int_0^\infty \frac{\exp(-k_2 C_{A0} t)}{1+k_2 C_{A0} t} E(t)dt$

(GATE 2001)

2.The E-curve for a non-ideal reactor defines the fraction of fluid having age between t and t +dt

(a) at the inlet

(b) at outlet

(c) in the reactor

(d) averaged over the inlet and outlet

(GATE 2001)

3.A pulse tracer is introduced in an ideal CSTR (with a mean residence time τ) at time t=0. The time taken for the exit concentration of the tracer to reach half of its initial value will be

(a) 2τ (b) 0.5τ

(c) τ /0.693 (d) 0.69τ

(GATE 2002)

4.For an ideal plug flow reactor the value of the peclet number is

(a) Zero (b) infinity

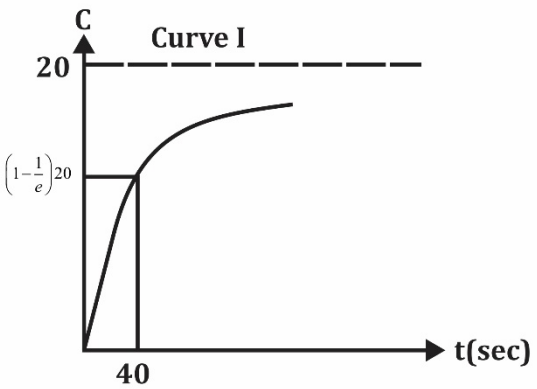
(c) 1 (d) 10

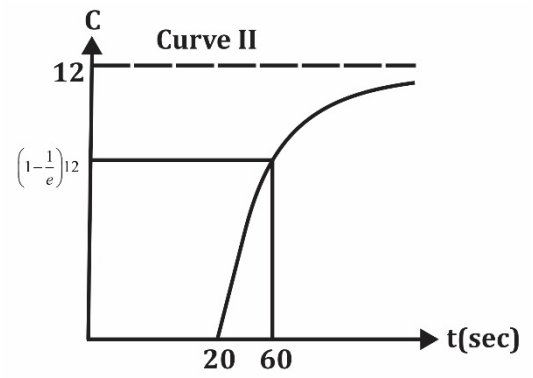
(GATE 2002)

5. A step input tracer test is used to explore the flow pattern of fluid through a vessel of total volume equal to 1 m^3 /min.

Identify for each curve in Group I a suitable flow model from the list given under Group II.

Group 1	**Group 2**
P. Curve 1 **Q.** Curve 2	**1.** PFR and CSTR in series **2.** CSTR with dead space **3.** PFR in series with a CSTR and dead space **4.** CSTR





(a) P-4, Q-3 (b) P-4, Q-1

(c) P-2, Q-3 (d) P-2, Q-1

(GATE 2003)

6.For a packed bed reactor, the presence of a long tail in the residence time distribution curve is an indication of

(a) ideal plug flow (b) bypass

(c) dead zone (d) channelling

(GATE 2004)

7. Match the items in Group I with those in Group II.

GROUP I	GROUP II
(P) porous catalyst	1.Selectivity
(Q)parallel reaction	2.Shrinking core model
(R)Non-ideal tubular reactor	3.Thiele modulus
(S)Gas solid non-catalytic reaction	4.Dispersion number

(a) P-3, Q-1, R-4, S-2

(b) P-1, Q-3, R-2, S-2

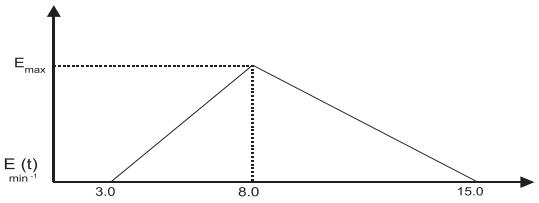
(c) P-1, Q-4, R-2, S-3

(d) P-3, Q-4, R-1, S-2

(GATE 2005)

COMMON DATA QUESTION

The residence time distribution E(t) (as shown below) of a reactor is zero until 3 min and then increases linearly to a maximum value E_{max} 8min after which it decreases linearly back to zero-at 15 min.



8. What is the value of E_{max} ?

(a) 1/6 (b) 1/8

(c) ¼ (d) 1/3

(GATE 2005)

9. What is the value of the mean residence time in min?

(a) 5.7 (b) 8

(c) 8.7 (d) 12

(GATE 2005)

10. The exit age distribution in a stirred reactor is given by $E(t)=\frac{1}{\tau}e^{-t/\tau}$. Fluid elements e_1 and e_2 enter the reactor at times t=0 and t=θ>0, respectively. The probability that e_2 exits the reactor before e_1 is

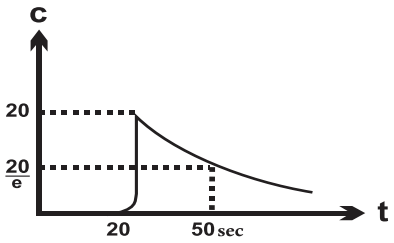
(a) $\frac{1}{2}$ (b) $\frac{1}{2}e^{-\theta/\tau}$

(c) $e^{-\theta/\tau}$ (d) zero

(GATE 2006)

11. A pulse of concentrated KCI solution is introduced as tracer into the fluid entering a reaction vessel having volume equal to 1 m^3 and flow rate equal to

$1\ m^3/min$. The concentration of tracer measured in the fluid leaving the vessel is shown in the figure given below. The flow model parameters that fit the measured RTD in terms of one or all of the following mixing elements, namely, volume of p lug flow reactor $V_{p,}$ mixed flow volume V_m and dead space $V_{d,}$ are



(a) $V_p = 1/6m^3, V_m = 1/2m^3, V_d = 1/3m^3$

(b) $V_p = V_m = V_d = 1/3m^3$

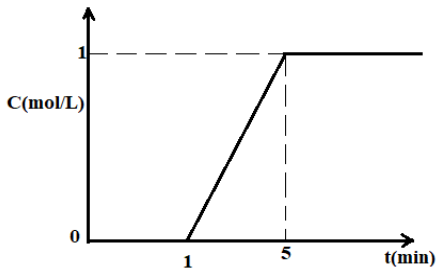
(c) $V_p = 1/3m^3, V_m = 1/2m^3, V_d = 1/6m^3$

(d) $V_m = 5/6m^3, V_d = 1/6m^3$

(GATE 2007)

COMMON DATA QUESTION

A liquid is flowing through a reactor at a constant flow rate. A step input of tracer at a molar flow rate of 1 mol/min is given to the reactor at time t=0. The time variation of the concentration (C), of the tracer at the exit of the reactor is as shown in the figure.



12. The volumetric flow rate of the liquid through the reactor (in L/min) is

(a) 1 (b) 2

(c) 1.5 (d) 4

(GATE 2008)

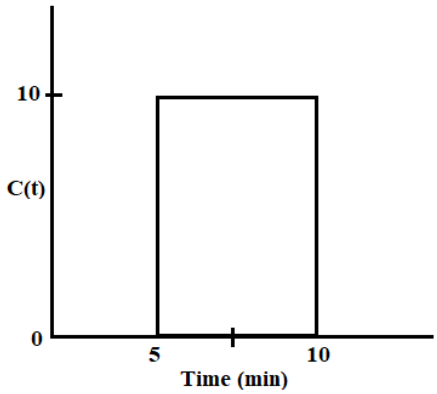
13. The mean residence time of the fluid in the reactor (in min) is

(a) 1 (b) 2

(c) 3 (d) 4

(GATE 2008)

14. An **isothermal** pulse test is conducted on a reactor and the variation of the outlet tracer concentration with time is shown below.



The mean residence time of the fluid in the reactor (in min) is

(a) 5.0 (b) 7.5

(c) 10.0 (d) 15.0

(GATE 2009)

15. Two reactors (reactor 1 and reactor 2) with average residence times τ_1 and τ_2, respectively are placed in series. Reactor 1 has zero dispersion and reactor 2 has infinite dispersion. The residence time distribution E(t)

(a) $\left\{\frac{1}{\tau_1}\exp\left(-\frac{t-\tau_1}{\tau_2}\right)\right.^{0}_{for t\le\tau_1}$

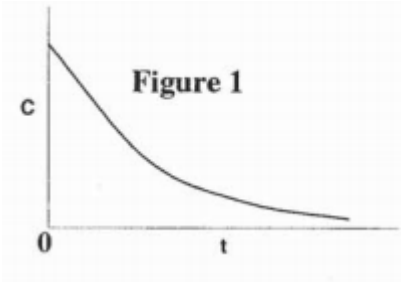
(b) $\begin{cases} \frac{1}{\tau_1}\exp\left(-\frac{t-\tau_2}{\tau_1}\right) & for t \le \tau_2 \\ 0 & for t > \tau_2 \end{cases}$

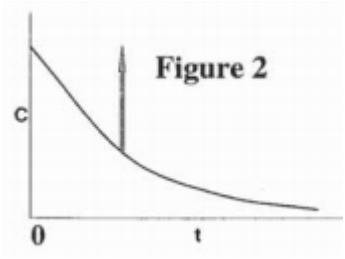
(c) $\begin{cases} \frac{1}{\tau_1}\exp\left(-\frac{t-\tau_1}{\tau_2}\right) & for t \le \tau_2 \\ 0 & for t > \tau_2 \end{cases}$

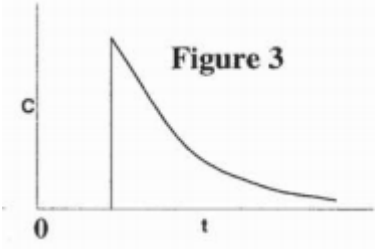
(d) $\begin{cases} \frac{1}{\tau_2}\exp\left(-\frac{t}{\tau_1}\right) & for t \le \tau_1 \\ 0 & for t > \tau_2 \end{cases}$

(GATE 2010)

16. The following figure show the outlet tracer concentration profiles (C vs time) for a pulse input.







Match the figures in Group 1 with the reaction configuration in Group 2.

Group 1	Group 2
P. Figure 1	**1.** PFR
Q. Figure 2	**2.** CSTR
R. Figure 3	**3.**PFR and CSTR in series
	4. PFR and CSTR in parallel

(a)P-2 Q-4 , R- 3 (b)P-4,Q-3, R-1

(c)P-3,Q-4, R-2 (d)P-1, Q-3, R-2

(GATE 2011)

17. The exit age distribution for reactor is given by E(t)= ∂ (t-4), where t is in seconds. A first order liquid phase reaction ($k = 0.25s^{-1}$) is carried out in this reactor under steady state and isothermal conditions. The mean conversion of the reactant at the exit of the reactor, up to 2 digits after the decimal point, is

(a) 0.50 (b)0.60

(c) 0.59 (d) 0.63

(GATE 2013)

18. Match the following :

GROUP 1	GROUP 2
(P) Tank in series	(I)Non-isothermal reactors
(Q)Liquid-Liquid extraction	(II) mixer-Settler
(R)Optimum temperature progression	(III)PFR with axial mixing
(S) Thiele modulus	(IV)Solid catalysed reaction

(a)P-2,Q-4,R-1,S-3 (b) P-1,Q-2,R-3,S-4

(c)P-3,Q-1,R-2,S-4 (d) P-3,Q-2,R-1,S-4

(GATE 2014)

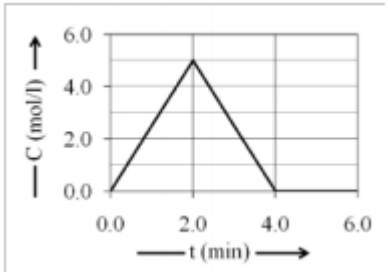
19.The vessel dispersion number for an ideal CSTR is

(a) -1 (b) 0

(c) 1 (d) ∞

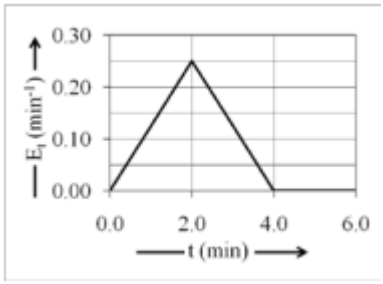
(GATE 2014)

20. The impulse response to a tracer pulse experiment for a flow reactor is given below

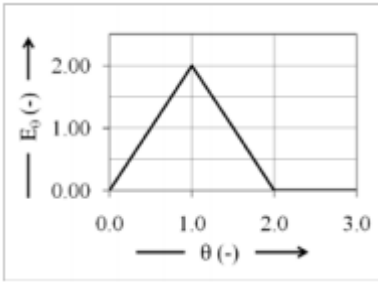


In the above figure, C is the exit tracer concentration. The corresponding E or E_θ (normalized E) curve is correctly represented by which of the following choices? Here, θ is dimensionless time.

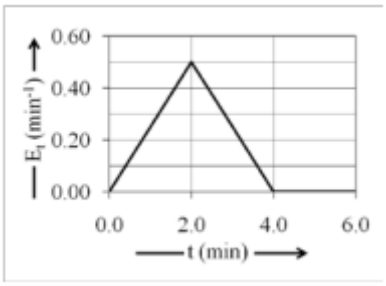
(a)



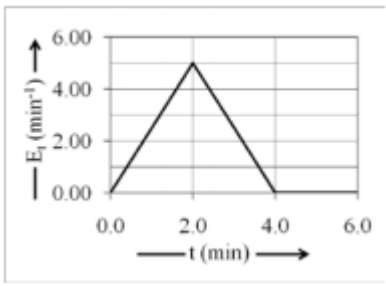
(b)



(c)

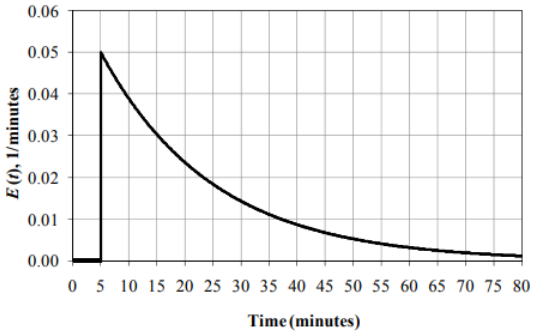


(d)



(GATE 2015)

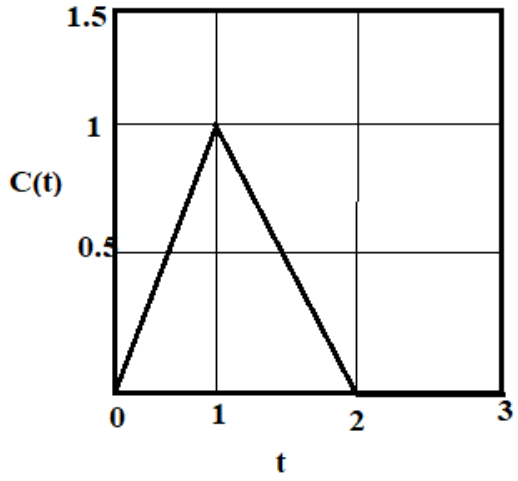
21. A CSTR has a long inlet pipe. A tracer is injected at the entrance of the pipe. The E-curve obtained at the exit of the CSTR is shown in the figure below.



Assuming plug flow in the inlet pipe, the ratio (rounded off to the second decimal place) of the volume of the pipe to that of the CSTR is_____

(GATE 2016)

22. The curve measured during a pulse tracer experiment is shown below. In the figure c(t) is concentration of the measure at the reactor exit in mol/litre at time t seconds. Calculate t_m.



(GATE 2017)

ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(A)	(B)	(D)	(B)	(C)	(C)	(A)	(A)	(C)	(B)
11	12	13	14	15	16	17	18	19	20
(B)	(A)	(C)	(B)	(A)	(A)	(D)	(D)	(D)	(C)
21	22								
(0.25)	(1)								

EXPLANATIONS

1.Answer:(a)

$A \xrightarrow{k_2} B$

For second order reaction in batch reactor,

$$-\frac{dC_A}{dt} = k_2 C_A^2$$

$$\int_{C_{A_o}}^{C_A} -\frac{dC_A}{C_A^2} = \int_0^t k_2 dt$$

$$\frac{1}{C_A} - \frac{1}{C_{A_o}} = k_2 t$$

$$\frac{1}{C_A} = \frac{1}{C_{A_o}} + k_2 t$$

$$C_A = \frac{C_{A_o}}{1 + k_2 C_{A_o} t}$$

Now, for non-ideal reactor,

$$\frac{\overline{C_A}}{C_A} = \int_0^\infty \left(\frac{C_A}{C_{A_o}}\right)_{batch} E(t)dt$$

$$1 - \overline{X_A} = \int_0^\infty \left(\frac{1}{1 + k_2 C_{A_o} t}\right) E(t)dt$$

$$\overline{X_A} = 1 - \int_0^\infty \left(\frac{1}{1 + k_2 C_{A_o} t}\right) E(t)dt$$

$$\overline{X_A} = \int_0^\infty E(t)dt - \int_0^\infty \left(\frac{1}{1 + k_2 C_{A_o} t}\right) E(t)dt$$

$$\overline{X_A} = \int_0^\infty \left[1 - \left(\frac{1}{1 + k_2 C_{A_o} t}\right)\right] E(t)dt$$

$$\overline{X_A} = \int_0^\infty \left(\frac{k_2 C_{A_o} t}{1 + k_2 C_{A_o} t}\right) E(t)dt$$

2.Answer:(b)

E-curve or exit age distribution is distribution of time for the stream of fluid leaving the vessel.

Thus E-curve defines the fraction of fluid having age between t and t+dt at the outlet of the reactor.

3.Answer:(d)

At time t=0 tracer is injected. During the tracer coming out of the reactor tracer balance

Tracer in-tracer out = Accumulation

$$-vc = \frac{d(VC)}{dt}$$

$$\frac{-v}{V} C = \frac{dc}{dt}$$

$$-C/\tau = \frac{dc}{dt}$$

$$\int_{c_o}^{c} \frac{-dc}{c} = \int_0^t dt/\tau$$

$$-In\left(C/C_o\right) = \frac{t}{\tau}$$

$$C = C_o e^{-t/\tau}$$

When $C = C_o/2$

$$C_o/2 = C_o e^{-t/\tau}$$

$$e^{-t/\tau} = \frac{1}{2}$$

$$\frac{t}{\tau} = \ln(2)$$

$$t = 0.693\tau$$

4.Answer:(b)

For ideal PFR, peclet number = infinity . Peclet number is ul/D and is dispersion coefficient. D is zero for PFR.

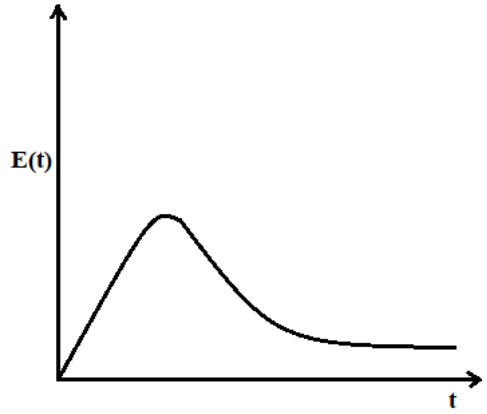
5.Answer:(d)

Curve 1- CSTR with dead space

Curve 2- PFR and CSTR in series

6.Answer:(c)

For packed bed reactor, RTD curve is shown below.



Here , long tail represents the dead zone. If we have in the reactor, in the pulse experiment particles will go to the dead zone and slowly come out of the reactor.

7.Answer:(a)

Porous catalyst-Thiele modulus

Parallel reactions-Selectivity

Non-ideal tubular reactor-Dispersion

Gas-solid non-catalytic reaction-Shrinking core model

8.Answer:- (a)

We know that,

$$\int_0^\infty E(t)dt = 1$$

Area of shaded portion =1

$$\frac{1}{2}(8-3)E_{\max} + \frac{1}{2}(15-8)E_{\max} = 1$$

Or $E_{\max} = \frac{1}{6}$

9.Answer:(c)

$$\frac{1}{2}\times(12)(x) = 1 \Rightarrow x = \frac{2}{12} \Rightarrow \therefore E_{\max} = \frac{1}{6}$$

$$t = ? \Rightarrow t = \int_0^\infty Etdt$$

$$E_1 = \frac{1/6}{5}t + K$$

$$0 = \frac{1/6}{5}\times 3 + K \Rightarrow K = -0.1$$

$$\Rightarrow E_1 = 0.033t - 0.1$$

$$\left(8, \frac{1}{6}\right), (15, 0) \Rightarrow E_2 = \frac{1/6}{-7}t + K_1$$

$$0 = -\frac{1}{42}\times 15 + K_1 \Rightarrow 0.36$$

$$E_2 = -0.024t + 0.36$$

$$\therefore \bar{t} = \int_3^\infty (0.033t^2 - 0.1t)dt + \int_8^{15} (-0.024t^2 + 0.36t)dt$$

$$= 5.335 - 2.75 + 22.904 + 28.98 = 8.67$$

10.Answer:(b)

Given $E(t) = \frac{1}{\tau}e^{\frac{-t}{\tau}}$

e_1 enters at t=0

e_2 enters at t= $\theta > 0$

Probability of e_1 & e_2 stays together in the reactor=probability to e_1 exiting between θ and $\infty = \int_0^\infty \frac{1}{\tau} e^{-t/\tau} dt$

$= e^{-\theta/\tau} dt$

When e_1 & e_2 stays inside the reactor e_2 exiting before e_1 is $= \frac{1}{2}[e^{-\theta/\tau} dt]$

½ because when e_1 & e_2 stays together e_1 can exit before e_2 or e_2 can exit before e_1

11.Answer:(c)

Given,

$V = 1m^3$

$V_0 = 1m^3 / \min = \frac{1}{60} m^3 / s$

For PFR, $\tau_\rho = 20s$ (see the figure)

$\therefore \frac{V_P}{V} = \tau_\rho$

$\therefore V_P = \frac{1}{60} \times 20 = \frac{1}{3} m^3$

$\therefore \frac{V_P + V_m}{V} = \frac{50}{60} \sec$

$V_m = \frac{1}{2} \mathrm{m}^3$

$\therefore V_d = V - V_m - V_P$

$V_d = 1 - \frac{1}{2} - \frac{1}{3}$

$V_d = \frac{6-3-2}{6} = \frac{1}{6}$

12.Answer: (a)

We have,

$C_{\max} = \frac{m}{V}$

Given, $C_{\max} = 1mol / L$

$m = 1mol / \min$

$V = ?$

Thus, $1 = \frac{1}{V}$

$V = 1\, L / \min$

13.Answer:(c)

$\bar{t} \frac{1}{C_{\max}} \int_0^{C_{\max}} tdc$

$= \frac{1}{1} \int_0^1 tdc$

$= \int_0^1 tdc$

When C is varying from 0 to 1, the varies from 1 to 5.

$\frac{C-0}{t-1} = \frac{1-0}{5-1}$

t=4c+1

$\bar{t} = \int_0^1 (4c+1) dc = 3 \min$

14.Answer:(b)

Area of the curve = $5 \times 10 = 50$

$$\bar{t} = \int_0^{\infty} t\ E(t)\ dt$$

$$\bar{t} = \int_5^{10} t\ E(t)\, dt \qquad \begin{matrix} 0 < t < 5,\ E = 0 \\ t > 10,\ E = 0 \end{matrix}$$

$$5 < t < 10, E = \frac{10}{50}$$

$$\bar{t} = \int_5^{10} \frac{10}{50} t dt$$

$$\bar{t} = \frac{10}{50}\left[\frac{t^2}{2}\right]_5^{10}$$

$$\bar{t} = 7.5 \min$$

15.Answer:(a)

Reactor 1 is PFR and reactor 2 is MFR.

$$E(t) = 0 \text{ for } t \le \tau_1$$

And

$$E(t) = \frac{1}{\tau_2} \exp\left[-\left(\frac{t-\tau_1}{\tau_2}\right)\right], \text{ for } t > \tau_1$$

16.Answer:(a)

Figure 1-CSTR

Figure 2-PFR and CSTR in parallel

Figure 3-PFR and CSTR in series

17.Answer:(d)

We have

$$\frac{C_A}{C_{A0}} = \int_0^{\infty} e^{-kt} E(t) dt$$

$$1 - x_A = \int_0^{\infty} e^{-kt} \delta(t-4) dt$$

$$1 - x_A = e^{-4k}$$

$$1 - x_A = e^{-4\times 0.25}$$

$$1 - x_A = \frac{1}{e}$$

$$x_A = 1 - \frac{1}{e} = 0.6$$

18.Answer:(d)

Tank in series model $\rightarrow PFR$ with axial mixing

Liquid-liquid extraction $\rightarrow$ Mixer settler

Optimum temperature progression $\rightarrow$ Non-isothermal reaction

Thiele modulus $\rightarrow$ solid catalyst reaction

19.Answer: (d)

$$\text{Dispersion number} = \frac{D}{UL}$$

For an ideal CSTR,

$$\frac{D}{UL} \rightarrow \infty$$

20.Answer:(c)

Area under the 'C' curve

$$= \frac{1}{2} \times base \times height$$

$$= \frac{1}{2} \times 4 \times 5 = 10$$

E curve is generated by dividing the Y Coordinate of C Curve with area. Max Y in C curve in 5 which will become 0.5 in E curve. Area under the E curve should be one.

21.Answer: 0.25

Solution:- It's obvious there is delay so it can be assumed to be PFR & CSTR in series so the delay equal to τ_p (space time PFR)

So here delay 5 min(τ_p =5min)

We know that for CSTR E(t)= $\frac{e^{-t/\tau_m}}{\tau_m}$

$$t = 0, E(t) = \frac{1}{\tau_m}$$

$$E(t-\tau_p) = \frac{1}{\tau_m}$$

$$\frac{1}{\tau_m = 0.05}\tau_m = 20\,\text{min}$$

$$So, \frac{\tau_p}{\tau_m} = \frac{5}{20} = 0.25$$

22. Answer: (1)

$$t_m = X_0 + \frac{2}{3}a + \frac{1}{3}b$$

$$\text{t}t_m = 0 + \frac{2}{3}\times 1 + \frac{1}{3}\times 1$$

$$t_m = 1\text{sec}$$

7 HETEROGENEOUS SYSTEM

The reaction system where more than one phase exists is called *Heterogeneous System.* In heterogeneous reaction systems, the rate of reaction is usually expressed in measures other than volume, such as reaction surface area or weight of catalyst. There are two types of heterogeneous reactions:

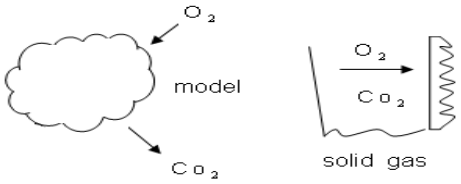
Non- Catalytic Reaction

Catalytic Reaction

7.1 NON -CATALYTIC REACTION SYSTEM

Due to more than one phase reaction is called heterogeneous reaction. The rate of reaction therefore depends upon the M.T and chemical reaction kinetics.

ex. $C + O_2 \rightarrow CO_2$



Over all reaction rate

(1) Series: $r_{overall}$ $r_1 = r_2 = r_3$

(2) Parallel: $r_{overall} = r_1 + r_2 + ... + r_n$

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt}; \frac{mol}{m^3 - s}$$

$$-r_A^{'} = \frac{1}{w}\frac{dN_A}{dt}; \frac{mol}{kg - s}$$

$$-r_A^{''} = \frac{1}{S}\frac{dN_A}{dt}; \frac{mol}{m^2 - s}$$

7.1.1 RATE EQUATION

A heterogeneous reaction takes place in a number of steps

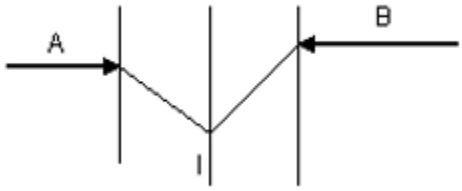
A + B → product

The overall rate expression consist mass transfer terms in addition with kinetic terms.

- If a heterogeneous reaction consists of parallel steps, then overall rate equation is equal to sum of the individual rates.

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

- For Series steps



$$\boxed{r_{overall} = r_1 = r_2 = ... = r_n}$$

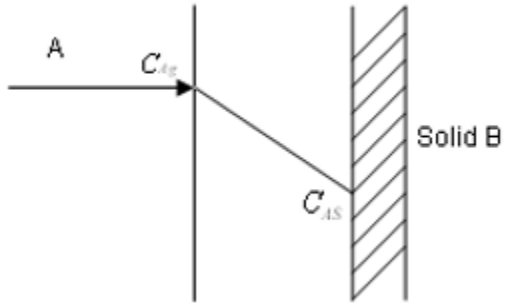
- When mass transfer takes please the rate is defined in terms of molar flux $\left(\frac{moles}{surface\ area - time}\right)$. Hence rare of reaction is based on unit

surface area $\boxed{-r_A^{"} = -\frac{1}{S}\frac{dN_A}{dt}}$ we express overall rate in term of overall concentration difference.

Heterogeneous rate depends upon:

1. Surface kinetics
2. Pore diffusion resistance
3. Film diffusion resistance

7.1.2 THE CONCEPT OF RARE CONTROLLING TO DEVELOP OVERALL RATE EXPRESSION



$A(g) + B(s) \longrightarrow R(g)$

Rate of disappearance of A can be expressed in two ways.

(1) Rate of transport of A to surface B,

(2) Rate of reaction

$$-r_{A1}^{"} = \frac{-1}{S}\frac{dN_A}{dt} = k_g\left(C_{Ag} - C_{As}\right)$$

$$-r_{A2}^{"} = \frac{-1}{S}\frac{dN_A}{dt} = k^{"}C_{As} \quad --(1)$$

$\because$ *These step are in series*

$$\therefore -r_A^{"} = -r_{A1}^{"} = -r_{A2}^{"}$$

$$k_g\left(C_{Ag} - C_{As}\right) = k^{"}C_{As}$$

$$C_{As} = \frac{k_g}{k^{"} + k_g}C_{Ag}$$

put this in equation(1)

$$\boxed{-r_A^{"} = -r_{A2}^{"} = \frac{k^{"}.k_g}{k^{"} + k_g}C_{Ag}}$$

$$\boxed{-r_A^{"} = \frac{1}{\left(\frac{1}{k_g} + \frac{1}{k^{"}}\right)}C_{Ag}}$$

if $k_g >> k"$

$$-r_A^{"} = k"C_{Ag}$$

$\rightarrow$ *chemical reaction is the rate controlling step*

$\rightarrow$ *slowest step*

if $k" >> k_g$

$$-r_A^{"} = k_g.C_{Ag}$$

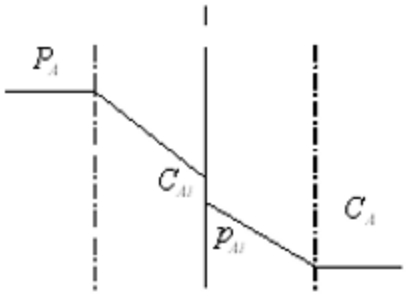
$\rightarrow$ *mass taransfer is the rate controlling step* $\rightarrow$ *slowest step*

Note: $\boxed{f_e = \frac{V_l}{V_r}}$ = *liquid hold up*

$$\boxed{a = \frac{S}{V_r}} = \frac{\text{interfaeial area}}{\text{Reactor volume}}$$

- There are several theories of mass transfer between two fluid phases but we will used two film theory.
  - Resistance on both hypothesized film on each side of interface.
  - Equilibrium is assumed at interface.

Concentration gradient is linear.



7.1.3 RATE EQUATION FOR PHYSICAL ABSORPTION OF A

$P_{Ai} = H_A C_{Ai}$ – *Henry's law* (*dilute Solution*)

(1) *gas film*

$-r_A'' = k_{Ag}\left(P_A - P_{Ai}\right)$ – *unit surface area*

$-r_A' = k_{Ag} a\ \left(P_A - P_{Ai}\right)$ – *unit volume*

Or

$$\frac{-r_A'}{k_{Ag}} = \left(P_A - P_{Ai}\right) \text{\_\_\_\_(1)}$$

(2) *liquid film*

$-r_A'' = k_{Al}\left(C_{Ai} - C_A\right)$ – *unit surface area*

$-r_A' = k_{Al} a\ \left(C_{Ai} - C_A\right)$ – *unit volume*

$$-r_A'' = k_{Al}.a\left(C_{Ai} - C_A\right)$$

$$\frac{-r_A'}{k_{Al}.a} = \left(C_{Ai} - C_A\right)$$

$$= \frac{P_{Ai}}{H_A} - C_A$$

$$\frac{H_A}{K_{Al}.a}\left(-r_A'\right) = \left(P_{Ai} - H_A C_A\right) \text{\_\_\_\_\_(2)}$$

adding (1) & (2)

$$\frac{-r_A'}{k_{Ag}.a} + \frac{-r_A' H_A}{k_{Al}.a} = P_A - H_A C_A$$

$$-r_A'\left[\frac{1}{k_{Ag}.a} + \frac{H_A}{k_{Al}.a}\right] = P_A - H_A C_A$$

$$-r_A' = \frac{1}{\frac{1}{k_{Ag}.a} + \frac{H_A}{k_{Al}.a}}\left(P_A - H_A C_A\right)$$

Q $P_A^* = H_A C_A$

$$\boxed{-r_A' = \frac{1}{\frac{1}{k_{Ag}.a} + \frac{H_A}{k_{Al}.a}}\left(P_A - P_A^*\right)}$$

Or

$$\boxed{\frac{1}{K_{Ag}.a} = \frac{1}{k_{Ag}.a} + \frac{H_A}{k_{Al}.a}}$$

$$-r_A' = a\left(-r_A''\right)$$

$$-r_A'' = \frac{-r_A'}{a}$$

$$-r_A'' = -\frac{1}{S}\frac{dN_A}{dt} = \frac{1}{a}\left[\frac{1}{\frac{1}{k_{Ag}.a} + \frac{H_A}{k_{Al}.a}}\right]\Delta P_A$$

$$\boxed{-r_A'' = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{k_A l}}\Delta P_A.}$$

$$\boxed{\frac{1}{K_{Ag}} = \frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}}$$

7.1.4 RATE EQUATION FOR ABSORPTION WITH CHEMICAL REACTION

There are eight cases.

Case A: Instantaneous reaction with low C,

Case B: Instantaneous reaction with high CB

Case C: Fast reaction in liquid film, with low CB

Case D: Fast reaction in liquid film, with high C,

Case E and F: Intermediate rate with reaction in the film and in the main body of the liquid

Case G: Slow reaction in main body but with film resistance

Case H: Slow reaction, no mass transfer resistance

$$-r_A' = \frac{1}{\frac{1}{k_{Ag}.a} + \frac{H_A}{k_{Al}.a.E} + \frac{H_A}{k.C_B.f_l}} \Delta P_A$$

where

$\frac{1}{k_{Ag}.a} \rightarrow$ *gas film resistence*

$\frac{H_A}{k_{Al}.a.E} \rightarrow$ *liquid film resistence*

$\frac{H_A}{k.C_B.f_l} \rightarrow$ *liquid bulk resistence*

The effect of chemical reaction is to accelerate the rate of absorption of A.

THE LIQUID FILM ENHANCEMENT FACTOR (E)

$$E = \frac{\text{Rate of take up of A when reaction occurs}}{\text{Rate of take up of A for straight mass transfer}}$$

$E \geq 1$ always

$E = E\left(E_i, M_H\right)$

Where

E_i - Enhancement factor for an infinitely fast reaction.

$M_H{}^2$ – Maximum possible conversion in the film compared to maximum possible diffusion through film

Or $M_H{}^2$ – Hatta modulus

if $E_i > 5M_H \rightarrow$ *pseudo first order reaction* $\Rightarrow E = M_H$

if $E_i < \frac{M_H}{5} \rightarrow$ *instantaneous reaction* $\Rightarrow E = E_i$

Hatta number indicates whether reaction is fast or slow

7.1.4 HATTA NUMBER (M_H)

$$M_H{}^2 = \frac{\text{Maximum possible cnversion in film}}{\text{Maximum possible diffusion through film}}$$

$$M_H = \sqrt{\frac{k\ C_B P_A}{k_{Al}}}$$

It Provides indication of whether a large interfacial area *(a)* or a large liquid hold up *(f_l)* is required in a reactor to be designed for particular reaction.

If $M_H > 2$ all reaction occurs in liquid film

If 0. 02 < M_H <2 reaction occurs in liquid film & liquid bulk

If M_H < 0.02 reaction is in liquid bulk

When M_H is large (fast reaction), we required large interfacial Area. → packed column, plate column

When M_H is very small (slow reaction), we required large Volume of liquid

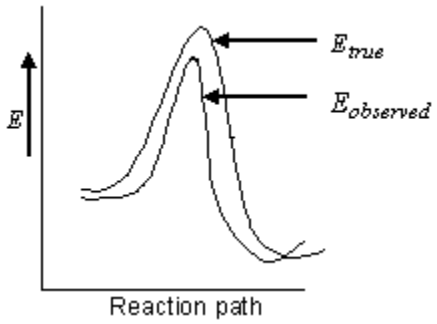
hold up → packed bubble column.

When required both → Agitated Tank.

7.2 CATALYTIC REACTION SYSTEM

A catalytic reaction occurs at the fluid solid interface so a large interfacial area is essential to provide. This solid catalyst is normally porous. It usually speeds up a reaction by promoting a different reaction mechanism for formation of products that requires lower activation energy that for the non- catalyzed reaction.

A catalyst remains unchanged in its amount & chemical composition at the end of reaction.



7.2.1Steps in solid catalysed fluid reaction

(1) Diffusion of A From bulk to external surface of catalyst → surface diffusion step.

(2) Diffusion of A form pore mouth to into the catalyst pares → pore diffusion step

(3) Adsorption of A on to the catalyst surface

(4) Chemical reaction → surface reaction

(5) De-Sorption of the product

(6) Diffusion of product from pores diffusion

(7) Diffusion of the product from pore mouth to bulk fluid

The overall rate of reaction is equal to the rate of slowest step.

We can reduce the resistance to pore diffusion by reducing the catalyst particle size.

7.2.2 RATE EQUATION FOR PORE DIFFUSION AND SURFACE REACTION

$$A \longrightarrow P \quad -r_A'' = -\frac{1}{S}\frac{dN_A}{dt} = k''C_A$$

$$Input\ of\ A = \left(\frac{dN_A}{dt}\right)_{in} = -D\left(\frac{dC_A}{dx}\right)_{in}.\pi r^2$$

$$Output\ of\ A = \left(\frac{dN_A}{dt}\right)_{out} = -D\left(\frac{dC_A}{dx}\right)_{out}.\pi r^2$$

$$Disappearance\ of\ A = \left(k''C_A\right).2\pi r.dx$$

therefore, material balance equation

$$\boxed{Input\ of\ A = Output\ of\ A + Disappearance\ of\ A}$$

$$\Rightarrow -D\left(\frac{dC_A}{dx}\right)_{in}.\pi r^2 = -D\left(\frac{dC_A}{dx}\right)_{out}.\pi r^2 + \left(k''C_A\right).2\pi r.dx$$

dividing by $\pi r^2 D.dx$

$$\frac{-\left(\frac{dC_A}{dx}\right)_{in}}{dx} = \frac{-\left(\frac{dC_A}{dx}\right)_{out}}{dx} + \frac{2k''}{D.r}$$

$$\Rightarrow \frac{\left(\frac{dC_A}{dx}\right)_{out} - \left(\frac{dC_A}{dx}\right)_{in}}{dx} = \frac{2k''}{D.r}$$

by derivative of first approximation,

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

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kC_A$$

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

$$\Rightarrow k^{"}C_A.S = kV.C_A$$

$$\Rightarrow k^{"} = \frac{k.V}{S}$$

$$\Rightarrow k^{"} = \frac{k.\left(\pi r^2.L\right)}{(2\pi r.L)}$$

$$\Rightarrow \boxed{k^{"} = \frac{k.r}{2}}$$

Hence,

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

$$let\ \frac{k}{D} = m^2$$

$$\frac{d^2C_A}{dx^2} - m^2C_A = 0$$

$$\therefore \left(D^2 - m^2\right)C_A = 0$$

D= $\pm$m

$$\boxed{C_A = C_1e^{mx} + C_2e^{-mx}}$$

Using B.C. *at* x = 0 $\Rightarrow C_A = C_{AS}$

$$C_{AS} = C_1 + C_2 \_\_\_\_\_(1)$$

$$at\ x = L \Rightarrow \frac{dC_A}{dx} = 0$$

$$\Rightarrow \frac{dC_A}{dx} = m\ M,e^{m_x} - m\ M_2e^{-mx}$$

$$0 = C_1e^{mL} - C_2e^{-mL} \_\_\_\_\_(2)$$

from equation (1) *and* (2),

$$\boxed{C_1 = \frac{C_{AS}.e^{-mL}}{e^{mL} + e^{-mL}}}$$

$$\boxed{C_2 = \frac{C_{AS}.e^{mL}}{e^{mL} + e^{-mL}}}$$

hence

$$C_A = \frac{C_{AS}.e^{-mL}}{e^{mL} + e^{-mL}}.e^{mx} + \frac{C_{AS}\ e^{mL}.e^{-mx}}{e^{mL} + e^{-mL}}$$

$$\boxed{C_A = C_{AS}\left[\frac{e^{+m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}}\right]}$$

$$\Rightarrow \boxed{\frac{C_A}{C_{AS}} = \frac{\cosh m(L-x)}{\cosh mL}}$$

The *mL* is a dimensionless quantity and called *Thiele modulus (Φ).*

7.2.3 EFFECTIVENESS FACTOR (ή)

Effectiveness factor is used to measure how much reaction rate is lower, due to the resistance of pore diffusion.

$$\boxed{\eta = \frac{-\bar{r}_A\ with\ diffusion\ resistance}{-r_A\ without\ diffusion\ resistance}}$$

η = *ranges form* 0 *to* 1

For first order reaction

$$\eta = \frac{-\overline{r_A}}{-r_A} = \frac{k\overline{C_A}}{kC_{AS}} = \frac{\overline{C}_A}{C_{AS}}$$

we know that,

$$\overline{C}_A = \frac{\int_0^L C_A.dx}{\int_0^L dx} = \frac{1}{L}\int_0^L C_A.dx$$

$$\overline{C}_A = \frac{1}{L}\left[\int_0^L C_{AS}\frac{\cosh m(L-x)}{\cosh mL}dx\right]$$

$$\overline{C}_A = \frac{C_{AS}}{L.\cosh mL}\left[\frac{\sinh m(L-x)}{-m}\right]_0^L$$

$$\overline{C}_A = -\frac{C_{AS}}{mL.\cosh mL}\left[-\sinh mL\right]$$

$$\overline{C}_A = \frac{C_{AS}.\sinh mL}{mL}$$

$$\Rightarrow \eta = \frac{\left(\frac{C_{AS}.\tanh mL}{mL}\right)}{C_{AS}}$$

$$\boxed{\eta = \frac{\tanh mL}{mL}}$$

- **NOTES**:

° *when* $mL < 0.4 \Rightarrow \tan mL = mL$

$$\Rightarrow \boxed{\eta = 1}$$

This is the case where

→ *catalyst pore is short ,*

→ *slow reaction* (*small k*)

→ *fast diffusion* (*high D*)

° *when* $mL > 4 \Rightarrow \tan mL = 1$

$$\Rightarrow \boxed{\eta = \frac{1}{mL} = \frac{1}{\phi}}$$

This is the case where

→ *catalyst pore is large*

→ *fast reaction* (*high k*)

→ *slow diffusion* (*small D*)

° *when* $0.4 < mL < 4$

This is the case where

→ *the pore diffusion resistance and reaction rate resistance are approximately same.*

$$\frac{\eta_1}{\eta_2} = \frac{-r_{A1}}{-r_{A2}} = \frac{\phi_2}{\phi_1} = \frac{R_2}{R_1}$$

$$\phi = L\sqrt{\frac{(n+1)K''C_A^{n-1}}{2D_e}}$$

$$\phi^2 = \frac{\text{Surface reaction rate}}{\text{Diffusion late}}$$

Mass Transfer → high temperature region. → Not much effect of temperature.

Chemical Reaction → Lower temp reign → $e^{-E/RT}$ temperature effect is strong

7.2.4 CHARACTERISTIC LENGTH (L)

$$\boxed{L = \frac{Volume\ of\ particle}{external\ surface\ area}}$$

e.g.

$\boxed{L = \frac{thickness}{2}}$ → *for flat plate*

$\boxed{L = \frac{R}{2}}$ → *for cylinder*

$\boxed{L = \frac{R}{3}}$ → *for sphere*

RELATIONSHIP BETWEEN THIELE MODULUS AND SIZE OF PARTICLE

Q $\phi \propto L$

$\Rightarrow \phi \propto R$ (*size of pore*)

$$\boxed{\frac{-r_{A1}}{-r_{A2}} = \frac{\phi_2}{\phi_1} = \frac{R_2}{R_1}}$$

7.2.5 THIELE MODULUS (Φ *or* M_T)

Thiele Modulus can be generalized as

$$\phi = \frac{\left(-r_{AS}^{"}\right).L}{\left[2D_e \int_0^{C_{AS}} \left(-r_A^{"}\right)\right]^{1/2}}$$

for n^{th} order reaction

$$\phi = L\sqrt{\frac{(n+1)K^{"}C_{As}^{\,n-1}}{2D_e}}$$

hence for 0^{th} order reaction

$$\phi = L\sqrt{\frac{K^{"}}{2D_e.C_{As}}}$$

7.2.6 FOR STRONG PORE DIFFUSION RESISTANCE

In the regime of stong pore resis tance

$$-r_A^{"} = k^{"}C_{AS}^{\,n}.\eta$$

$$Or = k^{"}C_{AS}^{\,n}\frac{1}{M_T}$$

$$-r_A^{"} = k^{"}C_{AS}^{\,n}\ \frac{1}{L\left[\frac{(n+1)k^{"}C_{AS}^{\,(n-1)}}{2D_e}\right]^{1/2}}$$

$$-r_A^{"} = k^{"}C_{AS}^{\,n}\frac{1}{L}\left(\frac{2D_e}{(n+1)k^{"}C_{AS}^{\,n-1}}\right)^{1/2}$$

$$-r_A^{"} = \left[\left(\frac{2}{n+1}\right)\frac{k^{"}D_e}{L^2}\right]^{1/2} C_{AS}^{\left(\frac{n+1}{2}\right)}$$

↓ ↓

Temperature *Concentration*

the general chemical reaction can be defined as,

$-r_A^{"} = k_{obs}^{"}C_{AS}^{\,n'}$

On Comaparing

$C_{AS}^{\left(\frac{n+1}{2}\right)} \rightarrow C_{AS}^{\,n'}$

$$\Rightarrow \boxed{n^1 = \frac{n+1}{2}}$$

where

n - true order of reaction

n' - observed order of reaction

and

$$k_{obs}^{"} = \left[\left(\frac{2}{n+1}\right)\frac{k^{"}D_e}{L^2}\right]^{1/2}$$

where

$k^{"}$ - actual rate Constant

$k_{obs}^{"}$ - observed actual rate Constant

7.2.7 EFFECTIVE DIFFUSIVITY (D_e)

It is used when

Not all area is normal to direction to flux flow.

The path of diffusion is tortuous in catalyst.

If cross section area of pores is varying.

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

where

D_{AB} = *Diffusivity*

ϕ_p = *Porosity*

σ_c = *Constriction factor*

$\bar{\tau}$ = *Tourtuosity*

7.3 DESIGN EQUATION FOR REACTORS CONTAINING POROUS CATALYST

PFR

$Input = Output + disappearance\ of\ A$

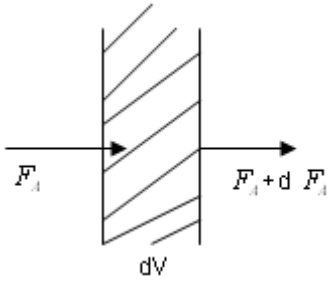
$F_A = F_A + dF_A + (-r_A')dW$

Q $F_A = F_{Ao}(1 - X_A)$

$\therefore dF_A = F_{Ao}.dX_A$

$\Rightarrow F_{Ao}dX_A = (-r_A')dW$

$$\frac{dW}{F_{Ao}} = \frac{dX_A}{(-r_A')}$$



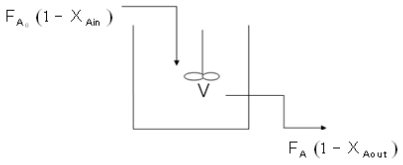
$$\int_0^W \frac{dW}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A')}$$

$$\boxed{\frac{W}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A')}}$$

$$By\ \tau' = \frac{WC_{Ao}}{F_{Ao}} \rightarrow Weight - time$$

$$\boxed{\tau' = C_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A')}}$$

Mixed flow



$$\frac{W}{F_{A0}} = \frac{X_{Aout} - X_{Ain}}{-r_{Aout}}$$

For Batch :

$$\frac{t}{C_{Ao}} = \frac{V}{W_s}\int_o^{X_{Aout}} \frac{dX_A}{-r_A'}$$

$$\frac{t}{C_{Ao}} = \frac{V}{V_s}\int_o^{X_{Aout}} \frac{dx_A}{-r_A^{111}}$$

For 1st order with $\varepsilon \neq 0$

$$PFR\ : K'\tau' = K'''\tau''' = (1+\varepsilon_A)\ln\frac{1}{1-X_{Aout}} - \varepsilon_A\ X_{Aout}$$

$$CSTR = X_{Aow}\ \frac{(1+\varepsilon_A\ X_{Aout}}{1-X_{AouL}}$$

7.4 ACTIVITY OF CATALYST (a)

$$a = \frac{\text{Rate of reaction of A with catalyst at time t}}{\text{Rate of reaction of A when catalyst is fresh}}$$

Activity of catalyst 'a'

$-r_A = K^1 C_A^n\ d$

$a = 1, t = 0$

$a < 1, t = t$

$$-\frac{da}{dt} = K_d^1\ C^m\ a^d \rightarrow \text{order of Deactivation}$$

$$a = \frac{\text{Rate of } R_{xn} \text{ with catalyst at time } t}{\text{Rate of } R_{xn} \text{ with catalyst at time } t = 0}$$

7.5 Deactivation of Catalyst

The continuous decrease in the activity of catalyst with time is called *deactivation of catalyst.*

- Types of catalyst deactivation
  - By sintering (aging)
  - By fouling
  - By poisoning
- **By sintering** – due to a loss of active surface area resulting from the prolonged exposure to high temp in the rector
- **By fouling** – due to physical deposition of coke material on the surface of catalyst. This is rapid deactivation.
- **By poisoning** – due to reversible or irreversible chemisorption of the poisoning materials on the active sites.

There is many factor affect deactivation but mainly decay reaction & pore diffusion.

How catalyst get deactivated: -

(1) Decay reaction

1. Parallel
2. Series
3. Side by side

(2) Pore diffusion

$\phi < 0.3 \rightarrow \eta = 1$ uniform distribution

$\phi > 3 \rightarrow n = \frac{1}{\phi} \rightarrow$ at exterior $\rightarrow$ slowly penetrate with $\rightarrow$ parallel R_{xn}

$\phi < 0.3 \rightarrow \eta = 1 \rightarrow$ uniform distribution

(3) Temperature / operating condition

$\rightarrow$ Structural modification

$\rightarrow$ Sintering (Aging) of catalyst surface $\rightarrow$ due to extreme dependent upon : time temp environment

Activity w.r.t to t : $\frac{-da}{dt}$

Negative sign $\rightarrow$ as activity is decreasing

$$-\frac{da}{dt} = kd\, C_A^m\, a^d \rightarrow \text{parallel}$$

$$-\frac{da}{dt} = kd\, C_R^m\, a^d \rightarrow \text{Series}$$

$$-\frac{da}{dt} = kd\, C_P^m\, a^d \rightarrow \text{side by side}$$

$$-\frac{da}{dt} = k_d\, a^d \rightarrow \text{temperature}$$

7.6 Observed rate of Reaction:

$$-r_A^{11} = k^{11} C_{AS}^{\ n}$$

$$-r_A^{11} = k^{11} C_{AS}^{\ n} \frac{1}{L\sqrt{\frac{(n+1)k^{11} C_{AS}^{\ (n-1)}}{2D_e}}}$$

$$-r_A^{11} = \frac{K^{11}\, C_{AS}^n}{L} \sqrt{\frac{2D_e}{(n+1)k^{11} C_{AS}^{\ (n-1)}}}$$

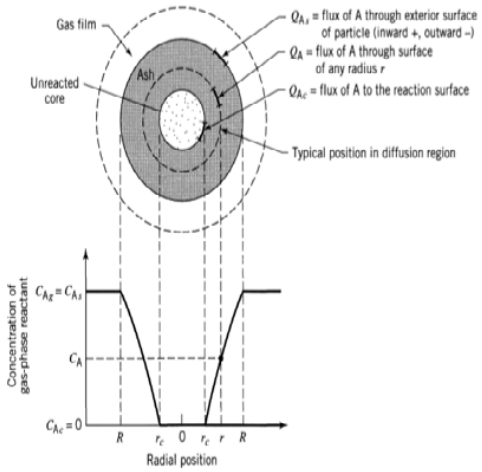
$$-r_A^{11} = \sqrt{\frac{k^{11}.2D_e}{L^2\,(n+1)}} \cdot \frac{C_{AS}^{\ n}}{C_A^{\ (n-1)/2}}$$

$$-r_A^{11} = \sqrt{\frac{k^{11}2.De}{L^2\,(n+1)}}\ C_{As}^{\ n-\left(\frac{n-1}{2}\right)}$$

$$-r_A^{1} = \sqrt{\frac{k^{11}2\ De}{L^2\ (n+1)}}\ C_{AS}^{\ \frac{n+1}{2}}$$

$$-r_A^{11} = k_{lobs}^{11}\ C_{AS}^{\ n'}$$

7.7 Shrinking care model:-



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

Resistance through ash layer is rate controlling

(1) Write the flux relationship for partially reacted particle

(2) Then apply for all value of r_c $\left(\int_O^R r\ c\right)$

(3) Integrate then for time t $\left(\int_o^t \frac{aw}{dt}\right)$

$\frac{p_{solid}}{p_{Gas}}$ = 1000 $\rightarrow$ this is rate by which the gas movement toward core & core reduction is taking place

So we can assume flat the core greediest of A in as layer at any time that the unreacted core is stationary

At steadys state:

$$-\frac{1}{5}\frac{dN_A}{dt} = Q_A$$

$$-\frac{dN_A}{dt} = Q_{AS}$$

$$-\frac{dN_A}{dt} = Q_a\, 4\pi r^2 = Q_{As}\, 4\pi rc^2 = \text{constsant}$$

$$Q_A = De\frac{dC_A}{dr}\ (\text{Ficks law for counter diffustion}$$

$$-\frac{dN_A}{dt} = 4\pi r^2\, De\frac{dC_A}{dr} = \text{constant}$$

– step1ends

$$\frac{-dN_A}{dt}\int_R^{rc}\frac{dr}{r^2} = 4\pi De\int_{C_{Ag}=C_{As}}^{C_{AC}=0} dC_A$$

$$-\frac{dN_A}{dt}\left(\frac{1}{r_C}-\frac{1}{R}\right) = 4\pi De\ C_{Ag}$$

This represents the condition of reacting particle at any time – t

2nd steps: here we are considering change in size of core is not constant with time as ash layer gets thicker and thicker which makes more resistance for A.

$$dN_A = p_A\, dv$$

$$= p_A\, d\left(\frac{4}{3}\pi r_c^3\right)$$

$$dN_A - p_A\ 4\pi_c^2\ drc$$

$$p_A\, 4\pi r_C^2\ \frac{drc}{dt}\left(\frac{1}{r_c}-\frac{1}{r}\right)d = De\, C_{Ag}\int_0^t dt$$

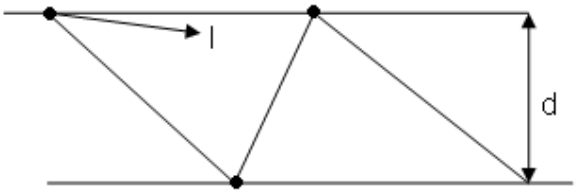
$$t = \frac{p_A R^2}{6De\, C_{Ag}}\left[1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{rc}{R}\right)^3\right]$$

$$\tau = \frac{p_A R^2}{6De\, C_{Ag}}\ (r_c = 0)$$

$$\frac{t}{\tau}=1-3\left(\frac{r_c}{k}\right)^2+2\left(\frac{r_c}{k}\right)^3$$

$$\frac{t}{\tau}=1-3\left(1-\alpha_3\right)^{2/3}+2\left(1-X_B\right)$$

7.8 Knudsen Diffusion and Knudsen transport



Depends upon:-

→Velocity of molecule

→Diameter of pore

→Mean free path

MFP more → diameter small → KD → more wall Collisions

MFP less → Diameter large → KD → more molecular Collisions

GATE QUESTIONS

1. For a vapor phase catalytic reaction $A+B \rightarrow P$. which follows the Rideal mechanism and the reaction step is rate controlling, the rate of reaction is given by (reaction step is irreversible, product also adsorbs)

(a) $-r_A = \dfrac{kP_AP_B}{1+K_AP_A+K_PP_P}$

(b) $-r_A = \dfrac{kP_A^2 - k_1P_P}{1+K_AP_A+K_PP_P}$

(c) $-r_A = \dfrac{kP_AP_B}{1+K_AP_A+K_BP_B+K_PP_P}$

(d) $-r_A = \dfrac{kP_AP_B}{1+K_AP_A}$

(GATE 2001)

2. Following isothermal kinetic data are obtained in basket type of mixed flow reactor for a porous catalyst. Determine the role of pore diffusion and) external mass process

Pellet Diameter	Leaving conc. of reactant	Basket spinning rate	($-r_A$)
1	1	high	2
2	1	low	1
2	1	high	1

(a) Strong pore diffusion control and mass transfer not controlling
(b) Both pore diffusion and mass transfer not controlling
(c) Bothe diffusion and mass transfer controlling
(d) Mass transfer controlling

(GATE 2003)

3. A first order gaseous phase reaction is catalysed by a non-porous solid. The kinetic rate constant and the external mass transfer coefficient are k and k_g respectively. The effective rate constant (k_{eff}) is given by

(a) $k_{eff} = k + k_g$ (b) $k_{eff} = \dfrac{(k+k_g)}{2}$

(c) $k_{eff} = (kk_g)^{\frac{1}{2}}$ (d) $\dfrac{1}{k_{eff}} = \dfrac{1}{k} + \dfrac{1}{k_g}$

(GATE 2004)

4. The first order reaction of $A \rightarrow R$ is run in an experimental mixed flow reactor. Find the role played by pore diffusion in the run given below. C_{A0} is 100 and W is fixed. Agitation rate was found to have no effect on conversion.

Found to have no effect on conversion.

d_p	F_{A0}	X_A
2	2	0.8
6	4	0.4

(a)Strong pore diffusion control

(b)Diffusion free

(c)Intermediate role by pore diffusion

(d)External mass transfer

(GATE 2007)

5. A packed bed reactor converts A to R by first order reaction with 9 mm pellets in strong pore diffusion regime to 63.2% level. If 18 mm pellets are used what is the conversion.

(a) 0.39 (b) 0.61

(c) 0.632 (d) 0.865

(GATE 2007)

6. A species (A) reacts on a solid catalyst to produce R and S as follows

(1) $A \rightarrow R : r_R = k_1 C_A^2$

(2) $A \rightarrow S : r_S = k_2 C_A^2$

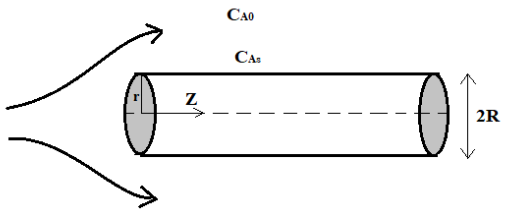
Assume film resistance to mass transfer is negligible. The ratio of instantaneous fractional yield of R in the presence of pore diffusion to that in the absence of pore diffusion is

(a) 1 (b) >1

(c) <1 (d) zero

(GATE 2008)

7. The irreversible zero order reaction $A \rightarrow B$ takes place in a porous cylindrical catalyst that is sealed at both ends as shown in the figure. Assume dilute concentration and neglect any variations in the axial direction.



The steady state concentration profile is $\frac{C_A}{C_{AS}} = 1 + \frac{\phi_0^2}{4}\left[\left(\frac{r}{R}\right)^2 - 1\right]$, where, ϕ_0 is the Thiele modulus. For ϕ_0 =4, the range of r, where, C_A=0, is

(a) $0 < r < \frac{R}{4}$

(b) $0 < r < \frac{R}{2}$

(c) $0 \le r \le R\sqrt{\frac{3}{4}}$

(d) $0 \le r \le R$

(GATE 2008)

8. For a solid-catalysed reaction, the Thiele modulus is proportional to

(a) $\sqrt{\frac{\text{intrinsic reaction rate}}{\text{Diffusion rate}}}$

(b) $\sqrt{\frac{\text{Diffusion rate}}{\text{intrinsic reaction rate}}}$

(c) $\frac{\text{intrinsic reaction rate}}{\text{diffusion rate}}$

(d) $\frac{\text{diffusion rate}}{\text{intrinsic reaction rate}}$

(GATE 2009)

9. Consider an irreversible, solid catalysed, liquid phase first order reaction. The diffusion and the reaction resistances are comparable. The overall rate constant (k_0) and the reaction rate constant (k) as

(a) $k_0 = \frac{kk_m}{k + k_m}$ (b) $k_0 = \frac{k + k_m}{kk_m}$

(c) $k_0 = \frac{k + k_m}{2}$ (d) $k_0 = k + k_m$

(GATE 2011)

10. For a first order isothermal catalytic reaction $A \rightarrow P$, occurring in an infinitely long cylindrical pore, the relationship between effectiveness factor $\in$, and Thiele modulus ϕ, is

(a) $\varepsilon = \frac{1}{\phi^2}$ (b) $\varepsilon = \phi$

(c) $\varepsilon = 1$ (d) $\varepsilon = \frac{1}{\phi}$

(GATE 2011)

11. For a first order catalytic reaction, the Thiele modulus (ϕ) of a spherical pellet is defined as

$$\phi = \frac{R_p}{3}\sqrt{\frac{kp_p}{D_e}}$$

Where, p_p = pellet density

R_p =pellet radius

D_e =effective diffusivity

K = first order reaction rate constant

If $\phi = 5$, then the apparent activation energy (Ea)is related to the intrinsic (or true) activation Energy (E) as

(a) $E_a = E^{0.5}$
(b) $E_a = 0.5E$
(c) $E_a = 2E$
(d) $E_a = E^2$

(GATE 2012)

12. The rate controlling step for the solid catalysed irreversible reaction $A + B \rightarrow C$ is known to be the reaction of adsorbed A with adsorbed B to give adsorbed C. If p, is the partial pressure of component i with k_i is the adsorption equilibrium constant of component i, then the form of the Langmuir-Hinshelwood rate expression will

(a) Rate $a\frac{p_A p_B}{1 + k_A p_A + k_B p_B + k_C p_C}$

(b) Rate $a\frac{p_A p_B}{\left(1 + k_A p_A + k_B p_B + k_C p_C\right)^2}$

(c) Rate $a\frac{p_A p_B}{\left(1 + k_A p_A + k_B p_B + k_C p_C\right)^{0.5}}$

(d) Rate $a\frac{p_A p_B}{p_C}$

(GATE 2012)

13. The overall rates of an isothermal catalytic reaction using spherical catalyst particles of diameter 1mm and 2 mm are r_{A1} and r_{A2} (in $\text{mol}(kg - catalyst)^{-1}h^{-1}$), respectively. The other physical properties of the catalyst particles are identical. If pore diffusion resistance is very high, the ratio r_{A2}/r_{A1} is

(a) 0.5 (b) 0.4

(c) 0.2 (d) 0.6

(GATE 2013)

14. A vapour phase catalytic reaction $(Q + R \rightarrow S)$ follows Rideal mechanism. R and S are not adsorbed. Initially, the mixture contains only the reactants in equimolar ratio. The surface reaction step is rate controlling. With constants a and b, the initial rate of reaction $(-r_0)$ in terms of total pressure (P_r) is given by

(a) $-r_0 = \frac{aP_r}{1 + bP_T}$ (b) $-r_0 = \frac{aP_r}{1 + bP_T^2}$

(c) $-r_0 = \frac{aP_T^2}{1 + bP_T}$ (d) $-r_0 = \frac{aP_T^2}{(1 + bP_T)^2}$

(GATE 2014)

15. A catalyst slab of half-thickness L (the width and length of the slab>>L) is used to conduct the first order reaction $A \rightarrow B$. At 450K, the Thiele modulus for this system is 0.5. The activation energy

for the first order rate constant is 100KJ/mol. The effective diffusivity of the reactant in the slab can he assumed to be independent of temperature, and external mass transfer resistance can be neglected. If the temperature of the reaction is increased to 470K, then the effectiveness factor at 470K (up to two decimal place) will be_____

(GATE 2015)

16. Which of the following can change if only the catalyst is changed for a reaction system?

(a) Enthalpy of reaction

(b) activation energy

(c) Free energy of the reaction

(d) Equilibrium constant

(GATE 2015)

17. A porous pellet with Pt dispersed in it is used to carry out a catalytic reaction. Following two scenarios are possible.

Scenario 1: Pt present throughout the pores of the pellet is used for catalysing the reaction.

Scenario 2: Pt present only in the immediate vicinity of the external surface of the pellet is used for catalysing the reaction.

At a large value of Thiele modulus. Which one of the following statements is TRUE?

(a) Since the reaction rate is much greater than the diffusion rate, scenario 1 occurs

(b) Since the reaction rate is much greater than the diffusion rate, scenario 2 occurs

(c) Since the reaction rate is much lower than the diffusion rate, scenario 1 occurs

(d) Since the reaction rate is much lower than the diffusion rate, scenario 2 occurs

(GATE 2016)

18. For a solid catalysed gas-phase reversible reaction, which of the following statement is always true.

(a) Adsorption is rate limiting

(b)Desorption is rate limiting

(c) Solid catalyst doesn't affect equilibrium conversion

(d) Temperature doesn't affect equilibrium conversion

(GATE 2017)

19.liquid phase isomerization of 0-xylene to p-xylene using a zeolite catalyst was carried out in a CSTR. There sets of kinetic data at different temperatures and stirring speeds were obtained as shown below.

	set A		
temperature (K)	500	500	500
stirring speed (rpm)	1000	2000	3000
reaction rate (mol L^{-1} s^{-1})	0.020	0.025	0.025

set B			set C		
600	600	600	700	700	700
1000	2000	3000	1000	2000	3000
0.037	0.047	0.047	0.069	0.078	0.086

The operating condition at which the reaction rate is not controlled by external mass transfer resistance is

(a) T=500K; rpm=3000

(b) T=600 K; rpm =1000

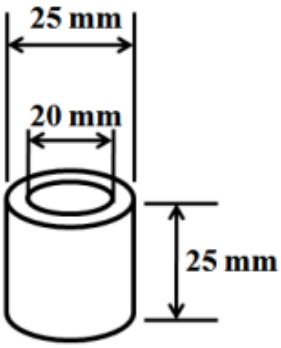
(c) T=700 K; rpm =1000

(d) T=700 K; rpm =2000

(GATE 2018)

20. Hydrogenation of benzene is to be carried out using Ni (density=8910kg/ m^3) as catalyst, cast in the form of non-porous hollow cylinders, as shown below. The reaction occurs on all the surfaces of the hollow cylinder. During an experiment, one such cylinder is suspended in the reactant stream. If the observed rate of reaction is 0.39 mol(kg of catalyst surface) $^{-1}$min $^{-1}$, then the rate of reaction inn mol (kg of catalyst) $^{-1}$ min $^{-1}$is _____(rounded off to three decimal places).

(GATE 2018)



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ANSWER KEYS

1	2	3	4	5	6	7	8	9	10
(A)	(A)	(D)	(A)	(A)	(A)	(C)	(A)	(A)	(D)
11	12	13	14	15	16	17	18	19	20
(B)	(B)	(A)	(C)	(0.8)	(B)	(B)	(C)	(A)	(0.033)

EXPLANATIONS

1.Answer:(a)

$A+B \rightarrow P$

Using equilibrium method to derive $-r_A = \frac{kp_A p_B}{1+k_A p_A + K_P P_P}$

2.Answer:(a)

it is of strong pore diffusion control where the mass transfer is not controlling

3.Answer:(d)

The effective rate constant can be written as

$$k_{eff} = \frac{1}{\left(\frac{1}{k}+\frac{1}{k_g}\right)}$$

$$\therefore \frac{1}{k_{eff}} = \frac{1}{k}+\frac{1}{k_g}$$

4.Answer:(a)

C_{Ao} =100

W = weight of catalyst fixed for the runs for CSTR

$$\frac{W}{F_{Ao}} = \frac{X_A}{-r_A}$$

$$(1)\ \frac{W}{2} = \frac{0.8}{-r_1} \rightarrow -r_1 = \frac{1.6}{W}$$

$$(2)\ \frac{W}{4} = \frac{0.4}{-r_2} \rightarrow -r_2 = \frac{1.6}{W}$$

C_{AOut} is changing from 20 to 60 which should increase the rate by three units. But the rate is constant because increasing diameter of the pellet from 2 to 6 decreasing the rate by three units. Diameter is affecting the rate so strong pore diffusion.

5.Answer: (a)

For a packed bed reactor with first order reaction,

$$\frac{W}{F_{Ao}} = \int_0^{x_A} \frac{dx_A}{(-\gamma_A)\xi}$$

$$\frac{W}{F_{Ao}} = \int_0^{x_A} \frac{dxA}{KC_{A_0}(1\times A)\xi}$$

$$\frac{W}{F_{Ao}} = KC_{A_0}\frac{-ln(1-X_A)}{\xi}$$

$$\frac{-ln(1-X_A)}{\xi} = cons\tan t$$

$\xi = \frac{1}{\phi}$ is strong diffusion

$$-\ln(1-X_A)\phi = \text{ constant}$$

$$\phi = \sqrt{\frac{K''}{\Delta}}L; -ln(1-X_A)L = \text{constant}$$

$$-\ln(1-X_A)L_1 = -\ln(1-X_{A_2})L_2$$

$$-\ln(1-0.632)\times 9 = -\ln(1-X_{A_2})\times 18$$

$$X_{A_2} = 0.39$$

In strong pore diffusion if L increases X_A decreases because if L increases ϕ will increases and efficiencies will decreases

6.Answer:(a)

$$A \rightarrow R, r_R = k_1.C_A^2$$

In pore diffusion case, $\frac{(C_A)\,pore}{(C_A)\,without pore} < 1$

But yield is $\frac{r_R}{-r_A} = \frac{k_1}{k_1 + k_2}$

Yield is not a function of C_A and hence the ratio of yield with and without diffusion is same.

7.Answer:(c)

Given, $\frac{C_A}{C_{As}} = 1 + \frac{\phi_0^2}{4}\left[\left(\frac{r}{R}\right)^2 - 1\right]$

Also given that, for $\phi_0 4, C_A = 0$

$$\therefore 0 = 1 + \frac{16}{4}\left[\left(\frac{r}{R}\right)^2 - 1\right]$$

$$\left(\frac{r}{R}\right)^2 - 1 = -\frac{1}{4}$$

$$\frac{r}{R} = \sqrt{\frac{3}{4}}$$

Thus, range of r would be $0 \le r \le R\sqrt{\frac{3}{4}}$

8.Answer:(a)

For solid catalyzed reaction,

Thiele modulus $\propto \sqrt{\frac{\text{Intrinsic reaction rate}}{\text{Diffusion rate}}}$

9.Answer:(a)

The overall rate constant is

$$\frac{1}{k_0} = \frac{1}{k_m} + \frac{1}{k}$$

$$\frac{1}{k_0} = \frac{k + k_m}{k k_m}$$

$$k_0 = \frac{k k_m}{k + k_m}$$

10.Answer:(d)

First order isothermal catalytic reaction in infinitely long cylindrical pore, theiele modulus, is high diffusion effects are strong in strong pore diffusion regime

$$\varepsilon = \frac{1}{\phi}$$

11.Answer:(b)

$$\phi \ \alpha \sqrt{\frac{k}{D_e}}$$

For $\phi > 5, E_a = 0.5E$

Strong pore diffusion regime as $\phi > 5$

12.Answer:(b)

For solid catalysed 2nd order reaction $A + B \rightarrow C$

The rate of reaction, $\gamma \alpha \frac{P_A P_B}{(1+K_A P_A + K_C P_C)^2}$

13.Answer: (a)

For a strong pore diffusion resistance

$r_A \alpha \frac{1}{d_p}, d_p$ is the diameter of the particle.

$\frac{r_{A2}}{r_{A1}} = \frac{d_1}{d_2} = \frac{1}{2} = 0.5$

14.Answer:(c)

Rideal mechanism

$A + (g)S \rightarrow AB - S$

$A - S + B(g) \rightarrow AB - S$ (rate controlling)

$AB - S \rightarrow AB$

Here S= adsorption site on catalyst surface

$K_1 = \frac{A-S}{(A)(S)} \_\_\_\_\_(I)$

And for rate controlling step $-r = K_2(A-S)(B) - K_{-2}(AB-S) \_\_\_\_(II)$

Also total number of site is $S_T = (S) + (A-S) + (AB-S) \_\_\_\_\_(III)$

Initially surface converage of AB will be very low, so (AB-S)=0

From (I),

$K_1 = \frac{A-S}{(A)(S_T - (A-S))}$

$\Rightarrow K_1(A)S_T - K_1(A-S)(A) =$

$(A-S) = \frac{K_1(A)S_T}{1+K_1(A)}$

Now , for rate controlling step, $-r = K_2(A-S)(B) - K_{-2}(AB-S)$

Initial rate mean concentration of $(AB-S) \rightarrow 0$

$-r_0 = K_2(A-S)(B)$

So, $-r_0 = \frac{K_2 K_1(A)(B)S_T}{1+K_1(A)}$

For the given reaction Q+R→S with reactants in equimolar ratio

$-r_0 = \frac{K_2 K_2 P_T . P_T}{1+K_1 P_T} = \frac{a P_T^2}{1+bP_T}$

15.Answer: 0.7 to 0.9

16.Answer:(b)

Catalyst changes the activation energy of the reaction

17.Answer:(b)

We know from the definition of Thiele modulus

$\text{Thiele Modulus} = \frac{\text{Reaction Rate}}{\text{Ditusion Rate}}$

For high value of thiele modulus reaction rate is higher than diffusion rate it would be difficult for reactants to diffuse into the pores of the pellet

18. Answer:(c)

19.Answer:(a)

20.Answer: 0.033