

# CHEMICAL REACTION ENGINEERING-I

## PART-A QUESTIONS & ANSWERS

1. Define the term 'specific reaction rate' or 'rate of reaction'.

The rate of reaction is defined as the rate of change in number of moles of any component 'i' due to chemical reaction per unit volume of the reacting fluid. It is given by the expression,  $r_i = (1/V) (dN_i/dt) = [\text{moles of 'i' formed}] / [(\text{volume of fluid}) (\text{time})]$

Significance: Negative sign for reactants & positive sign for products.

2. What are the variables affect the rate of reaction?

Many variables affect the rate of reaction of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables.

In heterogeneous systems, material may have to move from phase to phase during reaction; hence, the rate of mass transfer can be important. In addition, the rate of heat transfer may also become a factor.

3. What are single and multiple reactions?

Single reaction: When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, then it is said to be 'single reaction'.

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

4. Discuss the reaction rate of homogeneous reactions.

Suppose a single-phase reaction  $a A + b B \rightarrow r R + s S$ . The most useful measure of reaction rate for reactant 'A' is then

$$-r_A = - (1/V) (dN_A/dt) = [\text{Amount of A disappearing}] / [(\text{Volume}) (\text{Time})], [\text{mol}/\text{m}^3\text{-s}]$$

Where  $(-r_A)$  is the rate of disappearance of A and it is the intensive measure; Minus sign means disappearance.

In addition, rates of reaction of all materials are related by  $(-r_A) / a = (-r_B) / b = r_R / r = r_S / s$ .

5. Define the terms Molecularity & Order of an elementary reaction

- The number of molecules involved in the reaction is called Molecularity.
- The sum of the powers of the concentration terms involved in the rate equation of a reaction is called Order of that reaction.

6. Distinguish between homogeneous and heterogeneous reactions.

Homogeneous reactions:

- A reaction is homogeneous if it takes place in one phase alone.
- Most gas-phase reactions and fast reactions such as burning of a flame are non-catalytic type.
- Most liquid phase reactions, reactions in colloidal systems, and enzyme & microbial reactions are catalytic type.

Heterogeneous reactions:

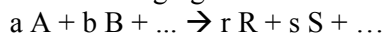
- A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate it does.
- Burning of coal, roasting of ores, attack of solids by acids, and gas-liquid absorption with reaction are non-catalytic type.
- Ammonia synthesis, oxidation of ammonia to produce nitric acid, cracking of crude oil, and oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  are catalytic type.

7. Differentiate elementary and non-elementary reactions.
- The reactions in which the rate equation corresponds to a stoichiometric equation are called elementary reaction.
  - The reactions in which there is no correspondence between stoichiometry and rate equation are known as Non-elementary reaction.

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

9. With suitable example, show the representation of an elementary reaction in terms of partial pressure.

For isothermal (elementary) gas reactions where the number of moles of material changes during reaction, the relation between the total pressure of the system ' $\pi$ ' to the changing concentration or partial pressure of any of the reaction component is



$$\text{For the component 'A', } p_A = C_A R T = p_{A0} - [(a/\Delta n) (\pi - \pi_0)]$$

$$\text{For the component 'R', } p_R = C_R R T = p_{R0} + [(r/\Delta n) (\pi - \pi_0)]$$

And the rate of the reaction, for any component 'i', is given by

$$r_i = (1/RT) (dp_i/dt)$$

10. How will test the kinetic models that involve a sequence of elementary reaction?

In testing the kinetic models that involve a sequence of elementary reaction, we hypothesize the existence of two types of intermediates;

Type-I: An unseen and unmeasured intermediate 'X' usually present at such small concentration that its rate of change in the mixture can be taken to be zero. Thus, we have [X] is small and  $d[X]/dt = 0$ . This is called the 'steady-state approximation'.

Type-II: Where a homogeneous catalyst of initial concentration  $C_0$  is present in two forms, either as free catalyst 'C' or combined in an appreciable extent to form the intermediate 'X', an accounting for the catalyst gives  $[C_0] = [C] + [X]$ . We then also assume that either  $(dX/dt) = 0$  or that the intermediate is in equilibrium with its reactants.

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

11. For the elementary reversible reaction,  $2A \rightarrow R + S$ , Derive the relation between equilibrium constant  $K_c$ ,  $k_1$  and  $k_2$ .

- For the given, the rate of reaction is  $-r_A = k_1 C_A^2 - k_2 C_R C_S$ .
- At equilibrium,  $-r_A = 0$ . Then,  $k_1 C_A^2 - k_2 C_R C_S = 0$  (or)  $K_c = k_1 / k_2 = (C_R C_S) / C_A^2$ .

12. For a reactant A (initial concentration  $C_{A0}$ ), its  $C_A$  varies according to  $(1/C_A) - (1/C_{A0}) = k t$ , where 't' is time and 'k' is kinetic constant. Derive an expression for the rate of reaction.

- The given expression can be rearranged as  $(1/C_A) = k t + (1/C_{A0})$  or  $C_A^{-1} = k t + C_{A0}^{-1}$
- Differentiating the above expression on both sides, we have  
 $-dC_A/C_A^2 = k dt + 0$  or  $-(dC_A/dt) = k C_A^2$  or  
 $-r_A$ , rate of the reaction =  $-(dC_A/dt) = k C_A^2$

13. Differentiate between differential and integral method of analysis of batch reactor data.

Integral method of analysis:

- It is simple to work and is recommended when testing specific mechanisms, or relatively simple rate expression. (elementary reactions)
- Order obtained is accurate.
- It has a disadvantage that it fails to test the rate expression involving fractional orders and involves multi-stage analysis in testing the rate form.

Differential method of analysis:

- Single stage analysis, tests any mechanism or rate form.

- It is the best analysis for fractional order reactions.
- It can be used to develop or build a rate equation to fit the data.
- It has a disadvantage that it requires more accurate or large amounts of data to evaluate  $(dC_i / dt)$ , which is the slope of the curve ' $C_i$ ' versus ' $t$ ', at different intervals of ' $t$ ' and it is difficult to work also.

14. A reaction has the stoichiometric equation  $A + B \rightarrow 2R$ . What is the order of reaction?

- By considering the given reaction as elementary, we can write the rate of reaction as  $-r_A = k C_A C_B$ . Where ' $k$ ' is the reaction rate constant.
- From the definition of order of reaction – sum of the powers of the concentration terms involved in the rate equation, we have Order,  $n = 1 + 1 = 2$

15. A certain reaction has a rate given by  $-r_A = 0.005C_A^2$ , mol/cm<sup>3</sup>-min. If the concentration is to be expressed in mol/liter and time in hours, what would be the value and units of the rate constant?

- If the concentration is to be expressed in mol/liter and time in hours, the given rate expression becomes  $-r_A = 0.005C_A^2 \times 60 \times 10^{-3} \text{ mol/lit-hr} = 0.0003 C_A^2 \text{ mol/lit-hr}$
- Then the value and the unit of rate constant,  $k = 0.0003 \text{ lit/mol-hr}$

16. For a gas reaction at 400K, the rate is reported as  $-dp_A/dt = 3.66 p_A^2$ , atm/hr.

a) What are the units of the rate constant?

b) What is the value of rate constant for the reaction if the rate equation is expressed as  $-r_A = - (1/V) dN_A/dt = kC_A^2$ , mol/liter-hr

Answer: (a) The unit for rate constant is

$$k = 3.66 = - (dp_A/dt) / p_A^2 = (\text{atm/hr}) / (\text{atm})^2 = 1/\text{atm-hr} \text{ or } \text{atm}^{-1} \text{ hr}^{-1}$$

(b) We know,  $p_A = C_A R T$  or  $dp_A = (RT) dC_A$ . Then, the given expression becomes  $-(RT) dC_A/dt = 3.66 (C_A R T)^2$  or  $-dC_A/dt = (3.66 R T)C_A^2$   
or  $-r_A = - (1/V) dN_A/dt = -dC_A/dt = (3.66 R T)C_A^2$ .

$$\text{On comparing, we get 'k' } = 3.66 R T = 3.66 (0.0820575) (400) = 120.1322$$

lit/mol-hr

17. On doubling the concentration of a reactant the rate of reaction triples. Find the reaction order.

- We know, the general rate of reaction is  $-r_A = k C_A^n$
- For the given statement, On doubling the concentration of a reactant the rate of reaction triples, the above rate can be written as  $3 (-r_A) = k (2C_A)^n$
- On combining the above rate expressions, we get  $3 = 2^n$  or  $n = \log(3) / \log(2) = 1.585$

18. Give the basis on which chemical reactions and reactors are classified.

- Based on number of phases: Homogeneous & Heterogeneous reactions.
- Based on progress: Reversible & Irreversible reactions.
- Based on stoichiometric equation: Single reaction & multiple reaction (Series & parallel reaction)

19. Differentiate constant volume and variable volume methods of analysis of reactors.

Constant volume method:

- It refers to the volume of reaction mixture, and not the volume of reactor. It actually means a constant density reaction system, that is, the composition of reaction mixture is constant.
- Most of the liquid phase as well as gas phase reactions occurring in a constant volume bomb fall in this class.
- In a constant volume system, the measure of reaction rate of component ' $i$ ' (reactant

or product) becomes  $r_i = (1/V) (dN_i/dt) = dC_i/dt$ .

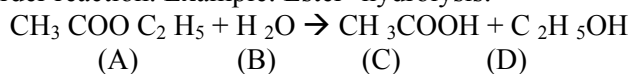
- Conversion of reactant 'A' in this method is given by  $X_A = 1 - (C_A/C_{A0})$ .

Variable volume method:

- It actually means the composition of reaction mixture varies with time by the presence of inerts.
- Gas phase reactions involving the presence of inerts or of impure reactants occurring in a reactor fall in this class.
- The measure of reaction rate of component 'i' (reactant or product), in this method, becomes  $r_i = (C_{i0}/\epsilon_i) [d(\ln V)/dt]$ .
- In variable volume system, the fractional change in volume of the system between the initial and final stage of the reaction will be accounted. Thus, conversion of reactant 'A' becomes  $X_A = [1 - (C_A/C_{A0})] / [1 + \epsilon_A (C_A/C_{A0})]$ .

20. What is a pseudo first order reaction? Give an Example.

A second order rate equation which follows the first order rate equation is defined as pseudo First order reaction. Example: Ester hydrolysis.



When  $C_{B0} \gg C_{A0}$ , Concentration of  $\text{H}_2\text{O}$  is very large,  $-r_A = -dC_A/dt = k' C_A$ .

21. What is a zero order reaction?

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

22. Explain bimolecular reactions with examples.

An irreversible bimolecular-type second-order reaction may fall on two categories;

(1) The reaction  $A + B \rightarrow \text{Products}$  with corresponding rate equation

$$-r_A = - (dC_A/dt) = - (dC_B/dt) = k C_A C_B$$

Here the amounts of A and B that have reacted at any time 't' are equal.

(2) The reaction  $2A \rightarrow \text{Products}$  with corresponding rate equation

$$-r_A = - (dC_A/dt) = k C_A^2$$

Here in practice that the reactant ratios either equal to or widely different from the stoichiometric ratio.

23. Explain third order reaction with example.

An irreversible trimolecular-type third-order reaction may fall on two categories;

(1) The reaction  $A + B + D \rightarrow \text{Products}$  with corresponding rate equation

$$-r_A = - (dC_A/dt) = k C_A C_B C_D.$$

If  $C_{D0}$  is much greater than both  $C_{A0}$  and  $C_{B0}$ , the reaction becomes second order.

(2) The reaction  $A + 2B \rightarrow \text{Products}$  with corresponding rate equation

$$-r_A = - (dC_A/dt) = k C_A C_B^2.$$

24. Write the empirical rate equation of  $n^{\text{th}}$  order.

The empirical rate equation of  $n^{\text{th}}$  order,  $-r_A = -dC_A/dt = k C_A^n$  (constant volume).

Separating the variables and integrating, we get  $C_A^{1-n} - C_{A0}^{1-n} = (n-1) k t$ .

Case i)  $n > 1$ ,  $C_{A0}^{1-n} = (1-n) k t$ . The slope is  $(1-n)$

$k$  is negative Or the time decreases.

Case ii)  $n < 1$ ,  $C_{A0}^{1-n} = (1-n) k t$ . The slope is  $(1-n)$   $k$  is positive.

The rate of the reaction predicts that the reaction will drop to zero at some infinite time which is completion of the reaction ( $C_A = 0$ ).

25. What are autocatalytic Reactions?

A reaction in which one of the products of reaction acts as a catalyst is called autocatalytic reaction. Example:  $A+R \rightarrow R+R$

26. What are multiple reactions? Explain.

When more than one stoichiometric equation is used to represent a reaction and more than one rate equation is required to follow the change in concentration of all the components, the reactions are said to be 'Multiple reactions'. It can be classified as Series, Parallel or Series-Parallel reactions.

27. Give the variables affecting the rate of reaction.

The variables affecting the rate of the reaction are (1) temperature (2) Pressure and (3) Composition of materials involved.

28. What is activation energy?

The excess energy of the reactants required to dissociate into products is known as activation energy.

29. Write Arrhenius Law.

The temperature dependency on the reaction rate constant is given by Arrhenius Law. That is,  $k = k_0 e^{-E/RT}$   
Where  $k$  = rate constant,  $k_0$  = frequency factor,  $E$  = Activation energy

30. Define Half life of the reaction.

The half life of the reaction ' $t_{1/2}$ ' is defined as the time needed for the concentration of reactants to drop to one half its original value.

31. Define Fractional Conversion ' $X_A$ '.

Fractional conversion of a reactant A is defined as fractional reactant converted into product at any time. It is given by the equation,  $X_A = (N_{A0} - N_A) / N_{A0}$   
Where ' $N_{A0}$ ' is the initial no. of moles of reactant 'A' at  $t = 0$ .  
' $N_A$ ' is the remaining no. of moles of reactant at any time 't' in the reaction.

32. For an irreversible gas phase reaction  $2A \rightarrow 3R$ , determine the value of  $\epsilon_A$  if the feed is a mixture of 50% A and 50% inert.

Component	Initial ( $X_A=0$ )	Final ( $X_A=1$ )
A	0.5	0
Inert	0.5	0.5
R	0	$0.5 * 3/2 = 0.75$
<b>Total</b>	<b>1.0</b>	<b>1.25</b>

Therefore,  $\epsilon_A = [V_{X=1} - V_{X=0}] / V_{X=0} = [1.25 - 1.0] / 1.0 = 0.25$

33. Half-life of a first order reaction  $A \rightarrow B$  is 10 min. What percent of A remains after 60 min?

- We know, the performance equation of a first order reaction taking place in the batch reactor as  $-\ln(1 - X_A) = k t$
- Given, at  $t = 10$  min  $X_A = 0.5$  (Half-life). Then, from the above equation, we get  $k = 0.069315$ .
- Thus, at  $t = 60$  min, we get  
Remaining A,  $(1 - X_A) = \exp(-k t) = \exp(-0.069315 * 60) = 0.0156$  or 1.56%

34. For  $(-r_A) = k C_A / (M + C_A)$ , how will you graphically determine 'k' & 'M' from  $C_A$  vs.  $(-r_A)$  data?

- Taking reciprocal of the given expression, we get  $1/(-r_A) = (M/k) (1/C_A) + (1/k)$ .
- Then plot a graph of  $1/(-r_A)$  vs.  $(1/C_A)$ , using the given data, which forms a straight line with slope as  $(M/k)$  and intercept as  $(1/k)$ .
- From the intercept, we get 'k' and (slope/intercept) will give 'M'.

35. The rate equation of a reaction  $2A + B \rightarrow C$  is  $-r_A = k C_A^2 C_B$ . Find the unit of 'k'.

- The given reaction, and from the rate equation, is third order.
- We know, the unit for the rate constant, in general, is
$$k = [\text{time}]^{-1} [\text{concentration}]^{1-n} = [\text{min}]^{-1} [\text{mol/lit}]^{1-3} = \text{lit}^2/\text{mol}^2\text{-min}$$

36. What are the different factors to be considered for reactor design?

The different factors required for reactor design are (i) Size of reactor (ii) Type of reactor (iii) Time or duration of reaction (iv) Temperature & Composition of reacting material in the reactor (v) Heat removal or added and (vi) Flow pattern of fluid in the reactor.

37. What are ideal reactors?

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

38. What is a Batch reactor?

A batch reactor (BR) is one in which reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady state operation where composition changes with time; however at any instant the composition throughout the reactor is uniform.

39. What are the advantages and disadvantages of a batch reactor?

The advantages of a batch reactor are (i) small instrumentation cost and (ii) flexibility of operation.

A batch reactor has the disadvantages of (i) high labour (ii) poor quality control of the product and (iii) considerable shutdown time has taken to empty, clean out and refill.

40. What is a Mixed flow reactor?

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

41. What is a Plug flow reactor?

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

42. Differentiate between MFR and PFR.

MFR: i) there is no concentration gradient within the reactor, since there is uniform mixing.  
ii) Rate of reaction varies with concentration alone.

PFR: i) There is concentration gradient within the reactor in the axial direction, since there is no mixing in this direction.  
ii) Rate of reaction varies with position.

43. Define space time & space velocity.

The time required to process one reactor volume of feed measured at specified conditions is called space time.

Space velocity is defined as the number of reactor volumes of feed at specified

conditions which can be treated in unit time.

44. Explain conservation of mass in reactors.

Rate of accumulation of the component within the system = Rate of flow of a into the system — Rate of flow of A out of the system — Rate of consumption of component a in the system.

45. Write the classification of chemical reactors based on the method of operation and the number of phases in the reaction mixture.

Method of operation: Unsteady state reactors → batch and Semi-batch  
Steady state reactor → Tubular reactor, Back mix

Phases: Homogeneous reactor → Batch, PFR, MFR reactors  
Heterogeneous reactor → Biochemical Reactor

46. What do you mean by a space velocity of  $5 \text{ hr}^{-1}$ ?

In one hour, five reactor volumes of feed at specified conditions are being treated by the reactor.

47. Distinguish between Holding time and Space time for flow reactors.

▪ Holding time: It is the mean residence time of flowing material in the reactor. It is given by the expression  $t = C_{A0} \int dX_A / [(-r_A) (1 + \epsilon_A X_A)]$

▪ Space time: It is the time needed to treat one reactor volume of feed at specified conditions. It is given by the expression  $\tau = V/v_0 = (C_{A0} V) / F_{A0}$

For constant density systems (all liquids and constant density gases)  $t = \tau = V/v$

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

48. Which reactors performance is identical for constant density systems?

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

49. At what situation the ratio of the volume of MFR's to PFR's is greater than unity?

The ratio of the volume of MFR's to PFR's is always greater than unity for identical feed composition ( $C_{A0}$ ), flow rate ( $F_{A0}$ ) and conversion and for all positive reaction orders.

50. Consider a gas phase reaction  $2A \rightarrow R+2S$  with unknown kinetics. If a space velocity of  $1 \text{ min}^{-1}$  is needed for 90% conversion of A in a PFR find the corresponding space time and mean residence time or holding time of the fluid in the reactor.

Given,  $X_A=0.9$ , space velocity= $1 \text{ min}^{-1}$ .

(i) Space time= $1/\text{space velocity}=1 \text{ min}$ .

(ii)  $t_M = V/v_f = V/v_0 (1 + \epsilon_A X_A)$ ; where  $\epsilon_A = (3 - 2)/2 = 0.5$  and  $V/v_0 = 1$

Therefore,  $t_M = V/v_f = V/v_0 (1 + \epsilon_A X_A) = 1/1.45 = 0.6897 \text{ min}$ .

51. A 2<sup>nd</sup> order reaction is to be carried out in 3 CSTR's of Volume 100 lit, 150 lit and 200 lit. Explain how they are connected.

For 2<sup>nd</sup> order ( $n > 1$ ) reaction, to be carried out in CSTR's of different sizes, the reactors should be ordered so as to keep the concentration of reactant as high as possible. This can be performed by arranging them in the ascending order with respect to volume or size. Hence, the best arrangement should be

100 liter ↔ 150 liter ↔ 200 liter

52. Differentiate between PFR's and batch reactors. How would you compare them?

PFR: (i) It is a steady state flow reactor (ii) As space time increases concentration of reactant decreases (iii) Better quality control (iv) For high rate of reaction PFR is employed.

Batch reactor: (i) It is unsteady state reactor (ii) As reaction time increases concentration of reactants decreases (iii) No better quality control (iv) For very slow reactions or low rate of reaction batch reactors are employed.

53. What are steady and unsteady state reactors? Explain.

Steady state reactor

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

Total mass inflow = Total mass outflow

Unsteady state reactor

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

54. What are semi batch reactors? Give the different types.

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

55. Which achieves higher conversion among the flow reactors for identical conditions? Why?

For identical conditions i.e. for same reactor volume conversion achieved in PFR is higher than in MFR. Since in a PFR, all the properties vary gradually along the length of the reactor. Hence concentration is maintained at high value throughout and the rate of reaction is maintained at high value. Therefore Conversion achieved in PFR for same volume is greater or higher than in MFR.

56. Why does rate of reaction vary in a PFR? How does it vary in a MFR?

Rate of reaction varies, for isothermal reactions, in PFR as there is no mixing in the axial direction since rate of reaction is directly proportional to concentration. As concentration of reactant varies with distance rate of reaction also varies.

In PFR, rate of reaction is independent of time and dependent on position or distance.

In MFR, rate of reaction is independent of position & depends on concentration of reactants.

57. Which reactors are most suitable for very high pressure gas phase reaction and for isothermal operation?

Tubular flow reactor is most suitable for very high pressure gas phase reaction and Back-mix reactor is most suitable for isothermal operation.

58. What are the operating conditions for an exothermic reversible reaction-taking place in a plug-flow reactor? Give the uses of PFR.

The operating conditions for an exothermic reversible reaction-taking place in a PFR are the temperature should be high in the beginning and decreased towards end of the reaction. Uses of PFR: (i) For reactions where the reaction rate is fairly to extremely high, (ii) For large scale production, and (iii) For good quality control.

59. For two CSTR's operating in series, state the principle involved to determine the minimum volume of reactors. Given, feed concentration is  $C_{A0}$  and final concentration is  $C_{A2}$ . The reaction is first order.

For a system of two CSTR's connected in series, in which first order reaction is taking place and for the given conversion, the minimum volume of reactors will be obtained when both the reactors are operated with equal volume. This was obtained by using the



minimum concentration of 'A' as  $C_{A, \text{MIN}} = \text{SQRT}(C_{A0} C_{A2})$  in the performance equation.

60. How does intermediate conversion affect the volume of the multiple reactor system for single reactions?

Intermediate conversion affects the volume of the multiple reactor system for single reactions in case of MFR only. In case of PFR intermediate conversion does not determine the total reactor volume; in the case of PFR's whatever be the intermediate conversion the total reactor volume required to achieve a given conversion is identical. In case of MFR, there is a particular intermediate conversion.

At this conversion the total volume of the reactor required is minimum. This conversion is called as "the best intermediate conversion". If the intermediate conversion is changed the size ratio and volume of the units will change.

61. A large CSTR, small CSTR and PFR of fixed volume are available. In general, how would you arrange them for getting maximum conversion for reactions of order  $>1$  and  $<1$ . Why?

- For  $n > 1$  arrangement is PFR followed by small CSTR followed by large CSTR to maintain the reactant concentration as high as possible.
- For  $n < 1$  arrangement is large CSTR followed by small CSTR followed by PFR.
- For  $n = 1$  arrangement for first order reaction sequencing does not affect conversion. It can be either PFR followed by MFR or MFR followed by PFR.

62. If  $1/(-r_A)$  versus  $X_A$  graph decreases to a minimum from  $X_A = 0$  to  $X_A = 0.4$  and then increases, suggest a multiple reactor system with minimum volume for a desired conversion of  $X_A = 0.6$ .

For the given situation, the best reactor setup should be PFR followed by CSTR. That is, PFR should be operated up to the point of minimum (up to  $X_A = 0.4$ ) followed by a CSTR to fulfill the desired conversion ( $X_A = 0.6$ ).

Because minimum the area under the curve of  $1/(-r_A)$  versus  $X_A$  will lead to the minimum volume for the desired conversion. This was obtained only by the above said reactor arrangement.

63. What is a Recycle reactor?

In some reaction system, it is advantageous to divide the product stream and a part returned to reactor as recycle to increase the conversion rate. These reactors are called recycle reactors. The recycling provides a means for obtaining various degree of backmixing.

64. Define Recycle ratio and give its significance

Recycle ratio 'R' can be defined as the ratio of the volume fluid returned to the reactor entrance to the volume of fluid leaving the system or reactor.

Significance: Recycle ratio can be made to vary from zero to infinity. Reflection suggests that as the recycle ratio is raised, the behavior shifts from plug flow ( $R = 0$ ) to mixed flow ( $R = \infty$ ).

65. When will the recycle reactor behave like a CSTR?

When the recycle ratio 'R' becomes or tends to infinity ( $R = \infty$ ), the recycle reactor behaves like a CSTR.

66. What do you mean by optimum recycle operation?

When material is to be processed to some fixed final conversion in a recycle reactor, there must be a particular recycle ratio 'R' that minimizes the reactor volume or space time. That recycle ratio is said to be optimum and the operation is said to be optimum recycle

operation.

67. Suggest the most suitable reactor setup for all autocatalytic reactions.

The most suitable reactor setup for autocatalytic reactions is MFR operating at the point of maximum rate (low conversion) followed by a PFR (high conversion); that is, MFR operating to maximum rate followed by PFR. Because this will lead to a system with minimum volume for a desired conversion.

68. Define instantaneous and overall fractional yield.

Instantaneous fractional yield ( $\phi$ ) is the ratio of moles of desired product formed at any instant to moles of reactant (A) reacted at any instant. ' $\phi$ ' is a function of  $C_A$ . As  $C_A$  varies throughout the reactor, ' $\phi$ ' will also vary with position in the reactor.

Overall fraction yield ( $\bar{\phi}$ ) is the mean of the instantaneous fractional yields at all points within the reactor.

Both the yields depend on the type of flow within the reactor.

69. Explain the term "Selectivity" and "Yield".

Selectivity is defined as the ratio of moles of desired product to moles of undesired product.

Yield is defined as the ratio of moles of product formed to moles of reactant either fed or consumed.

70. What are the factors affected by the pattern of flow within the vessel for multiple reactions?

The factors affected by the pattern of flow within the vessel for multiple reactions are (i) The Volume of the vessel, (ii) The product distribution, (iii) Selectivity and yield of product.

71. How will you control the product distribution for reactions in parallel using  $k_2/k_1$ ?

The product distribution for reactions in parallel can be controlled by varying the ratio  $k_2/k_1$  (ratio of the rate constants of the formation of undesired product to the desired product). This can be done in two ways;

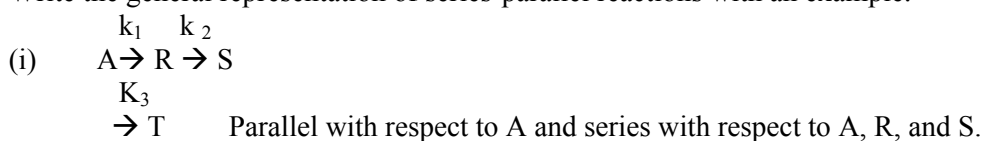
- By changing the temperature level of operation. (If the activation energy of the two reactions are different,  $k_2/k_1$  can be made to vary.)
- By using a catalyst. (One of the most important features of catalyst is its selectivity in depressing or accelerating specific reactions. This may be a much more effective way of controlling product distribution than any other way.)

72. How does the concentration level of reactants affect the product distribution in parallel reactions?

For reactions in parallel, the concentration level of reactants is the key to proper control of product distribution. That is,

- i) High reactant concentration favors the reaction of higher order.
- ii) Low reactant concentration favors the reaction of lower order.
- iii) The concentration level has no effect on the product distribution for reactions of the same order.

73. Write the general representation of series-parallel reactions with an example.



- (ii)  $A + B \rightarrow R$  and  $R + B \rightarrow S$   
 Parallel with respect to B and Series with respect to A, R, and S.

74. Explain the best operating conditions for parallel reactions.

For a desired conversion, the best operating condition for parallel reactions is that the reaction should be performed in the MFR first, up to the maximum yield with respect to the concentration of reactant in the  $\phi(S/A)$  versus  $C_A$ , and the followed by a PFR up to the desired conversion. Here, 'S' is the desired product.

75. For the parallel reactions

$$\begin{array}{ll} A \rightarrow R & r_R = 1 \\ A \rightarrow S & r_S = 2 C_A \\ A \rightarrow T & r_T = C_A^2 \end{array}$$

with  $C_{A0} = 2$  gmol/lit. What will be the frac. Yield of S when fractional conversion of A is 0.5?

- For the given parallel reaction, the instantaneous fraction yield of 'S' with respect to 'A' is  $\phi(S/A) = dC_S / (dC_A + dC_S + dC_T) = 2 C_A / (1 + 2 C_A + C_A^2) = 2 C_A / (1 + C_A)$
- Given,  $X_A = 0.5$  or  $C_A = C_{A0} (1 - X_A) = 2 (1 - 0.5) = 1$  gmol/lit. Thus,  
 $\phi(S/A) = 2 (1) / (1 + 1)^2 = 2 / 4 = 0.5$

76. For the reactions  $A + B \rightarrow R$  &  $R + B \rightarrow S$  A & B are mixed in a Batch reactor. What is the maximum concentration of R you obtain?

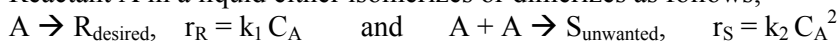
For the given series - parallel reactions, the maximum concentration of 'R', obtained in the batch reactor, is

$$\begin{array}{ll} C_{R, \max} / C_{A0} = [k_1/k_2]^{k_2/(k_2-k_1)} & k_2/k_1 \neq 1 \\ C_{R, \max} / C_{A0} = 1/e = 0.368 & k_2/k_1 = 1 \end{array}$$

77. For the first order reactions  $A \xrightarrow{k_1} R \xrightarrow{k_2} S$ , if  $k_1 = 0.5$  and  $\tau_{opt, CSTR} = 10$  secs, calculate  $\tau_{opt, PFR}$ .

- We know, for first order reactions in series - taking place in a CSTR, the expression for optimum space time is  $\tau_{opt, CSTR} = 1 / \text{SQRT}(k_1 k_2)$ .
- Given,  $k_1 = 0.5$  &  $\tau_{opt, CSTR} = 10$  secs. Using this given data, from the above expression, we have  $k_2 = 1 / (k_1 \tau_{opt, CSTR}^2) = 1 / [(0.5) (10^2)] = 0.02$
- We know, for first order reactions in series - taking place in a PFR, the expression for optimum space time is  $\tau_{opt, PFR} = \ln(k_2/k_1) / (k_2 - k_1)$ .
- Using the given value for 'k<sub>1</sub>' and the determined value of 'k<sub>2</sub>', the above expression yields  $\tau_{opt, PFR} = \ln(0.02/0.5) / (0.02 - 0.5) = 6.706$  secs.

78. Reactant A in a liquid either isomerizes or dimerizes as follows;

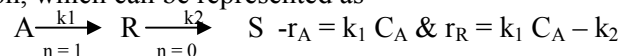


Write  $\phi(R/A)$  and  $\phi[R/(R + S)]$ .

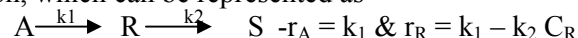
- For the given parallel reaction, the instantaneous fractional yields  
 $\phi(R/A) = \phi[R/(R + S)] = dC_R / (dC_R + dC_S) = k_1 C_A / (k_1 C_A + k_2 C_A^2) = k_1 / (k_1 + k_2 C_A)$

79. Explain "First-order reaction followed by Zero-order reaction" and vice-versa.

- "First-order reaction followed by Zero-order reaction" – It is a special case of series reaction, which can be represented as



- "Zero-order reaction followed by First-order reaction" – It is a special case of series reaction, which can be represented as



80. Explain qualitatively how to maximize the desired product in series reactions.

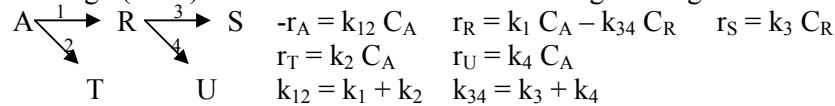
- For irreversible reactions in series the mixing of fluid of different composition is the key to the formation of intermediate, the desired reaction product. The maximum possible amount of any and all intermediates is obtained if fluids of different compositions and at different stages of conversion are not allowed.
- This also allows us to evaluate the effectiveness of various reactor systems. For example, plug flow and batch operations should both give a maximum R (the intermediate) yield because here there is no mixing of fluid streams of different compositions. On the other hand, the mixed reactor should not give as high a yield of R as possible because fresh stream of pure A (the reactant) is being mixed continually with an already reacted fluid in the reactor.

81. Give the application of irreversible series - parallel reactions.

- The field of polymerization affords an opportunity for a fruitful application of series - parallel reactions.
- Often hundreds or even thousands of reactions in series occur in the formation of polymers, and the type of cross linking and molecular weight distribution of these products depends on the physical and chemical properties of the products.
- For such reactions, PFR will yield a higher maximum concentration of any intermediate than does a MFR.

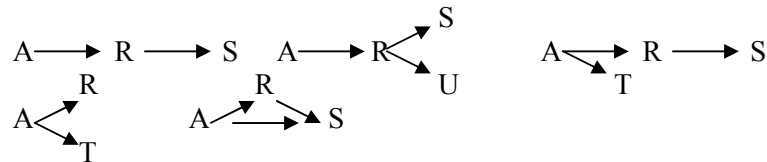
82. What are Denbigh reactions? Explain its special cases.

- Denbigh (1958) was the first to treat the following rather general reaction scheme



$$\text{With } C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0} = C_A + C_R + C_S + C_T + C_U$$

- The performance equation for this reaction scheme reduce directly to all the special cases, such as



- This scheme has wide application to a whole host of real reacting systems. These rate equations are all of first order and so to development of the performance expressions do not involve complex mathematics, although it may be a tedious task.

83. State the three step procedure of the selection of favorable system for any reaction.

- First, we must find how equilibrium composition, rate of reaction, and product distribution are affected by changes in operating temperature and pressures. This will allow us to determine the optimum temperature progression, and it strives to approximate with a real design.
- Second, chemical reactions are usually accomplished by heat effects, and we must know how these will change the temperature of favorable reactor and heat exchange systems – those which closely approach to optimum.
- Finally, economic considerations will select one of these favorable systems as the best.

84. What do you mean by heat of reaction?

The heat of reaction is the heat absorbed (or) evolved during the course of reaction and it is equal to the change in the enthalpy of the system for the reaction proceeding at constant pressure.

85. Explain Le-chatelier's principle.

If a system in equilibrium is subjected to a change in temperature, pressure or concentration the equilibrium of the reaction will shift in the direction, which tends to undergo the effect of the change impressed. This is known as Le-chatelier's Principle.

86. Give the relationship between standard free energy and equilibrium constant.

The relationship between standard free energy and equilibrium constant is given by

$$\Delta G^{\circ} = - R T \ln(K)$$

Where  $\Delta G^{\circ}$  is the std. free energy change of the reaction.

'K' is the equilibrium constant of the reaction.

'T' is the reaction temperature.

'R' is the universal gas constant.

87. What do you mean by equilibrium conversion?

It is the conversion obtained in the reactor with minimum ' $\Delta G$ ' (Gibb's free energy change) of the reaction.

88. What are the factors which affect the equilibrium conversion in chemical reaction?

The factors which affect the equilibrium conversion in chemical reaction are

(i) Temperature (ii) Pressure (iii) presence of inert (iv) presence of excess reactant and (iv) activities of reactants and products

89. What is the effect of pressure on equilibrium conversion?

The thermodynamic equilibrium constant is unaffected by the pressure of the system; though it is unaffected by the pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.

90. What is the effect of temperature on equilibrium conversion?

- The equilibrium conversion or composition, as governed by the equilibrium constant, changes with temperature, and from the thermodynamics the rate of change is given by

$$d(\ln K) / dT = \Delta H_r / (R T^2) \quad [\text{Van't Hoff equation}]$$

- When the heat of reaction  $\Delta H_r$  can be considered to be constant in the temperature interval, integration of the above equation yields

$$\ln (K_2 / K_1) = - (\Delta H_r / R) [(1/T_2) - (1/T_1)]$$

- This expression allows us to find the variation of the equilibrium constant, hence, equilibrium conversion, with temperature.

91. Give the conclusions drawn from thermodynamics for single reactions.

The following conclusions may be drawn from the thermodynamics;

- The thermodynamic equilibrium constant is unaffected by the pressure of the system, by the presence or absence of inerts, or by the kinetics of the reaction, but is affected by the temperature of the system.
- Though the thermodynamic equilibrium constant is unaffected by the pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.
- $K \gg 1$  indicates that practically complete conversion may be possible and that the reaction can be considered to be irreversible.  $K \ll 1$  indicates that reaction will not proceed to any appreciable extent.
- For an increase in temperature, equilibrium conversion rises for endothermic reactions and drops for exothermic reactions.

- For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction.
- A decrease in inerts for all reactions acts in the way that an increase in pressure acts for gas reactions.

92. Write short notes on Optimum temperature progression.

- Optimum temperature progression is the progression which minimizes  $(V / F_{A0})$  for a given conversion of reactant.
- This optimum may be an isothermal or it may be a changing temperature: in time for a batch reactor, along the length of a PFR, or from stage to stage for a series of MFR's.
- The optimum temperature progression in any type of reactor, at any composition, will always be at the temperature where the rate is a maximum.
- It is important to know this progression because it is the ideal which we try to approach with a real system. It also allows us to estimate how far any real system departs from the ideal.

93. How will you determine the size of reactor required for a given duty and for a given temperature progression?

The size of reactor required for a given duty and for a given temperature progression is determined as follows;

- Draw the reaction path on the  $X_A$  vs.  $T$  plot. This is the operating line for the given operation.
- Find the rates at various  $X_A$  along this path.
- Plot the  $1/(-r_A)$  vs.  $X_A$  curve for this path.
- Find the area under this curve, with respect to the given or desired conversion. This gives  $V/F_{A0}$  or  $\tau/C_{A0}$ .

94. Explain adiabatic operations of flow reactors.

In adiabatic operations, there is no heat interchange with surroundings. The conversion can be defined as the ratio of heat needed to raise the feed stream to  $T_2$  to the heat released by reaction at  $T_2$ . Thus,

$$X_A = C_p \Delta T / (-\Delta H_{r2}),$$

For complete conversion,  $-\Delta H_{r2} = C_p \Delta T$

Where  $C_p$  is the mean specific heat of either unreacted feed stream or of completely converted product stream per mole of entering reactant 'A';  $\Delta T = (T_2 - T_1)$ ;  $T_1$  &  $T_2$  are the temperatures of the entering and leaving streams.

95. How will you find the best reactor type for adiabatic operations?

The best reactor type for adiabatic operations, which minimizes  $V/F_{A0}$ , is found directly from the  $X_A$  vs.  $T$  graph.

- If the rate progressively decreases with conversion, then use plug flow. This is the case for endothermic reactions and close to isothermal exothermic reactions.
- For exothermic reactions that have a large temperature rise during reaction, the rate rises from a very low value to a maximum at some intermediate  $X_A$ , then falls. This behaviour is characteristic of autocatalytic reactions, thus recycle operations are best.
- The slope of the operating line,  $C_p/(-\Delta H_r)$ , will also determine the best reactor type for adiabatic operations as;
  1. For small  $C_p/(-\Delta H_r)$ , pure gaseous reactants, mixed flow is best.
  2. For large  $C_p/(-\Delta H_r)$ , gas with much inerts, or liquid systems, plug flow is best.

96. Explain Non-adiabatic operations of flow reactors.

In non-adiabatic operations, heat interchange with the surroundings will be accounted. The conversion can be defined as the ratio of the net heat still needed after heat transfer to raise the feed to  $T_2$  to the heat released by reaction at  $T_2$ . Thus,

$$X_A = (C'_p \Delta T - Q) / (-\Delta H_{r2})$$

Where  $C'_p$  is the mean specific heat of either unreacted feed stream or of completely converted product stream per mole of entering reactant 'A';  $\Delta T = (T_2 - T_1)$ ;  $T_1$  &  $T_2$  are the temperatures of the entering and leaving streams & 'Q' is the heat interchange to the surroundings per mole of entering reactant 'A'.

97. For an adiabatic flow reactor, fractional conversion  $X_A$  is usually calculated by  $X_A = C'_p (T_2 - T_1) / (-\Delta H_{r2})$ . State on what basis this equation is derived and what does each term denote.

- This equation was derived on the basis that the reactant 'A' has been taken as limiting reactant.
- $C'_p$  is the mean specific heat of unreacted feed stream per mole of entering reactant 'A'.
- $(-\Delta H_{r2})$  is the heat released by the reaction per mole of entering reactant 'A' at  $T_2$ .
- $T_1$  &  $T_2$  are the temperatures of the entering and leaving streams.

98. What is the conversion you expect from an adiabatic CSTR with the following operating condition:  $A \rightarrow R$ ; specific heat of pure feed 100 J/gmol-°C, heat of reaction = -20 KJ/gmol; Feed Temperature 30°C; operating temperature 150°C.

- We know, for an adiabatic flow reactor, fractional conversion  $X_A$  is usually calculated by  $X_A = C'_p (T_2 - T_1) / (-\Delta H_{r2})$
- Given  $C'_p = 100$  J/gmol-°C,  $-\Delta H_{r2} = -20$  KJ/gmol = -20000 J/gmol,  $T_1 = 30^\circ\text{C}$  and  $T_2 = 150^\circ\text{C}$ .
- Using this given data in the above expression, we get  

$$X_A = [100 (150 - 30)] / (20000) = 0.6 \text{ or } 60\%.$$

99. What are 'limit cycles' and 'Oscillating reactions'?

Limit cycle:

- It is an enclosed boundary for stable operation of any reactor, based on the mole fraction of reacting fluid with temperature.
- Limit cycle may also enclose a point of unstable equilibrium.
- The progress of reactor with time for mildly exothermic reaction could be controlled in a limit cycle of a period of a few minutes.

Oscillating reactions:

- Suppose an exothermic reaction is taking place in a CSTR, the progress of the reaction may exhibit a sustained oscillation with respect to time. Such behaviour of reactions is said to be 'Oscillating reactions'.
- This type of behavior has recently become more widely recognized; it can occur in many catalytic systems.
- In biological phenomena, oscillatory solutions are often positively preferred.

100. What do you mean by 'Parameter sensitivity' in flow reactors?

- Parameter sensitivity is defined as the situation where a small change in the operating variables leads to a very large change in the behaviour of the reactor.
- Usually the heat transfer parameters and the degree of dilution of the reaction mixture are very sensitive with respect to temperature (reacting fluid temperature) changes.
- For example, if the useful reaction is accompanied with exothermic degradation process, it will be evident that the onset of this process may occur rather quickly if the sensitive parameter exceeds a certain values.

- Nevertheless it may be necessary for this parameter to be kept close to its critical value in order to achieve an acceptable yield from the useful reaction. This may well occur in partial oxidation processes, and in such instances a CSTR can have advantages over a PFR.

## PART-B QUESTIONS

### UNIT-I

#### A. Searching For Mechanism:

1. The primary reaction occurring in the homogeneous decomposition of Nitrous Oxide is found to be  $N_2O \rightarrow N_2 + 1/2O_2$  with rate  $-r_{N_2O} = k_1 [N_2O]^2 / (1 + k_2[N_2O])$ . Devise a mechanism to explain the observed rate.
2. Experiment shows that the homogeneous decomposition of Ozone proceeds with a rate,  $-r_{O_3} = k[O_3]^2 [O_2]^{-1}$   
(a) What is the overall order of the reaction? (b) Suggest a two-step mechanism to explain this rate and state how you would further test this mechanism.
3. The decomposition of reactant A at 400°C for pressures between 1 and 10 atm follows a first-order rate law. Show that the mechanism,  $A + A \rightleftharpoons A^* + A$  &  $A^* \rightarrow R + S$  is consistent with observed kinetics. **(Dec-2003-Bio & May-2006-Bio)**
4. Discuss the theory of intermediate in explaining the kinetics of non-elementary reactions. What are the various intermediates suggested for this approach? **(May-2005)**

#### B. Temperature Dependency-Arrhenius Equation:

1. At 500K the rate of a bimolecular reaction is ten times the rate at 400K. (a) Find the activation energy of this reaction from Arrhenius theory and Collision theory. (b) What is the percentage difference in rate of equation at 600K predicted by these two methods? **(May-2005)**
2. (i) Pyrolysis of Ethane proceeds with an activation energy of 70000 calories. How much faster is the decomposition at 650°C than at 500°C? **(Dec-2004 & 2005-Bio)**  
(ii) Milk is pasteurized if it is heated to 63°C for 30 minutes, but if it is heated to 74°C it only needs 15 seconds for the same result. Find the activation energy for this sterilization. **(May-2006-Bio)**
3. Calculate the activation energy for the decomposition of benzene-diazonium-chloride to give chlorobenzene and nitrogen, first order reaction, using the following data;

k (sec <sup>-1</sup> )	0.00043	0.00103	0.0018	0.00355	0.00717
T (Kelvin)	313	318	323	328	333

Also find the rate equation.

4. In the mid-nineteenth century the entomologist Henri Fabre noted that French ants (garden verity) busily bustled about their business on hot days but were rather sluggish on cool days. Checking his results with Oregon ants, I find

Running speed, m/hr	150	160	230	295	370
Temperature, °C	13	16	22	24	28



What activation energy represents this change in bustliness?

5. Determine the activation energy and the frequency factor from the following data for the bimolecular formation of methyl ethyl ether. Also find the rate equation.

Temperature, °C	0	6	12	18	24	30
$K \times 10^5$ , lit/gmol-sec	5.6	11.8	24.5	48.8	100	208

C. Batch Reactor

Kinetics:

1. Explain the Integral and Differential method of analysis for finding the rate of reaction. **(May-2005)**
2. For the elementary reaction in series  $A \xrightarrow{k_1} R \xrightarrow{k_2} S$  if  $k_1 = k_2$  and at  $t = 0$ ,  $C_A = C_{A0}$  and  $C_{R0} = C_{S0} = 0$ , find the maximum concentration of R. **(May-2004)**
3. A zero order homogeneous gas reaction  $A \rightarrow r R$  proceeds in a constant volume reactor with 20% inerts and pressure rises from 1 atm to 1.3 atm in 2 minutes. If the same reaction takes place in a constant pressure batch reactor, What is the fractional change in volume in 4 minutes if the feed is at 3 atm and consists of 40% inerts? **(May-2004)**
4. The gaseous reaction  $2A \rightarrow R + 2S$  is second order with respect to 'A'. If pure 'A' is introduced at 1atm into a constant volume batch reactor, the pressure rises by 40% in 3 minutes. In case of a constant pressure batch reactor, find the (i) time require4d for the same conversion and (ii) fractional increase in volume at that time. **(Dec-2004 & Dec-2005)**
5. (i) In case of a first order irreversible reaction. Show that the time required for 75% conversion is double the time required for 50% conversion.  
(ii) For the aqueous reaction  $A \rightarrow$  Products, the following data were obtained at 25°C in which the concentration of 'A' is given at different intervals of time.

t (min)	0	10	20	30	40
$C_A$ (mol/lit)	0.86	0.74	0.635	0.546	0.405

Find the reaction order & calculate the rate constant and half-life period. **(Dec-2004)**

6. (i) Prove that  $t_{i/m} = [(m^{n-1} - 1) (C_{A0})^{1-n}] / [(n - 1) k]$ . Where ' $t_{i/m}$ ' is the time required for the reactant concentration to drop to  $(1/m)^{th}$  of its original value, ' $C_{A0}$ ' is the initial concentration of the reactant, ' $n$ ' is the order of the reaction and ' $k$ ' is the specific reaction rate. **(Dec-2004)**  
(ii) The decomposition of pure  $NH_3$  on tungsten wire at 856°C gave the following results;

Total pressure, mmHg (or) torr	228	250	273	318
Time, seconds	200	400	600	1000

Determine the reaction order and evaluate the rate constant in terms of moles, liters and seconds. **(Dec-2004 & Dec-2005)**

7. The first order reversible liquid reaction,  $A \rightleftharpoons R$ ,  $C_{A0} = 0.5$  mol/liter,  $C_{R0} = 0$ , takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction. **(Dec-2005)**
8. For the series reaction  $A \xrightarrow{k_1} R \xrightarrow{k_2} S$ , it is observed that the first step follows a first order kinetics while second step follows a zero order kinetics. If this reaction takes place in a batch reactor with  $C_{R0} = C_{S0} = 0$ , show that  $t_{R,max} = (1/k_1) \ln [(k_1 C_{A0})/k_2]$  and also  $C_{R,max}/C_{A0} = 1 - [k_2/(k_1 C_{A0})] \{1 - \ln [k_2/(k_1 C_{A0})]\}$ . Where ' $k_1$ ' and ' $k_2$ ' are rate constants,  $t_{R,max}$  is the time at which the maximum concentration of 'R' is obtain and  $C_{R,max}$  is the maximum concentration of 'R'. **(Dec-2005)**

9. The acetylation of Benzyl chloride in dilute solution at 102°C was studied. Equi-molal concentrations of Sodium acetate and Benzyl chloride ( $0.757\text{k-mol/m}^3$ ) were used. The following data on the fraction Benzyl chloride remaining with time was reported. **(May-2006)**

t, k-sec	10.80	24.48	46.08	54.72	69.48	88.56	109.44	126.72	133.74	140.76
$(\text{C}_6\text{H}_5\text{CH}_2\text{Cl})/(\text{C}_6\text{H}_5\text{CH}_2\text{Cl})_0$	0.945	0.912	0.846	0.809	0.779	0.730	0.678	0.638	0.619	0.590

Determine the order of the reaction and the reaction rate constant at this temperature.

10. Addition of HI to cyclohexane in benzene was studied. The reaction is believed to be first order in each reactant and second order overall. The following data were reported for their experiments at 20°C using an iodine concentration of  $0.422 \times 10^{-3} \text{ k-mol/m}^3$ .

time, sec	0	150	480	870	1500	2280
$C_{\text{HI}}, \text{ k-mol/m}^3$	0.106	0.099	0.087	0.076	0.062	0.050

The initial cyclohexane concentration was  $0.123 \text{ k-mol/m}^3$ . Are these data consistent with the proposed rate expression? If so determine the reaction rate constant. **(May-2006)**

11. Find the overall order of the irreversible reaction  $2\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$  from the following constant volume data using equi-molar amounts of hydrogen and nitric oxide;

Total pressure, mmHg	200	240	280	320	360
Half life, sec	265	186	115	104	67

12. Aqueous A at a concentration  $C_{A0} = 1 \text{ mol/lit}$  is introduced into a batch reactor where it reacts away to form product R according to stoichiometry  $\text{A} \rightarrow \text{R}$ . The concentration of A in the reactor is monitored at various rates as shown below;

t (min)	0	100	200	300	400
$C_{\text{A}}$ ( $\text{mol/m}^3$ )	1000	500	333	250	200

For  $C_{A0} = 500 \text{ mol/m}^3$  find the conversion of reactant after 5 hours in the batch reactor. Find the rate for the reaction also. **(Dec-2003-Bio)**

13. The aqueous reaction  $\text{A} \rightarrow \text{R} + \text{S}$  proceeds as follows;

t, min	0	36	65	100	160	$\infty$
$C_{\text{A}}, \text{ mol/lit}$	0.1823	0.1453	0.1216	0.1025	0.0795	0.0494

With  $C_{A0} = 0.1823 \text{ mol/liter}$ ,  $C_{R0} = 0$  and  $C_{S0} = 55 \text{ mol/liter}$ , find the rate equation for this reaction. **(Dec-2004-Bio & May-2005-Bio)**

14. (i) Explain the total pressure method of finding reaction rates.  
(ii) A 10 minute experimental run shows that 75% of liquid reactant is converted to product by a  $\frac{1}{2}$  order rate. What would be the amount converted in a half-hour run? **(May-2005-Bio)**

15. From the first principles, derive an expression for the maximum concentration of intermediate and time at which it occurs for a series reaction  $\text{A} \xrightarrow{k_1} \text{R} \xrightarrow{k_2} \text{S}$   
**(Dec-2005-Bio)**

16. A Small reaction bomb fitted with a sensitive pressure-measuring device is flushed out and filled with pure reactant A at 1atm. Pressure. The operation is carried out at 25°C, a temperature low enough that the reaction does not proceed to any appreciable extent. The temperature is then raised as rapidly as possible to 100°C and the following readings are recorded. The stoichiometry of the reaction is  $2\text{A} \rightarrow \text{B}$  and after leaving the bomb in the bath over the weekend the contents are analyzed for A, none can be found. Find a rate equation which will satisfactorily fit the data;

t, min	1	2	3	4	5	6	7	8	9	10	5	10
$\pi$ , atm	1.14	1.04	0.982	0.940	0.905	0.870	0.850	0.832	0.815	0.800	0.754	0.728

17. The following data are obtained at 0°C in a constant-volume batch reactor using pure gaseous A;

t, min	0	2	4	6	8	10	12	14	$\infty$
$p_A$ , mmHg	760	600	475	390	320	275	240	215	150

The stoichiometry of the decomposition is  $A \rightarrow 2.5 R$ . Find a rate equation. **(May-2006-Bio)**

## UNIT-II

### A. For Single Reactions:

- Derive the performance equation for (i) Plug flow reactor and (ii) Mixed flow reactor. **(May-2004, May-2005, Dec-2004-Bio & Dec-2005-Bio)**
- We are planning to operate a batch reactor to convert A into R. This is a liquid reaction, the stoichiometry is  $A \rightarrow R$ , and the rate of reaction is given in the table.

$C_A$ , mol/liter	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.3	2.0
$-r_A$ , mol/lit-min	0.1	0.3	0.5	0.6	0.5	0.25	0.10	0.06	0.05	0.045	0.042

- How long must we react each batch for the concentration drop from 1.3 mol/liter to 0.3 mol/liter?
  - What size of PFR is needed for 80% conversion of 1000 moles of A/hour feed at  $C_{A0} = 1.3$  mol/liter. **(May-2004, May-2005 & May-2004-Bio)**
- Assuming a stoichiometry of  $A \rightarrow R$  for a first order gas phase reaction, the volume of a PFR for 99% conversion of pure 'A' is calculated to be 32 liters. In fact the reaction stoichiometry is  $A \rightarrow 3R$ . With this corrected stoichiometry, determine the reactor volume required for the same conversion.
    - In an isothermal batch reactor in which a first order irreversible aqueous reaction takes place, 70% of reactant 'A' is converted in 13 minutes. Find the space time and space velocity required to effect the same in a PFR and in a MFR. **(Dec-2004)**
  - A gas phase reaction  $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$  has the following rate constants at 600K;  $k_1 = 500$  lit/mol-hr and  $k_2 = 0.032$  hr<sup>-1</sup>. If a PFR is to be fed at a rate of 600 m<sup>3</sup>/hr a gas mixture containing 60% Br<sub>2</sub>, 30% C<sub>2</sub>H<sub>4</sub> and 10% inerts by volume at 600K and 1.5 atm, calculate (i) the maximum possible fractional conversion of C<sub>2</sub>H<sub>4</sub> to C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> and (ii) the volume of the reaction vessel required to get 60% of this maximum conversion. **(Dec-2204)**
  - An aqueous phase reaction with a stoichiometry  $A \rightarrow 2R$  is carried out in a CSTR with a volume of 5 liters and the following data are obtained.

Run	Feed rate (cm <sup>3</sup> /sec)	Temperature of the run (°C)	Conc. of R in the effluent (mol/lit)
1	2	13	1.8
2	15	13	1.5
3	15	84	1.8

Find the rate equation for this reaction and also evaluate the activation energy of the reaction, assuming the applicability of Arrhenius law. **(Dec-2005)**

- The elementary gas phase reaction  $A_3 \rightarrow 3A$  is carried out in a PFR. The rate constant at 50°C is 10<sup>-1</sup> min<sup>-1</sup> and the activation energy is 85 kJ/mol. Pure A<sub>3</sub> enters the reactor at

10 atm and 127°C and a molar flow rate of 2.5 mol/min. Calculate the space time required to achieve 90% conversion of A<sub>3</sub>. Assume the applicability of Arrhenius law. **(Dec-2005)**

7. An alcohol 'A' and an acid 'B' are fed to a CSTR in equi-molal proportions. The mechanistic and stoichiometric equation for the reaction is  $A + B \rightleftharpoons E + H_2O$ . Where 'E' is the ester produced by the reaction. The reaction occurs at a constant temperature in an acetone solution of these species. The extent of reaction is limited by equilibrium conditions. Neglect volume change on the reaction. The following two data have been reported;

Space velocity k-sec <sup>-1</sup>	33	67.65
Fraction conversion of acid	0.50	0.40

What is the equilibrium degree of conversion? **(May-2006)**

8. Acetaldehyde is to be decomposed in a tubular reactor operating at 520°C and 101 kPa. The reaction stoichiometry is  $CH_3CHO \rightarrow CH_4 + CO$ . Under these conditions the reaction is known to be irreversible with a rate constant of 0.43 m<sup>3</sup>/kmol-sec. If 0.1 kg/sec of acetaldehyde is fed to the reactor, determine the reactor volume necessary to achieve 35% decomposition. **(May-2006)**
9. Pure gaseous reactant 'A' (C<sub>A0</sub> = 100 millimol/liter) is fed at steady state into a mixed reactor (V = 0.1 liter) where it dimerizes as  $2A \rightarrow R$ . For different gas feed rates the following data were obtained;

v <sub>0</sub> , liter/hr	30	9.0	3.6	1.5
C <sub>A</sub> , mol/liter	85.7	66.7	50	33.3

Find a rate equation for this reaction.

10. A high molecular weight Hydrocarbon gas is fed continuously to a heated high temperature mixed reactor where it thermally cracks (homogeneous gas reaction) into lower molecular weight materials collectively called R by a stoichiometry approximated by  $A \rightarrow 5R$ . By changing the feed rate different extents of cracking are obtained as follows:

F <sub>A0</sub> , m-mol/hr	300	1000	3000	5000
C <sub>A,out</sub> , m-mol/liter	16	30	50	60

The internal void volume of the reactor is V=0.1 liter and at the temperature of the reactor the feed concentration is C<sub>A0</sub> = 100 millimol/lit. Find a rate equation to represent the cracking reaction.

11. The data in the following table have been obtained on the decomposition of gaseous reactant A in a constant vol. batch reactor at 100°C.

t, sec	0	20	40	60	80	100	140	200	260	330	420
p <sub>A</sub> , atm	1.00	0.80	0.68	0.56	0.45	0.37	0.25	0.14	0.08	0.04	0.02

The stoichiometry of the reaction is  $2A \rightarrow R+S$ . What size PFR (in liters) operating at 100C and 1 atm can treat 100 mol A / hour in a feed consisting of 20% inerts to obtain 95% conversion of A.

12. A homogeneous liquid phase reaction  $A \rightarrow R$ ,  $-r_A = k C_A^2$ , takes place with 50% conversion in a mixed reactor.  
 (a) What will be the conversion, if one 6 times as large replaces this reactor – all else remaining unchanged?  
 (b) What will be the conversion, if this reactor is replaced by a PFR of equal size – all else remaining unchanged? **(Dec-2003-Bio, Dec-2004-Bio, Dec-Bio-2005 & May-2006-Bio)**
13. For the homogeneous gas phase reaction  $A \rightarrow R$ , find the space velocity from the following data;

\* Reaction temp. = 215°C.

- \* Feed consists of 50% A and 50% inerts.
- \* Initial concentration of A = 0.0625 mol/lit.
- \* Percentage conversion of A = 80%.
- \* Rate equation is  $-r_A = 10^{-2} C_A^{1/2}$

### B. Single Reaction & Multiple Reactor Design:

1. (i) Write a brief note on Optimum recycle operations.  
 (ii) For auto catalytic reaction  $1/(-r_A)$  decreasing to a min at  $X_A = 0.4$  and then increasing in  $1/(-r_A)$  versus  $X_A$  graph. Four engineers suggest the following;
  - Engineer 1: PFR
  - Engineer 2: CSTR
  - Engineer 3: PFR up to  $X_A = 0.4$
  - Engineer 4: CSTR up to  $X_A = 0.4$  followed by PFR.
 Discus which scheme provides a minimum reactor volume to achieve  $X_A = 0.98$ . **(May-2004)**
2. Obtain the optimum time and maximum concentration of 'R' in  $A \xrightarrow{k_1} R \xrightarrow{k_2} S$  (first order) conducted in a CSTR. **(May-2004, Dec-2005-Bio & May-2006-Bio)**
3. 100 lit/hr of a radioactive fluid having a half-life of 20hr is to be treated by passing it through two ideal stirred tanks in series. The volume of each stirred tank is 40,000 liters. In passing through this system, by how much has the activity decayed? The reaction follows first order kinetics with a constant density. **(Dec-2004)**
4. At present the conversion is 66.67% for an elementary, second order reaction  $2A \rightarrow 2R$  when operating in an isothermal PFR with  $R = 1$ . Determine the conversion, if the recycle stream is shut-off. **(Dec-2004 & Dec-2005)**
5. The kinetics of the aqueous phase decomposition of 'A' is investigated in two mixed reactors in series, the second having twice the volume of the first reactor. At steady state with a feed concentration of 1 mol(A)/liter and mean residence time of 96 seconds in the first reactor, the concentration in the first reactor is 0.5 mol(A)/liter and in the second is 0.25 mol(A)/liter. Find the kinetic equation for the decomposition. **(May-2005 & Dec-2005-Bio)**
6. Your company has two mixed reactors of unequal size for producing a specified product formed by homogeneous first order reaction. How these reactors should be connected to achieve a maximum production rate. **(May-2005 & Dec-2005-Bio)**
7. We wish to treat 10 liters/min of liquid feed containing 1mol A/liter to 99% conversion. The stoichiometry and kinetics of the reaction are given by
 
$$A \rightarrow R, \quad -r_A = \frac{C_A}{0.2+C_A} \quad (\text{mol / liter-min})$$
 Suggest a good arrangement for doing this using two MFR, and find the size of the two units needed. Sketch the final design chosen.
8. At present the elementary liquid phase reaction  $A+B \rightarrow R+S$  takes place in a PFR using equimolar quantities of A and B. Conversion is 96%,  $C_{A0}=C_{B0}=1$  mol./lit. If a Mixed reactor ten times as large as the PFR were hooked up in series with the existing unit, which unit should come first and by what fraction could productivity be increased for that setup?
9. The elementary irreversible aqueous-phase reaction  $A+B \rightarrow R+S$  is carried out isothermally as follows;
  - Equal volumetric flow rates of two liquid streams are introduced into a 4-liter mixing tank. One stream contains 0.02mol A/liter, while the other 1.40 mol B/liter.

- The mixed stream is then passed through a 16-liter PFR.
- We find that some R is formed in the mixed tank, its concentration being 0.002mol/liter.

Assuming that the mixing tank acts as a MFR, find the concentration of R at the exit of the PFR as well as the fraction of initial A that has been converted in the system.

10. Reactant A decomposes with stoichiometry  $A \rightarrow R$  and with rate dependent only on  $C_A$ . The following data on this aqueous decomposition are obtained in a MFR;

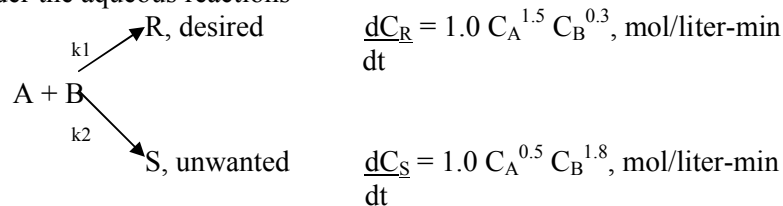
$\tau$ , sec	14	25	29	30	29	27	24	19	15	12	10
$C_{A0}$	200	190	180	170	160	150	140	130	120	110	101
$C_A$	100	90	80	70	60	50	40	30	20	10	1

Determine which setup, plug flow, mixed flow, or any two-reactor combination gives minimum  $\tau$  for 90% conversion of a feed consisting of  $C_{A0} = 100$ . Also find this  $\tau$  minimum.

11. Prove that the performance of series of 'N' mixed flow reactors is equivalent to single plug flow reactor. **(Dec-2003-Bio & May-2006-Bio)**
12. A reaction with rate expression  $-r_A = k C_A^2$  is carried out in 3-equal size mixed reactors in series. When  $(k \tau C_{A0}) = 1.2$ , find the fractional conversion in each reactor by an algebraic method. Assume constant volume operation. Where 'k' is the reaction rate constant, ' $\tau$ ' is the space time and ' $C_{A0}$ ' is the initial concentration of reactant. **(May-2004-Bio)**
13. It is Suspected that the gas reaction  $A + B \rightleftharpoons R$  is an elementary reversible reaction and the reaction is carried out in a PFR. Develop the isothermal performance equation for these kinetics, if the feed contains A, B, R and inert. Show how to test this equation for an equimolar feed of 'A' and 'B'. **(Dec-2005-Bio)**

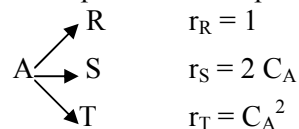
### UNIT-III

1. Consider the aqueous reactions



For 90% conversion of A, find the concentration of R in the product stream. Equal volumetric flow rates of the A and B streams are fed to the reactor, and each stream has a concentration of 20 mol/liter of reactant. The flow in the reactor follows (a) Plug flow (b) Mixed flow. **(Dec-2003-Bio)**

2. Consider the parallel decomposition of A,  $C_{A0} = 2$ ,



Find the maximum expected  $C_S$  for isothermal operations (a) in a MFR (b) in a PFR (c) in a reactor of your choice if unreacted A can be separated from the product stream and returned to the feed at  $C_{A0} = 2$ . **(May-2004-Bio)**

3. Reactant A decomposes in an isothermal batch reactor ( $C_{A0}=100$ ) to produce wanted R and unwanted S and the following progressive concentration readings are recorded;

$C_A$	100	90	80	70	60	50	40	30	20	10	0
$C_R$	0	1	4	9	10	25	35	45	55	64	71

Additional runs show that adding R or S does not affect the distribution of products formed and that only A does. Also, it is noted that the total number of moles of A, R, and S is consistent.

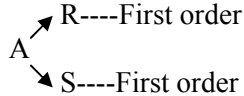
(a) Find the  $\phi$  versus  $C_A$  curve for this reaction

With a feed of  $C_{A0} = 100$  and  $C_{Af} = 10$ , find  $C_R$

(b) from a MFR (c) from a PFR

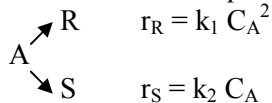
(d) Repeat part (b) & (c) with the modification that  $C_{A0} = 70$ .

4. Substance A in the Liquid phase produces R and S by the following reactions:



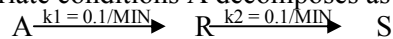
A feed ( $C_{A0} = 1.0$ ,  $C_{R0} = 0$ ,  $C_{S0} = 0$ ) enters two mixed reactors in series ( $\tau_1 = 2.5$  min,  $\tau_2 = 5$  min) knowing the composition in the first reactor ( $C_{A1} = 0.4$ ,  $C_{R1} = 0.4$ ,  $C_{S1} = 0.2$ ), find the composition leaving the second reactor. **(Dec-2004)**

5. Substance A in the Liquid phase produces R and S by the following reactions:



The feed ( $C_{A0} = 1.0$ ,  $C_{R0} = 0$ ,  $C_{S0} = 0$ ) enters two mixed reactors in series ( $\tau_1 = 2.5$  min,  $\tau_2 = 10$  min) knowing the composition in the first reactor ( $C_{A1} = 0.4$ ,  $C_{R1} = 0.4$ ,  $C_{S1} = 0.2$ ), find the composition leaving the second reactor (using fractional yield concept). **(May-2004 & May-2006-Bio)**

6. Under appropriate conditions A decomposes as follows;

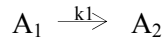


R is to be produced from 1000 liter/hr of feed in which  $C_{A0} = 1\text{mol/liter}$ ,  $C_{R0} = C_{S0} = 0$ .

(a) What size of PFR will maximize the concentration of R, and what is the concentration in the effluent stream from this reactor?

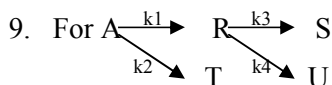
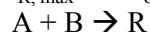
(b) What size of MFR will maximize the concentration of R, and what is  $C_{R,\text{max}}$  in the effluent stream from this reactor? **(Dec-2004-Bio)**

7. For the following parallel reactions



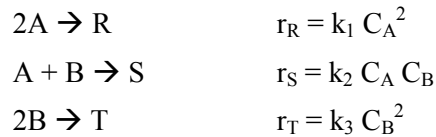
How will you determine the concentration  $C_{A2}$  as a function of  $C_{A1}$ ?

8. (b) Determination of  $C_{R,\text{max}}$  and  $\tau_{\text{opt}}$  in CSTR for the following Reactions;



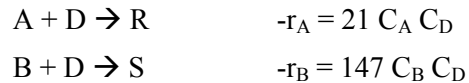
At  $t = 0$ ,  $C_A = C_{A0}$  and  $C_{R0} = 0$ ;  $-r_A = k_1 C_A$  for 'R',  $-r_A = k_2 C_A$  for 'T',  $-r_R = k_3 C_R$  for 'S' and  $-r_R = k_4 C_R$  for 'U'. Derive  $C_A/C_{A0}$  and  $C_R/C_{A0}$ . **(May-2004)**

10. 'A' and 'B' react with each other as follows;



Find what ratio of 'A' and 'B' should be maintained in a MFR so as to maximize the fractional yield of desired product 'S'. **(May-2006)**

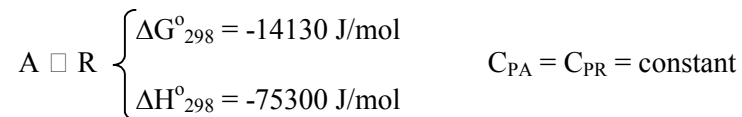
11. We have a mixture consisting of 90 mole% 'A' (45 mol/lit) and 10 mole% impurity 'B' (5 mol/lit). To be satisfactory quality the ratio of 'A' to 'B' in the mixture must be 100 to 1 or higher. 'D' reacts with both 'A' and 'B' as follows;



Assuming that the reaction go to completion, how much 'D' need be added to a batch of mixture to bring about the desired quality. **(May-2006)**

#### UNIT-IV & V

1. Explain the graphical design procedure for determining the size of given reactor for a given temperature progression. **(Dec-2003-Bio)**
2. Between 0°C and 100°C determine the equilibrium conversion for the elementary aqueous reaction



- (a) Present the result in the form of a plot of Temperature versus conversion.
- (b) What restrictions should be placed on the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

3. The reversible first-order gas reaction is to be carried out in a MFR. For operations at 300K the volume of reactor required is 100liters for 60% conversion of A. What should be the volume of the reactor for the same feed rate and conversion but with operations at 400K?



4. (i) Write brief notes on multiple stationary states in CSTR for Exothermic reactions.  
 (ii) For exothermic adiabatic reaction conducted in a CSTR, say for a reaction  $A \rightarrow B$ , you should be very careful of feed temperature, otherwise there may be unstable operation – Discuss. **(May-2004 & Dec-2005-Bio)**
5. (i) Derive the energy balance equation for the relation between temperature (T) and fractional conversion ( $X_A$ ) in an adiabatic batch reactor. **(May-2004)**  
 (ii) A liquid phase reaction  $A \rightarrow B$  is to be conducted in a CSTR at steady state at 163°C. The temperature of feed is 20°C and 90% conversion of A is required. Determine the volume of CSTR to produce 130 kg/hour of B and calculate heat load process. Use the following data;  $\Delta H_{R,A} = -87 \text{ KJ/mol}$ ,  $\rho = 0.95 \text{ kg/m}^3$ ,  $M_A = M_B = 200 \text{ gm/mol}$ ,  $C_P = 2.0 \text{ J/gm-K}$  &  $k_A = 0.8 \text{ hr}^{-1}$  at 163°C. **(May-2004)**



6. An irreversible Isomerization reaction  $A \rightarrow R$  is carried out in a liquid phase in MFR. The reaction is first order and the rate constant at  $165^\circ\text{C}$  is  $0.7 \text{ hr}^{-1}$ . The activation energy of the reaction is  $120 \text{ kJ/mol}$  and the heat of reaction is  $-350 \text{ kJ/kg}$ . The heat capacity of the reactants and products are  $1.95 \text{ kJ/kg-K}$ , the volumetric flow rate is  $0.33 \text{ m}^3/\text{hr}$ , and the feed temperature is  $20^\circ\text{C}$ . If the conversion is  $95\%$ , calculate (a) the reactor size and (b) the temperature of the reaction mixture, if the reactor is operated adiabatically. **(Dec-2004)**
7. Explain the graphical design procedure for finding the reactor size for adiabatic operations of Plug flow and Mixed flow reactors. **(May-2005 & Dec-2005)**
8. The flow through a tubular reactor, in which a first order irreversible liquid phase reaction takes place, is increased by  $20\%$  and in order to maintain the same fractional conversion it is decided to change the reactor operating conditions. The reaction has an activation energy of  $4 \text{ kcal/mol}$  and the initial temperature is  $150^\circ\text{C}$ . Find the new operating temperature of the reactor. **(Dec-2004 & Dec-2005)**
9. Discuss the stability criteria for exothermic reactions in Mixed flow reactors. **(May-2005)**
10. Methanol can be manufactured by the gas phase reaction  $\text{CO (g)} + 2\text{H}_2 \text{ (g)} \leftrightarrow \text{CH}_3\text{OH (g)}$  at  $400\text{K}$  and  $1.013 \text{ bar}$ . The following data are available;
- $$\Delta H_{298} = -90.71 \text{ kJ/mol} \qquad \Delta G_{298} = -24.33 \text{ kJ/mol.}$$
- (i) Calculate the equilibrium composition at  $400\text{K}$  ( $R = 8.319 \text{ J/mol-K}$ )  
(ii) If heat capacity of each reactants and products are equal, will heat of reaction be constant?  
(iii) If one mole of product is formed from one mole of reactant ( $A \rightarrow B$ ), will heat of reaction be independent of temperature? **(May-2004)**
11. Consider a CSTR that is used to carry out a reversible Isomerization reaction of the type  $A \leftrightarrow B$ ; where both the forward and reverse reactions are first order.  
Data: Feed is pure species A,  $C_{PA} = 1255 \text{ J/mol-K}$  &  $C_{PB} = 1172 \text{ J/mol-K}$ ,  
 $k_1 = 8.83 \times 10^4 \exp(-6290/T), \text{ sec}^{-1}$   
 $k_2 = 4.17 \times 10^{15} \exp(-14947/T), \text{ sec}^{-1}$ ; where 'T' is the temperature in degree Kelvin.  
(i) Is the reaction exothermic or endothermic? What is the standard enthalpy change for the reaction? (ii) What is the equilibrium fraction conversion at  $340\text{K}$ ?
12. A irreversible liquid phase dimerization reaction of the type  $2M \rightarrow D$  follows second order kinetics. You have been asked to estimate the fraction of the monomer that can be converted to dimer in an existing CSTR designed for adiabatic operation. The reactor volume is  $0.4 \text{ m}^3$  and the available input volumetric flow rate is  $1.3 \text{ m}^3/\text{ksec}$  of pure monomer. Data;  
Inlet temperature =  $312\text{K}$ ,  $\Delta H_{r, 300\text{K}} = -42 \text{ kJ/mol}$  'D' formed, liquid heat capacity =  $2.0 \text{ J/cm}^3\text{-K}$ , Monomer feed concentration =  $16 \text{ kmol/m}^3$ , Thermal expansion effects may be neglected and  $k = 2.7 \times 10^9 \exp(-12185/T), \text{ m}^3/\text{mol-ksec}$ ; 'T' is in degree Kelvin.
13. Write brief notes on the following;  
(i) Limit cycles and Oscillating reactions  
(ii) Parameter sensitivity in flow reactors. **(May-2004)**
14. A dissociation reaction of the type  $A \rightarrow B + C$  is being studied in a pilot plant reactor having a volume of  $0.5 \text{ m}^3$ . The reaction involves ideal gases with the following heat capacities;  $C_{P,A} = 160 \text{ J/mol-K}$ ,  $C_{P,B} = 120 \text{ J/mol-K}$  and  $C_{P,C} = 120 \text{ J/mol-K}$ . Pure 'A' is charged to the reactor at  $400 \text{ kPa}$  and  $300\text{K}$ . The reaction is first order in species 'A'. The variation of the reaction rate constant with temperature is given below;

T (Kelvin)	330	340	350	360	370	380
k (k-sec <sup>-1</sup> )	0.33	0.462	0.641	0.902	1.27	1.98

The standard heat of reaction is -11.63 kJ/mol. Determine the time necessary to achieve 90% conversion in a constant volume batch reactor under adiabatic conditions and under isothermal conditions. **(May-2006)**

15. Hydrogen can be manufactured from carbon monoxide by the water gas shift reaction  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ . At 700°C, the equilibrium constant for this reaction is 5.62. When the standard states for all the species are taken as unit fugacity. If the reaction is carried out at 75 atm, what molal ratio of the steam to carbon monoxide is required to produce a product mixture in which 90% of the inlet CO is converted to CO<sub>2</sub>. **(May-2006)**

16. At 25°C the standard Gibbs free energy change for the reaction  $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3$  is -70.04 kJ/mol, where the standard states are taken as the pure components at 10.13 kPa and 25°C. At 227°C and 1.013 kPa, the following equilibrium composition was determined experimentally;

Component	O <sub>2</sub>	SO <sub>2</sub>	SO <sub>3</sub>	Helium
Mole Percent	0.10	0.12	78.18	21.60

- (i) What is the equilibrium constant for the reaction at 25°C and 1.013 kPa?  
(ii) Will the equilibrium constant for the reaction at 25°C and 101.3 kPa be greater than, equal to or less than that calculated in part (i)? Explain your reasoning. **(May-2006)**

-----**ALL THE BEST**-----