SUMMER-17 EXAMINATION

Model Answer

Important Instructions to examiners:

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

Q No.	Answer	Marks
1	**Attempt any THREE of the following**	**12**
1A-a	**Difference between order and molecularity of reaction.**	1 mark each for any 4 points

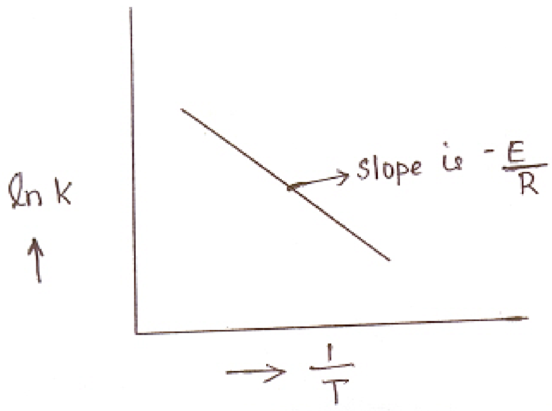
Sr.No.	Molecularity	Order of reaction
1	Molecularity is the number of molecules, atoms or ions in a chemical reaction.	Order of reaction is the sum of exponents of the concentration terms involved in the rate equation.
2	Molecularity always has an integer value 1, 2, 3…	Order of reaction can have a fractional value.
3	Shows the elementary mechanism or separate steps of a complicated process	Shows the kinetic dependence of the rate on the concentration of the reactants.
4	Depending upon the value of molecularity, reaction can be unimolecular ,bimolecular etc.	Depending upon the value of order, the reactions are termed as first order, second order reactions.
5	Molecularity is a theoretical quantity	Order of reaction is entirely an experimental value.

1A-b

T(min)	0	2	3	4
C_{N205}	0.16	0.113	0.056	0.04

	(mol / l) $C_{A0} = 0.16$ mol / l For first order reaction $-\ln(C_A / C_{A0}) = kt$ $k = -\ln(C_A / C_{A0}) / t$ When t = 2 minutes , $k = -\ln(0.113 / 0.16) / 2$ = **0.1738 min^{-1}** t = 3 minutes , $k = -\ln(0.056 / 0.16) / 3$ = **0.3499 min^{-1}** t = 4 minutes , $k = -\ln(0.04 / 0.16) / 4$ = **0.3465 min^{-1}** Since k values are not same, the decomposition reaction is not of first order.	1 3
1A-c	**Relation between Gibb's free energy (ΔG^0) and equilibrium constant** K_p Consider the reaction $aA + bB \rightarrow rR + sS$ ΔG reaction = ΔG product - ΔG reactant. $= (r\,\mu_R + s\,\mu_S) - (a\,\mu_A + b\,\mu_B)$. At equilibrium there is no Gibb's free energy change, $\Delta G = 0$ $(r\,\mu_R + s\,\mu_S) - (a\,\mu_A + b\,\mu_B) = 0$ $(r\,\mu_R + s\,\mu_S) = (a\,\mu_A + b\,\mu_B)$ But $\mu_i = \mu_i^0 + RT\ln p_i$ Therefore $r(\mu_R^0 + RT\ln p_R) + s(\mu_S^0 + RT\ln p_S) = a(\mu_A^0 + RT\ln p_A) + b(\mu_B^0 + RT\ln p_B)$ $RT\ln\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = (a\,\mu_A^0 + b\,\mu_B^0) - (r\,\mu_R^0 + s\,\mu_S^0)$ = - (ΔG product - ΔG reactant) = - ΔG reaction. $\ln\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = \frac{-\Delta G\text{ reaction}}{RT}$ But $\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = K_p$ Therefore $\Delta G = -RT\ln K_p$	2 2

1A-d	**Types of reactors used in industry:**	
	Based upon mode of operation, the reactors are classified as Batch reactors, Semi batch reactors & Continuous reactors. Reactors like packed bed reactors, fluidized bed reactors are also used in industry.	1
	Application of **Batch reactor**:	
	These are used when relatively small amount of material are to be treated. Also to produce different products using same reactor, for testing new products etc.	1 mark each for writing one application of any three reactors.
	Semi batch reactors: When good control of reaction is required, also used for liquid phase reactions & 2-phase reactions where gas is continuously bubbled through the pool of liquid in reactor.	
	Continuous reactors: Used for higher production rates with short reaction times, for producing high quality products, for carrying out reactions when rate of reaction is high.	
	Packed (fixed)bed reactor: Used when high conversion rate per catalyst weight is required.	
	Fluidized bed reactor: Used when good temperature control is required, when catalyst regeneration has to be done on a continuous basis without shutting down the reactor.	
1B	**Attempt any ONE of the following**	**6**
1B-a	**Arrhenius law**	
	The temperature dependence of the reaction rate constant k, is given by $k = k_0 e^{\frac{-E}{RT}}$ Where k_0 - frequency factor or pre exponential factor E - activation energy in J/ mol or cal/ mol R – universal gas constant	2

	T – temperature in Kelvin The activation energy is determined experimentally by carrying out the reaction at different temperatures. A plot of ln k vs$\frac{1}{T}$ should give a straight line with slope equal to $\frac{-E}{R}$.  Alternatively, if the rate is known at two different temperatures T_1 and T_2, then we can evaluate E with the help of equation $\ln\frac{k_2}{k_1} = \frac{-E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ Lower the value of activation energy, higher will be the rate at which reaction will proceed as the considerable part of collisions between the molecules result in a reaction and higher the value of activation energy, lower will be the rate at which the reaction proceeds.	2 2
1B-b	**General procedure for analysis of complete rate equation by integral method** The procedure for integral method of analysis is as follows : 1. In a constant volume system , the rate expression for the disappearance of reactant A will be of the following form	

$-r_A = -dC_A / dt = kf(c)$

2. Rate equation is rearranged as

   $-dC_A / f(c) = kdt$

   f(c) involves the concentration of materials which may be expressed in terms of C_A

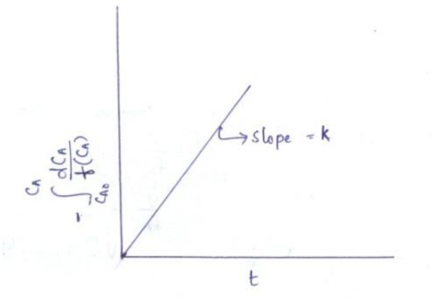
3. Above equation is integrated with appropriate limits

   $$-\int_{C_{A0}}^{C_A} \left(dC_A / f(c) \right) = k \int_{0}^{t} dt$$

5

4. The concentration function is proportional to time, so a plot of concentration vs time gives a straight line of slope k for this particular rate equation.
5. From experiment, determine the numerical value for the above integral and plot these at the corresponding time.
6. If the data fall on a reasonable straight line, then it may said that the particular rate equation being tested satisfactorily fits the data. If the data are being fitted by a curve, the rate equation and mechanism are rejected and another rate equation is tried.

Graph:



1

2	**Attempt any TWO of the following**	**16**

2-a

Chain reaction:

In chain reaction, the intermediate is formed in the first reaction called chain initiation step. It then combines with the reactant to form product and more intermediates in the chain propagation step. Occasionally these intermediates are destroyed in chain termination step.

$$R \rightarrow I^* \quad \text{Initiation step}$$

$$I^* + R \rightarrow I^* + P \quad \text{Propagation step}$$

$$I^* \rightarrow P \quad \text{Termination step.}$$

3

$-r_A = k\,C_A^{\,n}$

Taking log $\log -r_A = \log k + n \log C_A$ - (1)

2

On doubling the concentration of reactant, the rate of reaction triples

ie $3\text{-}r_A = k\,(2C_A)^{\,n}$

Taking log $\log(3\text{-}r_{A)} = \log k + n \log (2C_A)$ - (2)

(1) - (2) $\log 0.333 = n \log 0.5$

$n = 1.585$

3

2-b

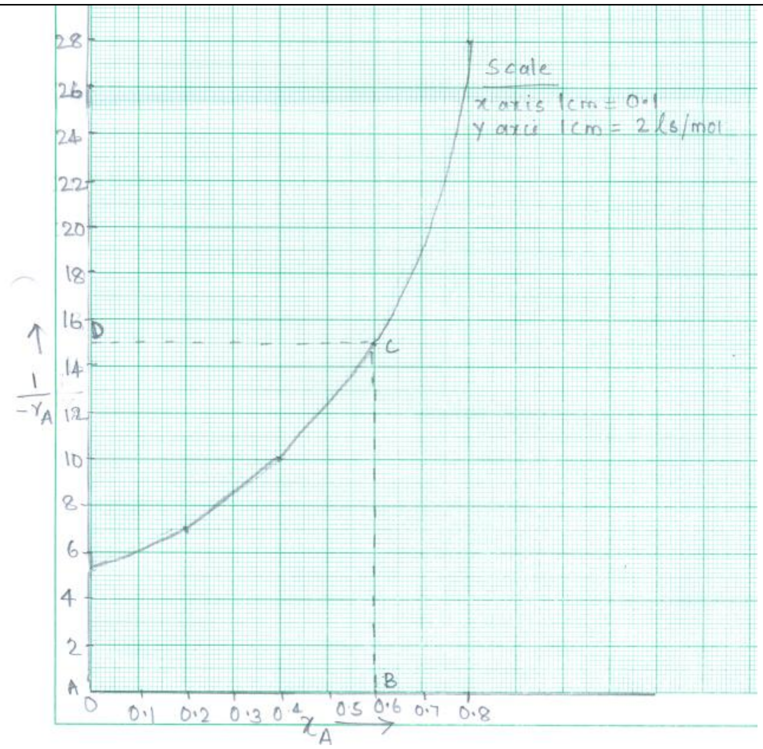
A → Products

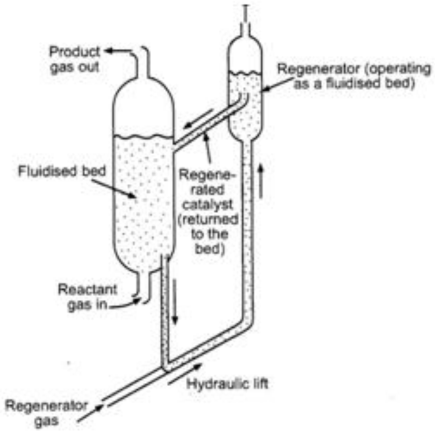
X_A	0	0.2	0.4	0.6	0.8
$-r_A$	0.182	0.143	0.1	0.0667	0.0357
$1/(-r_A)$	5.5	7	10	15	28

1

F_{A0} = 10 mol / s

Plot a graph between $1/(-r_A)$ and X_A

		2
	For a mixed flow reactor $$\frac{V}{F_{A0}} = \frac{X_A}{-r_A}$$ $\frac{V}{F_{A0}}$ **=** Area of the rectangle ABCD = 0.6*15 = 9 V = 9 X F_{A0}= 9 X 10 = 90 lit. Volume of CSTR **= 90 lit.**	2
	For a plug flow reactor $\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} = \int_0^{X_A} \frac{1}{(-r_A)} dX_A$ where $X_A = 0.6$ $\frac{V}{F_{A0}}$ = Area under the rate curve from $X_A = 0$ to $X_A = 0.6$ = Number of columns * scale of x axis * scale of y axis = 2710 * (0. 1 /10)*(2 / 10) = 5.42 V = 5.42 X F_{A0}= 5.42 * 10 =54.2lit	2

	Volume of PFR **= 54.2 lit** Volume of PFR is less than the volume of CSTR for the same conversion.	1
2-c	**Fluidized bed reactor:** **Diagram:** 	2
	Explanation: Consider a bed of fine particles and gases passing upward through them. On increasing the flow rate, a point is reached when the solids become suspended in the gas stream. In this state the bed is said to be fluidized and the particular inlet gas velocity is called minimum fluidizing velocity. If the gas velocity is much larger than this minimum, the bed takes the appearance of a violently boiling liquid with solids in vigorous motion and large bubbles rising rapidly through the bed. In this case we have the bubbling fluidized bed. Industrial reactors particularly for solid catalyzed gas phase reactions often operate as bubbling beds with gas velocities equal to 9 to 30 times minimum fluidizing velocity.	2
	Merits: 1. Good temperature control 2. Can use small size catalyst particles	1 mark each for any 2

	3. Regeneration is easily done without shut down of the reactor. **Demerits:** 1. Effective contacting require large amount of catalyst for high gas conversion 2. Catalyst loss is there. So recovery units are required.	points. 1 mark each
3	**Attempt any FOUR of the following**	**16**
3-a	$H_2 + I_2 \leftrightarrow 2HI$ Moles of H_2 present initially = 5 millimoles Moles of I_2 present initially = 2 millimoles $K_c = 16.34$ Let x moles of H_2 reacts at equilibrium Moles of H_2 present at equilibrium = 5-x Moles of I_2 present at equilibrium = 2-x Moles of HI present at equilibrium = 2x $K_c = \{(C_{HI})^2 / \{(C_{H2}) * (C_{I2})\}$ Concentration = moles / l $16.34 = \{ (2x)^2 / \{(5-x) * (2-x)\}$ $16.34 = 4x^2 / x^2 - 7x + 10$ $12.34x^2 - 114.38x + 163.4 = 0$ $x = \frac{-b \pm \sqrt{(b^2 - 4 * a * c)}}{2 *}$ $x = \frac{114.38 \pm \sqrt{(114.38^2 - 4 * 12.34 * 163.4)}}{2 * 12.34}$ = 7.504 or 1.76 Value of x = 1.76 Equilibrium concentration for H_2 = 5-x = 5- 1.76 = 3.24 millimoles / l	2

	Equilibrium concentration for I_2 = 2-x = 2- 1.76 = 0.24 millimoles / l Equilibrium concentration for HI = 2x = 2 * 1.76 = 3.52 millimoles / l	2
3-b	**Half life period:** It is the time required to reduce the concentration of the reactant to half of its original value Given Data: $$t_{1/2} = 2500 \text{ s}$$ $$t_{1/2} = \frac{0.693}{k}$$ $$2500 = \frac{0.693}{k}$$	2
	$k = 2.77 * 10^{-4}\ s^{-1}$ Let t be the time required to drop the concentration of the reactant to 1/4th of its initial concentration. $$C_{A0} = 1\ {}^{mol}/_{l}$$ $$C_A = 1/4\ {}^{mol}/_{l}$$ For first order reaction, $t = \frac{1}{k}\ln\left[\frac{C_{A0}}{C_A}\right]$	1
	t = 5000.5 s	1
3-c	**Expression for entropy change in constant volume process** From first law of thermodynamics, dU = dQ – dW dQ = dU + dW ……..(i) But dQ = TdS ………….(ii) dW = PdV ……(iii)	1
	For ideal gas dU= n C_vdT……… (iv) Substituting ii,iii and iv in i TdS = n C_vdT + PdV $dS = \frac{n\,C_v dT}{T} + \frac{PdV}{T}$	1

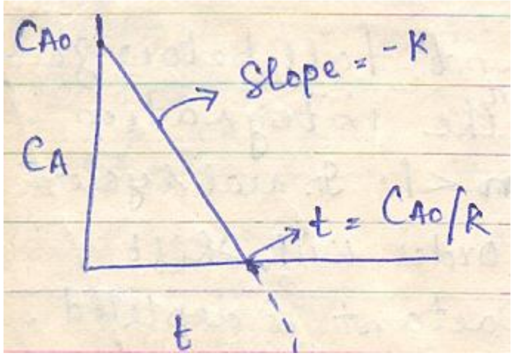
	For ideal gas P = $\frac{nRT}{V}$ Substituting dS = $\frac{n\,CvdT}{T} + \frac{nRdV}{V}$ Integrating between limits $\int_{S_1}^{S_2} dS = nC_v\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V}$ $\Delta S = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ ……(v) For constant volume system $v_1 = v_2$ $\Delta S = nC_v \ln\frac{T_2}{T_1}$	1 1
3-d	**Rate of a reaction:** It is defined as change in the moles of any reactant / product of the reaction per unit time per unit volume of reacting fluid. **Rate constant**: Rate constant of a chemical reaction is a measure of the rate of the reaction when all the reactants are at unit concentration. **Factors affecting the rate of a chemical reaction** : 1. In **homogeneous system** temperature, pressure and composition are the variables. 2. In **heterogeneous system**, since more than one phase is involved, material have to move from phase to phase during reaction, hence the rate of mass transfer is important. 3. rate of heat transfer 4. Catalyst 5. Nature of reactants 6. Surface area available. 7. Intensity of light if reaction is light sensitive.	1 1 2
3-e	**Catalyst ingredients** **Promoters** They are substances which do not act as catalyst but enhances the efficiency	1.5

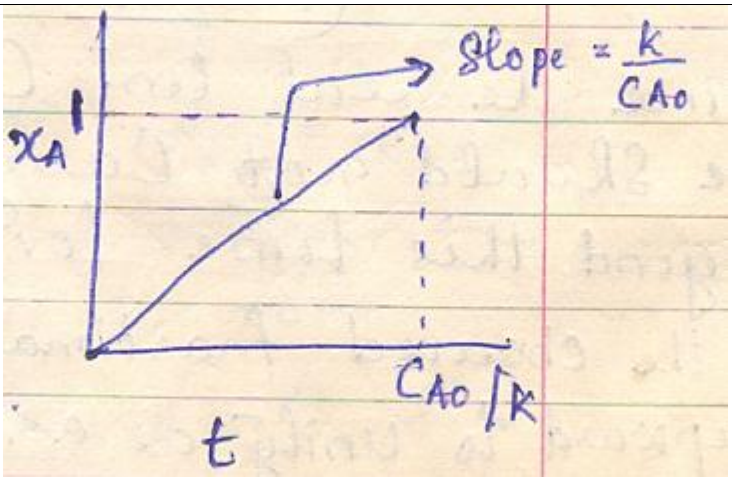
	and life of the catalyst. It is a substance added during the preparation of a catalyst which improves the activity or selectivity or stabilizes the catalytic agent so as to increase its life. Eg Al_2O_3 is used as a promoter to iron catalyst in the manufacture of ammonia **Inhibitors** It is the substance which decreases the performance of the catalyst. It lessens activity, stability or selectivity of a catalyst. It is useful for reducing the activity of a catalyst for an undesirable side reaction. Eg silver supported on alumina is an excellent oxidation catalyst and is used in the production of ethylene oxide from ethylene. But at the same conditions, complete oxidation to CO_2 and H_2O also occurs. So selectivity is poor. By adding halogen compounds to the catalyst inhibits the oxidation to CO_2 and H_2O and results in satisfactory selectivity. **Accelerators** They are substances added to the reactant streams to improve the performance of a catalyst. Eg steam added to butane feed of a dehydrogenation reactor reduces the amount of coke formed and increases the yield of butadiene.	1.5 1
4A	**Attempt any THREE of the following**	**12**
4A-a	**Relation between concentration and conversion for constant volume batch system:** Consider the reaction A → R Let N_{A0} and N_{R0} represent the number of moles of A and R present initially (t = 0). N_A and N_R represent the number of moles of A and R present at time t. X_A be the fractional conversion of A at time t Moles of A reacted at any time t = $N_{A0}\,X_A$	4

	When 1 mole of A reacts, I mole of R is produced. Ie $N_{A0} X_A = N_{R0} X_R$ where X_R represents fraction of R produced. At time t, moles of A present $N_A = N_{A0} - N_{A0} X_A$ Divide throughout by V, $(N_A / V) = (N_{A0} / V) - (N_{A0} X_A / V)$ But concentration = moles / l Therefore $C_A = C_{A0} - C_{A0} X_A$; $\mathbf{C_A = C_{A0} (1- X_A)}$ For product R, $\mathbf{C_R = C_{R0} (1+ X_R)}$	
4A-b	**Methods of catalyst Preparation:** 1. Precipitation 2. Gel formation 3. Simple mixing 4. Impregnation method **1.Precipitation method** : This method produces catalyst in porous form.It consists of adding a precipitating agent to the solution of the desired component. The precipitation is followed by washing,drying, calcinations & activation(or pretreatment) Eg. Magnesium oxide catalyst is prepared by this method. It is prepared by precipitating $MgCO_3$ from magnesium nitrate solution by adding sodium carbonate.The magnesium carbonate precipitate is washed, dried & calcined to obtain magnesium oxide. **2.Gel formation:**If the precipitate formed in the above method is colloidal, then gel is formed. Eg Catalyst containing silica and alumina are suitable for gel formation because their precipitates are colloidal in nature. **3. Simple mixing:** Some porous materials are obtained by mixing the components with water, milling to the desired grain size, drying and calcining. Such materials may be ground and sieved to obtain the particle size.	1 mark each

	Eg Mixed Mg and Ca oxide catalyst is prepared by this method **4. Impregnation method:** This method is used for the preparation of expensive catalysts like platinum, palladium, silver etc. A catalyst carrier provides a means of obtaining a large surface area with a small amount of catalyst. The steps in the preparation of a catalyst impregnated on a carrier include evacuating the carrier, contacting the carrier with the impregnating solution, removing the excess solution, drying, calcining and activation. Eg Nickel catalyst is prepared on alumina by soaking the evacuated alumina particles with nickel nitrate solution, draining to remove the excess solution and heating in an oven to decompose the nitrate to nickel oxide. The final step is activation in which nickel oxide is reduced to nickel. ***Any other appropriate method should also be given due consideration***	
4A-c	For second order reaction: $k = \frac{1}{t}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$ t = 50 min C_{A0} = $5*10^{-4}$ mol/l Gas is 40% decomposed $C_A = C_{A0}(1 - X_A) =$ $5x10^{-4}$ * 0.6= $3*10^{-4}$ mol/l $k = \frac{1}{50}\left[\frac{1}{3*10^{-4}} - \frac{1}{5*10^{-4}}\right]$ k = **26.67 l / (mol.min)**	1 1 2
4A-d	**Feasibility of a chemical reaction from Gibbs free energy change:** At chemical equilibrium $\Delta G^0 = 0$.For a chemical reaction at equilibrium at a given temperature &pressure, the free energy must be minimum. If $\Delta G^0 < 0$ i.e.it is negative, the reaction can take place spontaneously (reaction is possible under the given set of conditions).For spontaneous reaction, there should be decrease in Gibb's free energy change .	4

	If ΔG^0 is positive ,the reaction cannot take place under the given conditions	
4B	**Attempt any ONE of the following**	**6**
4B-a	$T_1 = 400$ K $T_2 = 500$K $k_2 = 10 k_1$ (i) **From Arrhenius law** $\ln\frac{k_2}{k_1} = \frac{-E}{R} (\frac{1}{T_2} - \frac{1}{T_1})$ $\ln 10 = (-E / 1.987) * (\frac{1}{500} - \frac{1}{400)} = 2.52 *10^{-4}E$ E = **9137.2 cal**	3
	(ii) From collision theory: $\ln\frac{k_2}{k_1} = \frac{-E}{R} (\frac{1}{T_2} - \frac{1}{T_1}) + 0.5 \ln (T_2 / T_1)$ $\ln 10 = (-E / 1.987) * (\frac{1}{500} - \frac{1}{400)} + 0.5 \ln(\frac{500}{400})$ E= **8694.5 cal**	3
4B-b	**Van't Hoff equation:** Consider the reaction aA + bB→rR+sS ΔG^0=- RTln K….. (1) ΔG^0 =(rμR+ s μs) –(a μA +b μB)……(2)	2
	From 1 and 2 - RTln K = (rμR+ s μs) –(a μA +b μB) Differentiating with respect to T at constant pressure d/dTlnk = -(1/R) ((r ∂/∂T μR/T + s ∂/∂T μs/T) –(a ∂/∂T μA/T+b ∂/∂T μb/T)	2
	Gibb's Helmholtz equation is a ∂/∂T (μi/T)=- Hi/RT^2 ie d/dTlnk = (1/RT^2) { [rH_R+ sH_s] - [aH_A+ bH_B]} = (1/RT^2)($\Sigma H^0_{product}$- $\Sigma H^0_{reactant}$) d/dT lnk = ΔH^0/ RT^2 is the Van't Hoff equation where ΔH^0 is molal enthalpy	2
5	**Attempt any TWO of the following**	**16**

5-a	**(i)Zero order reaction:** A reaction is of zero order when the rate of reaction is independent of the concentration of the reactant.	1
	Integrated form of rate expression for zero order reaction Rate equation is $-r_A = -\frac{dC_A}{dt} = C_{A0}\frac{dx_A}{dt} = k$ *In terms of concentration* $-\frac{dC_A}{dt} = k$ Integrating between appropriate limits $\int_{CA_0}^{CA} -dCA = k\int_0^t dt$ $C_{A0} - C_A = kt$ for t‹ $\frac{C_{A0}}{k}$  *In terms of fractional conversion* $C_{A0}\frac{d_{xA}}{dt} = k$ Integrating between appropriate limits $C_{A0}\int_0^{xA} d_{xA} = k\int_0^t dt$ $C_{A0}\,X_A = kt$ for t‹ $\frac{C_{A0}}{k}$	2



Important Characteristics of zero order reaction:

1. Conversion is proportional to time.
2. Reactions are zero order only at certain concentration ranges- the higher concentrations. If the concentration is lowered far enough, the reaction becomes concentration dependant, in which case the order rises from zero.
3. The half life of Zero order reaction is proportional to the initial concentration of the reactant. $t_{\frac{1}{2}} \propto C_{A0}$

1 mark for any one point

(ii) CA0'=0.405 mol/l $t_{1/2}'$= 420 sec

CA0'' = 0.64 mol/l $t_{1/2}''$ = 275 sec

$$t_{1/2} = \frac{C_{A0}^{1-n}}{k(n-1)}[(2^{n-1})-1]$$

$$(t_{1/2}' / t_{1/2}'') = (C_{A0}' / C_{A0}'')^{1-n}$$

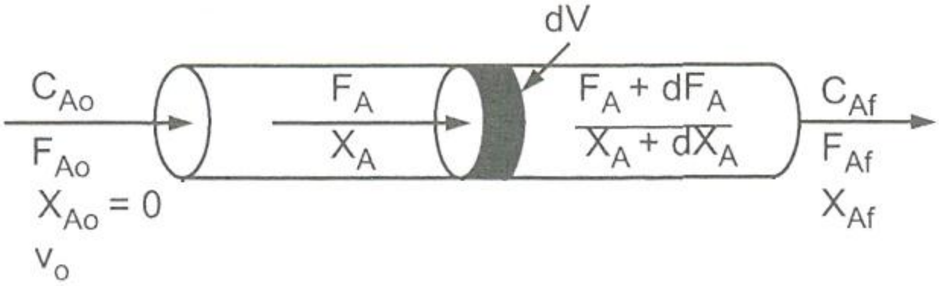
Taking log and rearranging

$n = 1-(\log(t_{1/2}'/t_{1/2}'') / \log(C_{A0}'/C_{A0}''))$

n = 1-(log (420 / 275) / (log (0.405/0.64))

n= 1 +0.92 = 1.925 =**2**

2

	$t_{\frac{1}{2}} = \frac{2^{n-1}-1}{(n-1)kC_{A0}^{n-1}}$ 420 = 1 / k 0.405 K= **5.88 $*10^{-3}$ l / (mol. Minute)**	2
5-b	**Derivation of performance equation for PFR** In PFR, the composition of the fluid varies from point to point along the flow path. So the material balance for a reaction component must be made for a differential element of volume dV.  Taking material balance of reactant A over the reactor, Input of A to reactor = Output of A from reactor + Disappearance of A due to chemical reaction + Accumulation of A within the reactor. For plug flow reactor, the last term is zero. Input of A to reactor = Output of A from reactor + Disappearance of A due to chemical reaction …………….(1) Let, F_{A0} = Molar feed rate to the reactor. C_{A0} = Molar concentration of A in stream entering the reactor (moles/volume) X_A = Fractional conversion of A $F_A = F_{A0} (1- X_A) = F_{A0} - F_{A0.} X_A$	2

$dF_A = - F_{A0}.dX_A$

For the differential volume dV

Input of A in moles/time = F_A

Output of A from reactor in moles/time = $F_A + dF_A$

Disappearance of A due to chemical reaction in moles/ time = $(-r_A)\,dV$

Substituting all the terms in the material balance equation (1)

$F_A = F_A + d\,F_A + (-r_A)\,.dV$

$-\quad d\,F_A = (-r_A)\,dV$

$F_{A0}.d\,X_A = (-r_A)\,dV$

$$\frac{dV}{F_{A0}} = \frac{dX_A}{-r_A}$$

This is the equation accounting for A in the differential section of the reactor of volume dV. For the whole reactor, the equation must be integrated.

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A}$$

3

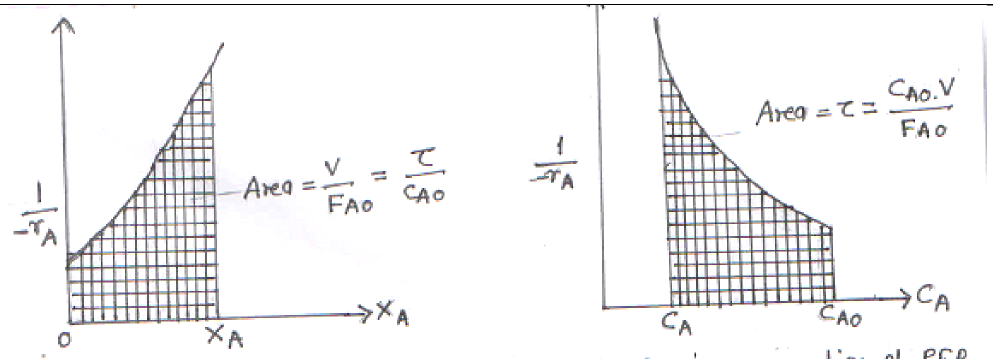
$$\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$$

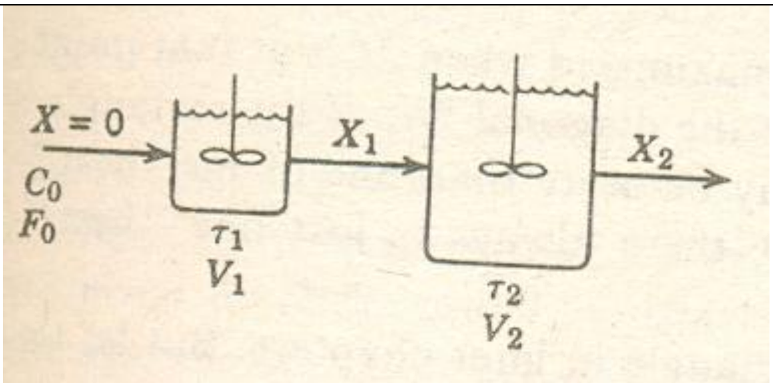
Where X_A and $(-r_A)$ are evaluated at the exit conditions

For constant volume system :

$$\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}} = \frac{-1}{C_{AO}} \int_{C_{Ao}}^{C_A} \frac{dC_A}{-r_A}$$

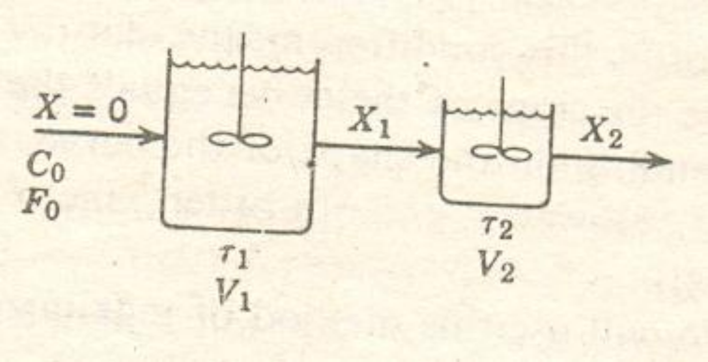
Graphical representation:

	 Graphical Representation of Design equation of PFR **Advantages of batch reactor:** 1. Simple in construction & operation 2. Low cost 3. Gives highest conversion by leaving the reactants for longer periods in reactor. 4. Requires small instrumentation & less supporting equipments 5. Suitable for small scale experimental studies on reaction kinetics **Disadvantages of batch reactor:** 1. High labor costs per unit volume of production. 2. Requires considerable time to empty, clean out & refill. 3. Poorer quality control of product. 4. Large scale production is difficult.	1 ½ mark each for any two points ½ mark each for any two points
5-c	**(i)Procedure to determine the best system for achieving desired conversion for different size MFR in series** Consider two different sizes MFR's connected in series. Two arrangements are possible 1^{st} arrangement	



1

2nd arrangement :



For the first reactor

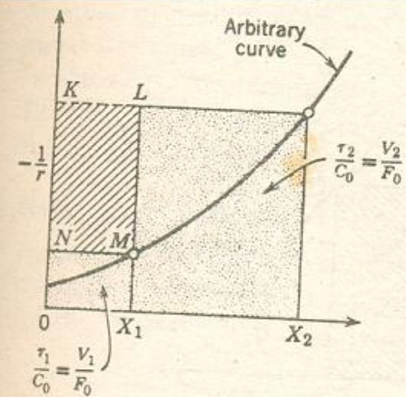
$$\frac{\tau_1}{C_0} = \frac{X_1}{(-r)_1}$$

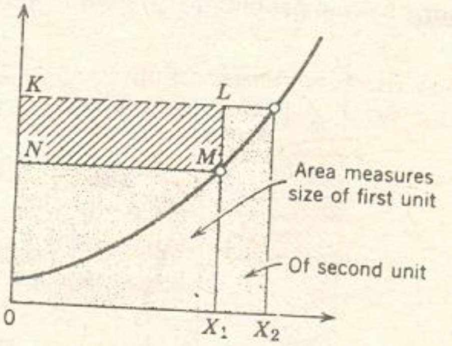
For the second reactor

$$\frac{\tau_2}{C_0} = \frac{X_2 - X_1}{(-r)_2}$$

The graphical representations of the variables for the two arrangements are given below.

For the first arrangement: For the second arrangement





2

Final conversion is the same in both the arrangements. Note, as the intermediate conversion X_1 changes, so does the size ratio of units (represented by the two shaded areas) as well as the total volume of the two reactors required. The total reactor volume is as small as possible (total shaded area is minimized) when the rectangle KLMN is as large as possible. The optimum size ratio of the two reactors is achieved when the slope of the rate curve at M equals the diagonal NL. The optimum size ratio for two mixed reactors in series is found in general to be dependent on reaction kinetics of the reaction and on the conversion level. It has been found that for first order reaction- equal size reactors are best, for n>1 - smaller reactor should come first, for n< 1 - larger reactor should come first.

2

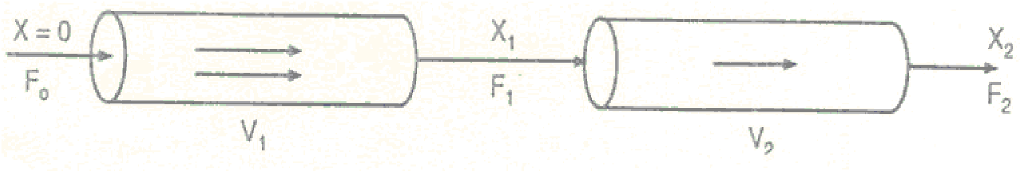
(ii)

$$C_{A0} = 100 \qquad C_{B0} = 200 \qquad X_A = 0.8$$

The reaction

$$A + B \rightarrow R + S$$

When 1 mole of A reacts, 1 mole of B also reacts and 1 mole each of R and S are formed.

	Therefore $\varepsilon_A = \frac{Total\ moles\ on\ complete\ conversion - initial\ total\ moles}{initial\ total\ moles} = 0$ $C_A = C_{A0}(1 - X_A)$ $C_A = 100(1 - 0.8) = \mathbf{20}$ $C_{A0}X_A = C_{B0}X_B$ $100 * 0.8 = 200 * X_B$ $X_B = \mathbf{0.4}$ $C_B = C_{B0}(1 - X_B) = 200\ (1 - 0.4) = \mathbf{120}$	1 1 1
6	**Attempt any FOUR of the following**	**16**
6-a	**Plug flow reactors in Series** :Assume two PFRs are placed in series as shown below Let X_1 & X_2 be the fractional conversions of a component A leaving reactors 1 &2 .  X_1 : conversion of A from first reactor X_2 : overall conversion of A from entire system The performance equation for PFR1 is $\frac{V_1}{F_0} = \int_0^{X_1} \frac{dX}{(-r)}$ The performance equation for PFR2 is $\frac{V_2}{F_0} = \int_{X_1}^{X_2} \frac{dX}{(-r)}$ Two PFRS in series $\frac{V}{F_0} = \frac{V_1}{F_0} + \frac{V_2}{F_0} = \int_0^{X_1} \frac{dX}{(-r)} + \int_{X_1}^{X_2} \frac{dX}{(-r)}$ EqI From eqI ,it is clear that the total volume of two PFRs in series is identical to that of one PFR(single reactor) for the same conversion. If the total volume of two PFRs in series is $V = V_1 + V_2$ for X_2, then the same conversion (X_2) can be	4

	achieved using one PFR of volume V. Thus it makes no difference if two PFRs are connected in series or one PFR of same reactor volume. Therefore PFR's are not connected in series.	
6-b	**Entropy**: Entropy(s) is the measure of the total disorder or randomness of the system or it is a measure of the unavailable energy to perform useful work. **Entropy Change for an Ideal Gas**: From first law of thermodynamics, dU = dQ – dW dQ = dU + dW ……..(i) But dQ = TdS ………….(ii) dW = PdV ……(iii) For ideal gas dU= n C_vdT……… (iv) Substituting ii,iii and iv in i TdS = n C_vdT + PdV $dS = \frac{n\,CvdT}{T} + \frac{PdV}{T}$ For ideal gas $P = \frac{nRT}{V}$ Substituting $dS = \frac{n\,CvdT}{T} + \frac{nRdV}{V}$ Integrating between limits $\int_{S_1}^{S_2} dS = nC_v\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V}$ $\Delta S = nC_v\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ ……(v) For isothermal operation, $\Delta S = nR\ln\frac{V_2}{V_1}$ For ideal gas PV = RT $\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$ Therefore $\frac{V_2}{V_1} = \frac{T_2P_1}{T_1P_2}$ ……… (vi) Also Cp – Cv = R ………..(vii)	1 2

<table>
<tr><td></td><td>Substituting vi and vii in v
$\Delta S = n(C_p - R)\ln\frac{T_2}{T_1} + nR\ln\frac{T_2P_1}{T_1P_2}$
$\Delta S = nC_p\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$
For isothermal operation, $\Delta S = nR\ln\frac{P_1}{P_2}$</td><td>1</td></tr>
<tr><td>6-c</td><td>Order of Reaction: It is the sum of exponents of the concentrations in the rate expressions OR it is the sum of powers to which concentrations are raised in the rate equation.
Classification of reactions on the basis of Order
1. First order reaction:
2. Second order reaction:
3. Third order reaction:
4. Zero order reaction:</td><td>2
2</td></tr>
<tr><td>6-d</td><td>Difference between integral method & differential method of analysis of kinetic data:
<table>
<tr><td>Sr.No.</td><td>Integral Method</td><td>Differential Method</td></tr>
<tr><td>1.</td><td>This method puts a particular rate equation to the test by integrating and comparing the predicted concentration versus time curve with the experimental C vs t data. If the fit is unsatisfactory, another rate equation is suggested and tested.</td><td>This method deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative dC_A / dt and testing the goodness of fit of the equation with experiment.</td></tr>
</table></td><td>1 mark each to any 4 points</td></tr>
</table>

2	Easy to use	This method is not that much easy, complicated & time consuming.
3	It is useful for testing relatively simple rate equations	It is useful for testing more complicated rate equations
4	It can be used when scattered data is available.	It is used only when more accurate &large amount of data are available.
5	This method can be only test probable form of rate equation.	It can be used to evolve the rate equation to fit the data

6-e **Given:**

X_A =0.70 ,t = 13 min

For constant volume batch reactor,

$$t = CAO \int_0^{X_A} \frac{dX_A}{-r_A}$$

First order chemical reaction is taking place

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

$$t = CAO \int_0^{X_A} \frac{dX_A}{\text{k. CA0 } (1 - \text{XA })}$$

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

$-\ln(1-0.70) = k * 13$ 1

$k = 0.0926\ \text{min}^{-1}$

For Plug flow reactor (constant –density system):

$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$ 1

$$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{k.C_{A0.(1-X_A)}}$$

$$\tau = \int_0^{X_A} \frac{dX_A}{k.(1 - X_{A})}$$

	Space time $\tau = \frac{1}{k}(-\ln(1-X_A)) = \frac{1}{0.0926}(-\ln(1-0.7)) = \mathbf{13\ min}.$ Space velocity = s = 1/ τ **= 1/13 = 0.07692 min^{-1}**	1 1