SUMMER-16 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.

<table>
<tr><th>Q No.</th><th>Answer</th><th>marks</th><th>Total marks</th></tr>
<tr><td>1A</td><td>Attempt any THREE</td><td></td><td>12</td></tr>
<tr><td>1A-a</td><td>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.
$R \rightarrow I^*$ Initiation step
$I^* + R \rightarrow I^* + P$ Propagation step
$I^* \rightarrow P$ Termination step
Non chain reaction:
In non-chain reaction, the intermediate is formed in the first reaction and then disappears as it reacts further to give products.
$R \rightarrow I^*$
$I \rightarrow P$</td><td>2
2</td><td>4</td></tr>
<tr><td>1A-b</td><td>Relation between conversion and equilibrium constant for second order reversible reaction
Reaction is $A + B \leftrightarrow R + S$
Let 1 mole of A and 1 mole of B is present initially.
x_A mole of A reacts at equilibrium
P is the total pressure.
When 1 mole of A reacts, 1mole of B also reacts. Then 1mole of R and 1 mole of S is produced
<table>
<tr><th></th><th>A</th><th>B</th><th>R</th><th>S</th><th>Total moles</th></tr>
<tr><td>Moles present initially</td><td>1</td><td>1</td><td>-</td><td>-</td><td></td></tr>
</table>
</td><td></td><td>4</td></tr>
</table>

<table>
<tr>
<td></td>
<td>
<table>
<tr><td>Moles reacted / produced at equilibrium</td><td>x_A</td><td>x_A</td><td>x_A</td><td>x_A</td><td></td></tr>
<tr><td>Moles present at equilibrium</td><td>$1- x_A$</td><td>$1- x_A$</td><td>x_A</td><td>x_A</td><td>2</td></tr>
<tr><td>Mole fraction</td><td>$1- x_A/2$</td><td>$1- x_A/2$</td><td>$x_A / 2$</td><td>$x_A / 2$</td><td></td></tr>
<tr><td>Partial pressure</td><td>$P(1- x_A) / 2$</td><td>$P(1- x_A) / 2$</td><td>$P x_A / 2$</td><td>$P x_A / 2$</td><td></td></tr>
</table>

$$K_p = \frac{P\left(\frac{X_A}{2}\right)P\left(\frac{X_A}{2}\right)}{P\left(\frac{1-X_A}{2}\right)P\left(\frac{1-X_A}{2}\right)} = \frac{x_A^2}{(1-x_A)^2}$$

$K_p\ (1- x_A)^2 = x_A^2$

$K_p(1-2x_A+ x_A^2) = x_A^2$

$K_p- 2 K_p x_A + K_p x_A^2 = x_A^2$

$(K_p - 1) x_A^2 - 2 K_p x_A + K_p = 0$

$$x_A = \frac{2K_P \pm \sqrt{(4K_P{}^2 - 4(K_P-1)K_P)}}{2(k_P-1)}$$
</td>
<td>2
2</td>
<td></td>
</tr>
<tr>
<td>1A-c</td>
<td>
$C_{A1} = 0.15$ mol / l $-r_{A1} = 2.7 * 10^{-3}$ mol / l min

$C_{A2} = 0.05$ mol / l $-r_{A1} = 0.3 * 10^{-3}$ mol / l min

$-r_A = KC_A{}^n$

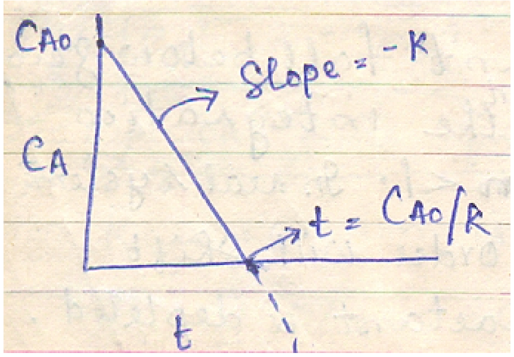
Taking log , $\log -r_A = \log K + n \log C_A$

$\text{Log} (-r_{A1} / -r_{A2}) = n \log (C_{A1} / C_{A2})$

$\text{Log} (2.7 * 10^{-3} / 0.3 * 10^{-3}) = n \log(0.15 / 0.05)$

$n = 2$

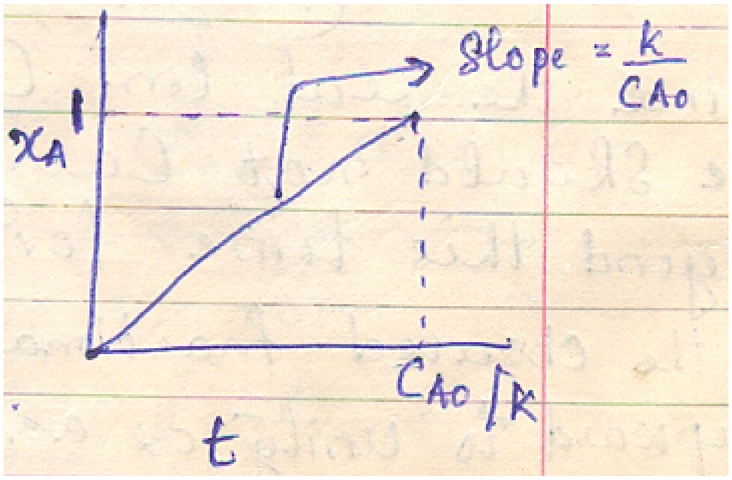
Order of the reaction is 2
</td>
<td>2
2</td>
<td>4</td>
</tr>
</table>

1A-d	**Relation between C_A and X_A**		4
	i)Constant volume System		
	$C_A=C_{A0}(1-X_A)$	2	
	ii)Variable volume system		
	$\frac{C_A}{C_{A0}}=\frac{(1-X_A)}{(1+\varepsilon_A X_A)}$	2	
1B	**Attempt any ONE**		**6**
1B-a	**Integrated form of rate expression for zero order reaction**		6
	Rate equation is $-r_A = -\frac{dC_A}{dt} = C_{A0}\frac{dx_A}{dt} = k$	1	
	In terms of concentration $-\frac{dC_A}{dt} = k$ Integrating between appropriate limits		
	$\int_{C_{A_0}}^{CA} -dCA = k\int_0^t dt$ $C_{A0} - C_A = kt$ for $t < \frac{C_{A0}}{k}$	1.5	
		1	
	In terms of fractional conversion $C_{A0}\frac{dx_A}{dt} = k$ Integrating between appropriate limits	1.5	

<table>
<tr>
<td></td>
<td>

$C_{A0}\int_0^{xA} d_{xA} = k\int_0^t dt$

$C_{A0} X_A = kt$ for $t < \frac{C_{A0}}{k}$



</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1B-b</td>
<td>

Theories of reaction rate constant:

1. Arrhenius theory
2. Collision theory
3. Transition state theory

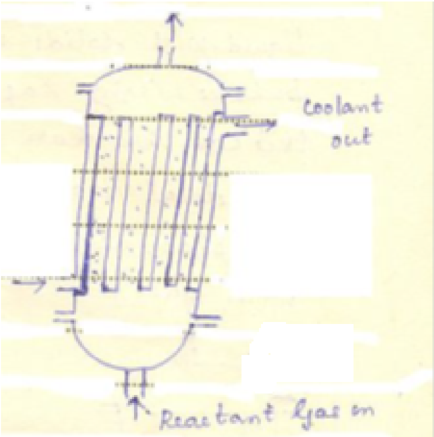
<table>
<tr><th></th><th>Transition State Theory</th><th>Collision Theory</th><th>Arrhenius theory</th></tr>
<tr><td>i) Experiment</td><td>Prediction of reaction rates is more accurate with experiment.</td><td>Prediction of reaction rates is less accurate with experiment.</td><td>Prediction of reaction rates is more accurate with experiment</td></tr>
<tr><td>ii) Mathematical</td><td>Temperature Dependency is</td><td>Temperature Dependency is</td><td>Temperature Dependency is</td></tr>
</table>

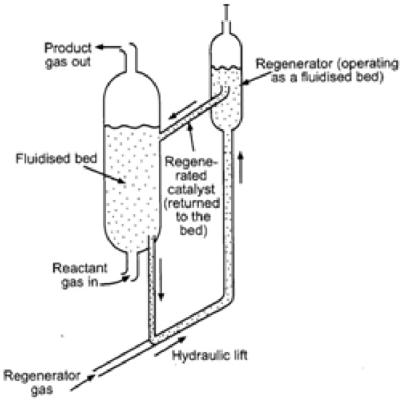
</td>
<td>1
5</td>
<td>6</td>
</tr>
</table>

equation	$k \propto T.e^{-E/RT}$	$k \propto T^{1/2}.e^{-E/RT}$	$k \propto .e^{-E/RT}$
iii) Activated complex	The theory views that the formation of activated complex is very rapid& decomposition of activated complex is slow.	The theory views that the decomposition of activated complex is very rapid & formation of activated complex is slow.	No activated complex is formed

2	**Attempt any TWO**		**16**
2-a	**Derivation for temperature dependency of rate constant from collision theory** The collision rate of molecules in a gas is found from the kinetic theory of gases. For the bimolecular collision of like molecules A , $Z_{AA} = \square_A^2 n_A^2 \sqrt{\frac{4\pi kt}{M_A}}$ $= \square_A^2 \frac{N^2}{10^6} \sqrt{\frac{4\pi kt}{M_A}} C_A^2$ ....(i) = number of collisions of A with A / sec.cm^3 Where $\square$ = diameter of molecule, cm M = (molecular weight) / N, mass of a molecule, gm N = Avogadro's number C_A = concentration of A, mol / liter $n_A = NC_A / 10^3$, number of molecules of A / cm^3 k = Boltzmann constant For the bimolecular collision of unlike molecules in a mixture of A and B, kinetic theory gives $Z_{AB} = \{(\square_A + \square_B)/2\}^2 n_A n_B \sqrt{8\pi kT\left(\frac{1}{M_A} + \frac{1}{M_B}\right)}$	2	8

	$= \{(\square_A + \square_B)/2\}^2 \frac{N^2}{10^6}\sqrt{8\pi kT\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}C_AC_B$.........(ii) If every collision between reactant molecules results in the transformation of reactants into product, these expressions give the rate of bimolecular reactions. The actual rate is much lower than that predicted and this indicates that only a small fraction of all collisions result in reaction. This suggests that only those collisions that involve energies in excess of a given minimum energy E lead to reaction. From the Maxwell distribution law of molecular energies the fraction of all bimolecular collisions that involves energies in excess of this minimum energy is given approximately by $e^{-E/RT}$ where E □□ RT. Thus the rate of reaction is given by $-r_A = -\frac{1}{V}\frac{dN_A}{dt} = k\,C_AC_B$ …….(iii) = (collision rate, mole / liter.sec)* (fraction of collision involving energies in excess of E) $= Z_{AB}\frac{10^3}{N}e^{-E/RT}$ $= \{(\square_A + \square_B)/2\}^2 \frac{N}{10^3}\sqrt{8\pi kT\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}e^{-E/RT}C_AC_B$ ……(iv) Comparing iii and iv, $\mathbf{k \propto T^{1/2} e^{-E/RT}}$	2 3 1	
2-b	**Given:** $X_A = 0.70$,t = 13 min For batch reactor, in which first order chemical reaction is taking place $-r_A = k.C_A$ $-\ln(1 - X_A) = kt$ $-\ln(1-0.70) = k * 13$ $k = 0.0926\ \text{min}^{-1}$ **For Plug flow reactor** (constant –density system): $\frac{V}{F_{A0}} = \int_0^{X_A}\frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$	2	8

	$\tau = C_{A0}\int_0^{X_A}\frac{dX_A}{k.C_{A0.(1-X_A)}}$ $\tau = \int_0^{X_A}\frac{dX_A}{k.(1-X_A)}$ Space time $\tau = \frac{1}{k}(-\ln(1-X_A))$ = $\frac{1}{0.0926}(-\ln(1-0.7)) =$ **13 *min*.** Space velocity = s = 1/ τ = **1/13 = 0.07692 min^{-1}** **For Mixed flow reactor** : $\tau = \frac{C_{A0}.X_A}{(-r_A)}$ $\tau = \frac{C_{A0}.X_A}{-r_A} = \frac{C_{A0}.X_A}{kC_{A0}(1-X_A)}$ **Space time**τ = $\frac{0.70}{0.0926(1-0.7)}$ **= 25.2 min.** **Space velocity = s = 1/ τ = 1/25.2 = 0.03968 min^{-1}**	2 1 2 1	
2-c	**Packed bed(Fixed bed) reactor**  **Explanation:**Fixed bed reactors normally consist of one or more tubes packed with catalyst particles and are generally operated in vertical position. The catalyst particles may be of a variety of sizes and shapes – granular, pelleted, cylinder, spheres etc. Wires of metals are made into screens in the case of expensive catalysts. Chances of hot spot formation are there in fixed bed reactor. In order to prolong the time between regeneration and shut down, the reactor tube may be made longer than required. The	2 2	8

	problem of regeneration of catalyst is a serious issue in this type of reactor. **Fluidized bed reactor with regenerator:**  **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 2	
3	**Attempt any FOUR**		16
3-a	$C_{NH3} = 0.105$ mol / l $C_{H2} = 1.5$ mol / l $C_{N2} = 1.1$ mol / l T = 1000K $N_2 + 3\ H_2 \leftrightarrow 2\ NH_3$		4

	$K_c = \underline{\hspace{2cm}} = 0.105^2 / (1.5^3 *1.1) = \mathbf{2.97 * 10^{-3} (g\ mol/ l)^{-2}}$ $Kp=Kc(RT)^{\Delta n}$ $\Delta n = 2-4 = -2$ $Kp = 2.97 * 10^{-3} * (0.08206 *1000)^{-2} = \mathbf{4.4 * 10^{-7}\ atm^{-2}}$	2 2	
3-b	**Definition of Half life :** Itisthetime requiredtoreducetheconcentrationofthereactantto halfofitsoriginalvalue. **Relation between half life and rate constant for first order reaction:** $\boxed{t_{1/2} = \frac{0.693}{k}}$ **Characteristics.** Half-life of first order reaction is independent of initial concentration of the reactant	1 2 1	4
3-c	**Definition:** **i)fugacity:** It is the fictitious (imaginary) pressure for real gases **ii) Chemical potential:** Itisdefined asthechangeinfree energyofasubstancewhenonemoleofitis addedtosuchalarge quantityofthesystemthatthere is noappreciablechangeinoverallcompositionofthesystematconstant temperature&pressure. **iii) chemical equilibrium constant:** It is the ratio of rate constants of forward and backward reaction. Or It is the ratio of product of the concentration of the products to the product of concentration of the reactants. **iv) Gibb's free energy:** Itistheenergyactuallyavailabletodousefulwork.It predicts thefeasibilityandequilibrium	1 1 1 1	4

	conditionsforchemicalreactionsat constanttemperatureandpressure.		
3-d	**Types of intermediates in non- chain reaction:** 1.Freeradicals**.**Freeatomsorlargerfragments of stable molecules which contain one or more unpaired electrons are called free radicals.The unpaired electrons designated by a dot in the chemical symbol for the substance. Eg.$C\dot{H}_3 C_2\dot{H}_5$ 2.Ions andpolarsubstances. Electrically charged atoms, moleculesorfragmentsofmoleculessuchasNa$^+$,OH$^-$**,**NH4$^+$arecalledions.Theymayact asintermediatesinreaction. 3.Molecules:ConsidertheconsecutivereactionA→R→S Thisisamultiple reaction.IftheproductRishighlyreactive,itsconcentration inthereactionmixturecanbecometoosmall tomeasure.Insuchasituation,R isnotobservedand canbeconsideredtobea reactiveintermediate. 4.Transitioncomplexes.The collisionbetweenreactantmoleculesresultina widedistributionofenergiesamongtheindividual molecules.Thiscanresultin strainedbonds,unstableformofmoleculesorunstableassociationofmolecules whichcantheneitherdecomposetogiveproductsorbyfurther collisionreturn tomolecules inthenormalstate.Suchunstableformsarecalledtransition complexes.	1 mark each	4
3-e	**Steps involved in solid catalyzed gas phase reactions** 1. Diffusion of the reactant from bulk fluid phase to external surface of catalyst 2. Diffusion of reactant tfrom pour mouth into catalyst pores 3. Adsorption of reactant into catalyst surface 4. Chemical reaction to form product 5. Deadsorption of product 6. Diffusion of deadsorped product from interior of catalyst pores to surface 7. Diffusion of product to the bulk of fluid phase	4	4

4	**Attempt any THREE**		12
4A-a	**Derivation of integrated rate expression for irreversible second order reaction2A →Products:**		4
	2A → product		
	In terms of conversion		
	$-r_A = -d_{CA}/dt = kC_A^2$	1	
	$C_A=C_{A0}(1-X_A)$		
	$d_{CA} = -C_{A0}.d_{XA}$	1	
	$- d_{CA}= C_{A0}. d_{XA}$		
	$C_{A0} (d_{XA}/dt)=k. C_{A0}^2(1-X_A)^2$	1	
	On integrating		
	$1/ C_{A0}\{ X_A/(1-X_A)\}= kt$	1	
4A-b	**Catalyst deactivation categories**		4
	1. Deactivation by Fouling 2. Chemical Deactivation - Poisoning 3. Deactivation by Thermal Degradation and Sintering	2	
	Description:		
	Deactivation by Fouling Generally fouling covers all phenomena where the surface is covered with adeposit. The most widely known form of fouling of catalysts is coke formation. Most of coke formation arises as a result of carbonaceous residues covering the active sites of a heterogeneous catalyst surface, subsequently decreasing the active surface area of the catalyst. In addition the deposition of rust and scale from elsewhere in the catalytic system is not uncommon. Coke-forming processes also involve chemisorption of different kinds of carbons or condensed hydrocarbons that may act as catalyst poisons causing the chemical deactivation of the catalyst. Eg. The fouling of zeolite catalysts occurs in the form of coke molecules limiting the access of the reactant hexane to the active sites of catalyst.	2	

	Due consideration should be given to any other method of catalyst deactivation		
4A-c	CA0’=0.1 mol/l $t_{1/2}$’= 1152 min CA0’’ = 0.2mol/l$t_{1/2}$’’ = 568 min $t_{1/2} = \frac{C_{AO}^{1-n}}{k(n-1)}[(2^{n-1})-1]$ $(t_{1/2}' / t_{1/2}'') = (C_{A0}' / C_{A0}'')^{1-n}$ Taking log and rearranging $n = 1-(\log(t_{1/2}'/ t_{1/2}'') / \log(C_{A0}''/ C_{A0}'))$ n = 1-(log (1152/5 68)/(log (0.1/0.2)) n= 1 +1.02 = 2.02 **Order of the reaction is 2**	2 2	4
4A-d	**Derivation of $K_p = K_c(RT)^{\Delta n}$** Consider the reaction aA +bB + …. → rR + sS……. $K_c = (C_R^r . C_S^s) / (C_A^a .C_B^b)$ For ideal gas $C_i = p_i / RT$ Therefore $K_c = \{(p_R / RT)^r . (p_S / RT)^s\} / \{ (p_A / RT)^a . (p_B / RT)^b\}$ $= (p_R^r .p_S^s) / (p_A^a . p_B^b) . (1 / RT)^{(r + s + … -(a+b=…))}$ R is the ideal gas constant T the absolute temperature in K P is the pressure in atm ie$K_c = K_p . (1 / RT)^{\Delta n}$where $K_p = (p_R^r . p_S^s) / (p_A^a . p_B^b)$ $\Delta n = (r + s + …-(a + b +….))$is the difference in the number of moles of product and reactant Or $K_p = K_c \times (RT)^{\Delta n}$	1 2 1	4
4B	**Attempt any one**		**6**
4B-a	Rate of disappearance of A is $-dC_A / dt = (0.1-0.05) / 2 = 0.025$ mol / l hr Rate of disappearance of B is $-dC_B / dt = (0.1-0.075) / 2 = 0.0125$ mol / l hr Since rate of disappearance of A is high, **the reaction A → R proceeds at a faster rate**	1 1 1	6

	Rate of formation of R is $dC_R / dt = (0.05-0) / 2$ = **0.025 mol / l hr** Rate of formation of S is $dC_S / dt = (0.025-0) / 2$ = **0.0125 mol / l hr**	1.5 1.5	
4B-b	**Derivation for entropy change of 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 $dU= nC_vdT$……… (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) Substituting vi and vii in v $\Delta S = n(C_p – R)\ln\frac{T_2}{T_1} + nR\ln\frac{T_2P_1}{T_1P_2}$	2 1 2	6

	$\Delta S = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$ **For isothermal operation,** $\Delta S = nR\ln\frac{P_1}{P_2}$ **For constant pressure process** $nC_p\ln\frac{T_2}{T_1}$	1	
5	**Attempt any TWO**		**16**

5-a	**Derivation of integrated rate expression for first order reversible reaction A ↔B** For first order unimolecular reaction: A $\rightleftharpoons$ B The net rate of disappearance of A $-r_A = k_1C_A - k_2C_B$ The rate of formation of B $r_B = k_1C_A - k_2C_B$ $\frac{dC_B}{dt} = \frac{-dC_A}{dt} = k_1C_A - k_2C_B$ $Let\ initial\ mole\ ratio\ of\ B\ to\ A\ to\ be\ M$ $M = \frac{C_{B0}}{C_{A0}}$ Concentration of A at time t is $C_A = C_{A0}(1 - X_A)$ Therefore on differentiating $-dC_A = C_{A0}dX_A$ Concentration of B at time t is $C_B = C_{B0} + C_{A0}X_A$ $-\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = k_1C_{A0}(1 - X_A) - k_2(C_{B0} + C_{A0}X_A)$ The reaction is composed of two elementary reaction $\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = C_{A0}[k_1(1 - X_A) - k_2(M + X_A)]$eq. **I** At equilibrium ,net rate is zero ,therefore $\frac{-dC_A}{dt} = 0$ and $X_A = X_{Ae}$ $(fractional\ conversion)$ $0 = C_{A0}[k_1(1 - X_{Ae}) - k_2(M + X_{Ae})]$ $k_1(1 - X_{Ae}) = k_2(M + X_{Ae})$ eq.II $K_C = \frac{C_{Re}}{C_{Ae}} = \frac{k_1}{k_2} = \frac{(M+X_{Ae})}{(1-X_{Ae})}$eq.III $From\ eq.I\ ,we\ have$ $\frac{dX_A}{dt} = [k_1(1 - X_A) - k_2(M + X_A)]$	2	8

Substituting the value of k_2 from eq.III in above equation

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

$$\frac{dX_A}{dt} = k_1\left[\frac{(1 - X_A)(M + X_{Ae}) - (1 - X_{Ae})(M + X_A)}{(M + X_{Ae})}\right]$$

$$\frac{dX_A}{dt} = k_1\left[\frac{M + X_{Ae} - MX_A - X_AX_{Ae} - M - X_A + MX_{Ae} + X_AX_{Ae}}{(M + X_{Ae})}\right]$$

2

Collecting the terms,we get

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

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

$$\int_0^{X_A} \frac{dX_A}{X_{Ae} - X_A} = \frac{k_1(M + 1)}{(M + X_{Ae})}\int_0^t dt$$

$$-ln\left(\frac{X_{Ae} - X_A}{X_{Ae}}\right) = \frac{(M+1)}{(M+X_{Ae})}k_{1.}t \qquad \text{eq. IV}$$

2

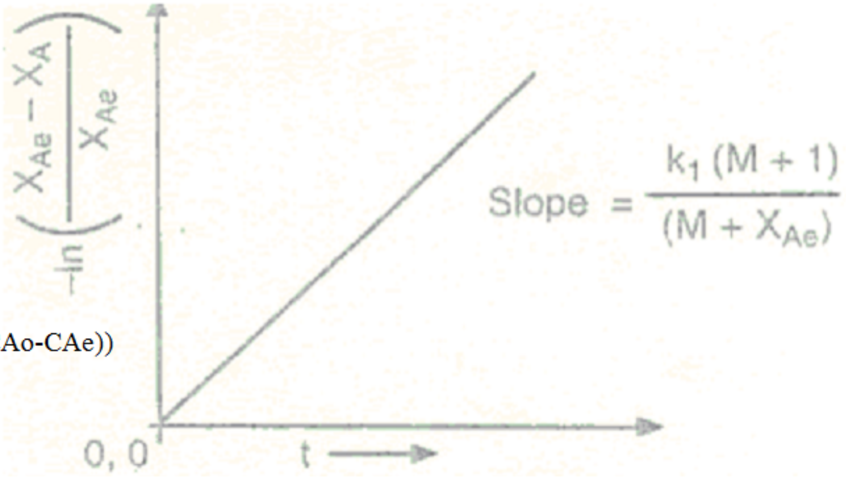
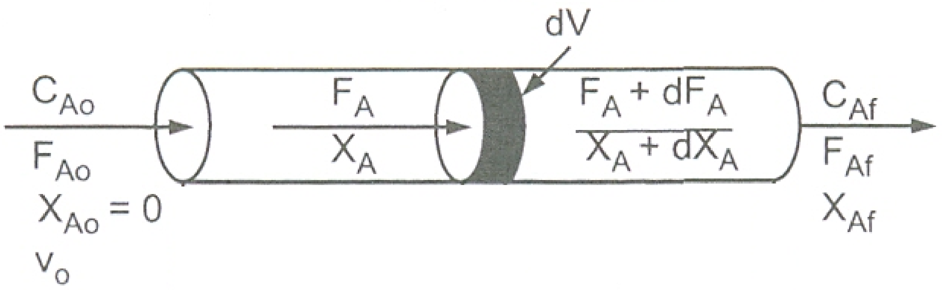
$$-ln\left(\frac{X_{Ae} - X_A}{X_{Ae}}\right) = -ln\left(\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}}\right) = \frac{(M+1)}{(M+X_{Ae})}k_{1.}t \qquad \text{eq.V}$$

Eq. V is the desired integrated rate equation for reversible first order reaction.

Graphical representation

A plot of

$-\,ln\left(\dfrac{X_{Ae} - X_A}{X_{Ae}}\right)$ *vs time gives a straight line with slope equal to* $\dfrac{(M + 1)}{(M + X_{Ae})}k_{1.}$

	 **or** -ln((CA -CAe) / (CAo-CAe))	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 flowreactor, the last term is zero. Input of A to reactor = Output of A from reactor + Disappearance of A due to chemical reaction …………….(1)	2	8

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

$F_A = F_{A0}(1- X_A) = F_{A0} - F_{A0}.X_A$

$dF_A = - F_{A0}.dX_A$

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)

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

$- dF_A = (-r_A)\,dV$

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

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

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. 2

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

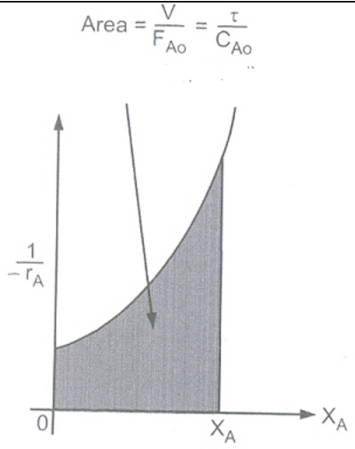
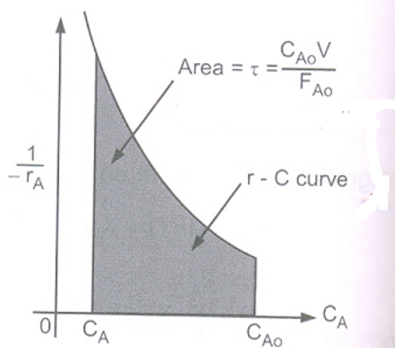
$$\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$$

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

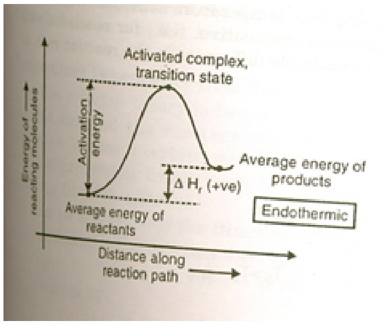
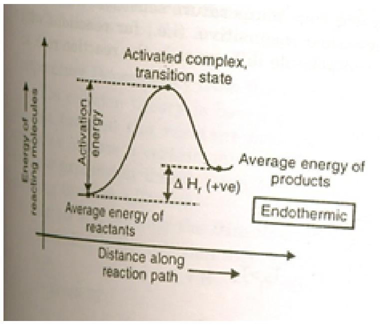
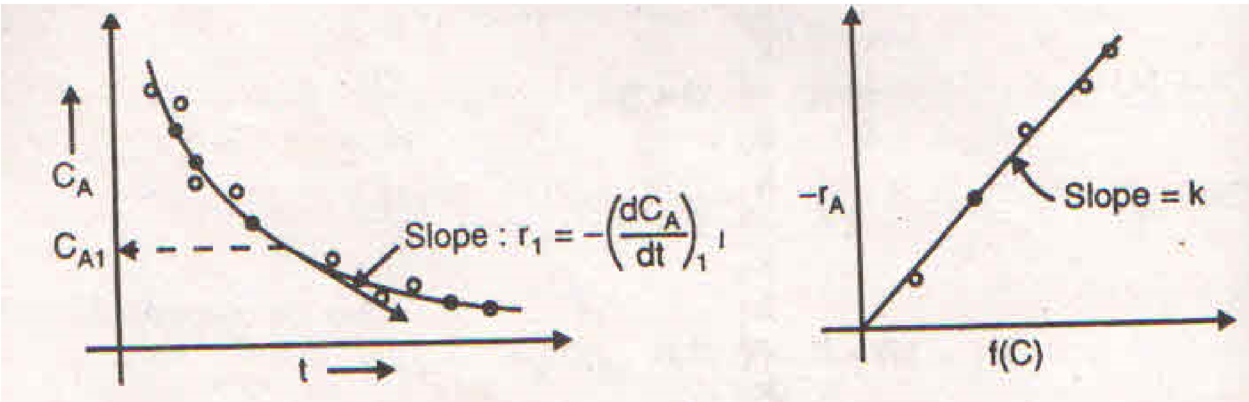
For constant volume system : 2

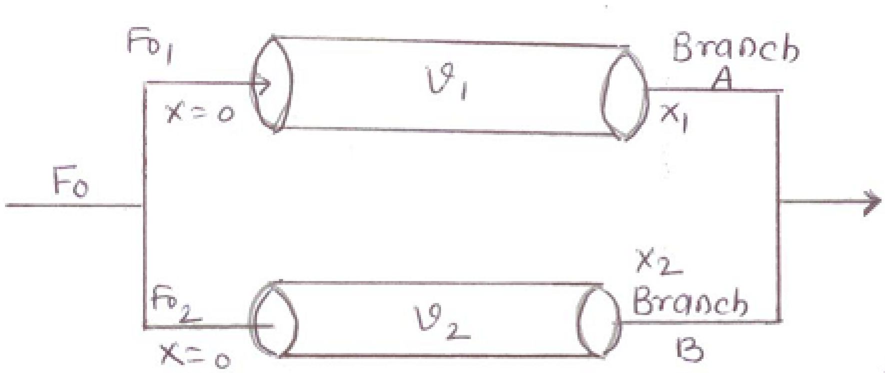
$$\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}} = \frac{-1}{C_{AO}} \int_{C_{Ao}}^{C_A} \frac{dC_A}{-r_A}$$

Graphical representation:

	 	2	
5-c	**Comparison of MFR and PFR** 1) For any given duty & for all positive reaction orders ,size of MFR is always larger than that of PFR. The volume ratio Vm / Vp increases with reaction order. 2) For low values of conversion,reactor size is only slightly affected by type of flow. As conversion approaches zero, volume / size ratio of these reactors approaches unity. The size ratio increases very rapidly at high values of conversion. 3) Design of reactor is affected by density variation during reaction. Expansion(density decrease) during reaction increases the size ratio.As density decreases, the effectiveness of CSTR wrt PFR. Density increase during reaction has the opposite effect. 4) The performance equation for MFR is $\tau_m . C_{A0}^{n-1} = \left(\frac{C_{A0}V}{F_{A0}}\right)_m = \frac{X_A(1+\varepsilon_A . X_A)^n}{k(1-X_A)^n}$ For PFR $\tau_p . C_{A0}^{n-1} = \left(\frac{C_{A0..}^{n} . V}{F_{A0}}\right)_p = \frac{1}{K}\int_0^{XA}\frac{(1+\ \varepsilon AXA)^n}{(1-X_A)^n} . dX_A$ **5)** For a given space time, conversion in a PFR is higher than in MFR. 6) It is possible to operate MFR under isothermal conditions whereas with PFR it is difficult.	2 marks each for any four points	8

	7) MFR have long residence time compared to PFR. 8) MFR is not suitable for high pressure reactionswhereas PFR is suitable.		
6	**Attempt any FOUR**		**16**
6-a	**Space time:**It is the time necessary to process one reactor volume of feed at specified conditions. **Unit:** (units of time) second,minute,hour **Space velocity:** It is the number of reactor volumes of feed at specified conditions which can be treated in unit time **Unit:** (reciprocal of time) second $^{-1}$,minute $^{-1}$,hour $^{-1}$	1 1 1 1	4
6-b	**Temperature increase is not desirable for exothermic reaction.** Van't Hoff equation is $\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$ For exothermic reaction, ΔH is negative. When temperature is increased, dT is positive; the overall equation is negative, which means ln K is negative. When ln K is negative, the value of K is low which denotes lower concentration of products. Therefore temperature increase is not desirable for exothermic reaction.	1 3	4
6-c	**Significance of activation energy.** Activation energy is the minimum energy that the reactants must acquire before reaction takes place to give the product. Activation energy can be considered as a potential energy barrier. Only those molecules that have sufficient energy to reach the top of the barrier and form activated complex react. Smaller the activation energy (low barrier), greater will be the number of activated molecules and faster will be the rate of reaction. It will help to find out the nature of the reaction (endothermic or exothermic)It will give the difference between activated complex and energy of reactant.	4	4

	 		
6-d	**Differential method of analysis of data** 1)Assume a mechanism and from it obtain a rate equation of the form $-r_A = \frac{-dC_A}{dt} = kf(c)$ 2) From experiment obtain concentration-time data and plot them. 3) Draw a smooth curve through this data. 4) Determine the slope of this curve at suitably selected concentration values.These slopes($\frac{-dC_A}{dt}$) are the rates of reaction at these composition. 5) Evaluate $f(c)$ for each composition. 6) Plot $\frac{-dC_A}{dt}$ $vs\ f(c)$ for each composition.If we get a straight line through origin ,the rate equation is consistent with the data.If not ,the another rate equation should be tested. 	1 2 1	4

6-e	**Method of feeding when PFR's are connected in parallel** Consider PFRs are connected as follows  Two PFRs in Parallel arrangement	1	4
	For the PFRs connected in parallel,the whole system can be treated as a single plug flow reactor of volume equal to total volume of the individual units if the feed is distributed in such a manner that fluid stream which meet have the same composition.Thus for reactors in parallel ,V/F must be the same for each parallel line. Let us consider from above figure that volume of reactor 1 in branch A is V_1& of reactor 2 in branch B is V_2. For branch A $\frac{V_1}{F0_1} = \int_0^{x_1} \frac{dX}{(-r)}$ For branch B $\frac{V_2}{F0_2} = \int_0^{x_2} \frac{dX}{(-r)}$ For the PFRs in parallel ,the ratio V/F must be identical if the conversion is to be the same in each branch. x1= x2 =x $\frac{V_1}{F0_1} = \frac{V_2}{Fo_2}$ $F0 = F0_1 + F0_2$ Therefore Feed flow to first branch should be multiple of $\frac{V_2}{F_{01}} . V_1$	3	

	For example: If V1 = 80 lit & V2 = 40 lit $\frac{F_A}{F_B} = \frac{V_A}{V_B} = \frac{80}{40} = 2$ Therefore 2/3 rd of feed must be fed to branch A.		