WINTER-16 EXAMINATION

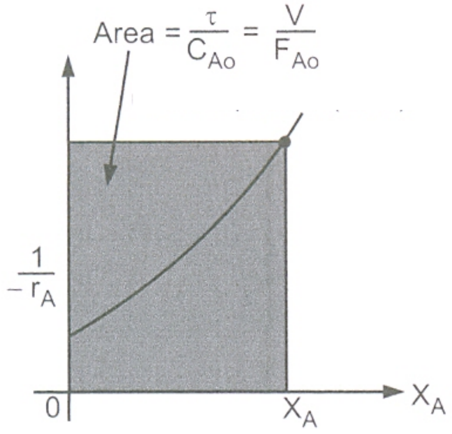
Model Answer

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></tr>
<tr><td>1</td><td>Attempt any THREE of the following</td><td>12</td></tr>
<tr><td>1A-a</td><td>Difference between order and molecularity of reaction.
<table>
<tr><th>Sr.No.</th><th>Molecularity</th><th>Order of reaction</th></tr>
<tr><td>1</td><td>Molecularity is the number of molecules,atoms or ions in a chemical reaction.</td><td>Order of reaction is the sum of exponents of the concentration terms involved in the rate equation.</td></tr>
<tr><td>2</td><td>Molecularity always have an integer value 1,2,3…</td><td>Order of reaction can have a fractional value.</td></tr>
<tr><td>3</td><td>Shows the elementary mechanism or separate steps of a complicated process</td><td>Shows the kinetic dependence of the rate on the concentration of the reactants.</td></tr>
<tr><td>4</td><td>Depending upon the value of molecularity, reaction can be unimolecular ,bimolecular etc.</td><td>Depending upon the value of order, the reactions are termed as first order, second order reactions</td></tr>
<tr><td>5</td><td>Molecularity is a theoretical quantity</td><td>Order of reaction is entirely an experimental value.</td></tr>
</table></td><td>1 mark each for any 4 points</td></tr>
<tr><td>1A-b</td><td>Relation between Kp and K_c(Derivation)
Consider the reaction aA +bB + …. → rR + sS…….</td><td>4</td></tr>
</table>

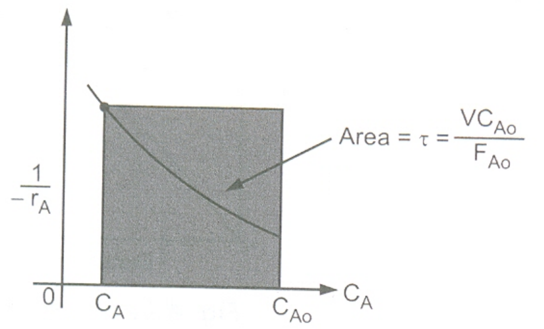
	$K_c = (C_R^r . C_S^s) / (C_A^a .C_B^b)$ For ideal gas $C_i = p_i / RT$ Therefore $K_c = \{(p_R / RT)^r . (p_S / RT)^s\} / \{ (p_A / RT)^a . (p_B / RT)^b\}$ $= (p_R^r .p_S^s) / (p_A^a . p_B^b) . (1 / RT)^{(r + s + \ldots -(a+b=\ldots))}$ R is the ideal gas constant T the absolute temperature in K P is the pressure in atm ie$K_c = K_p . (1 / RT)^{\Delta n}$where $K_p = (p_R^r . p_S^s) / (p_A^a . p_B^b)$ $\Delta n = (r + s + \ldots-(a + b +\ldots.))$is the difference in the number of moles of product and reactant Or $K_p = K_c \times (RT)^{\Delta n}$	
1A-c	**Autocatalytic reactions**:A reaction in which one of the products of the reaction acts as a catalyst is called as an autocatalytic reactions. Eg1. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ Here CH_3COOH acts as catalyst 2. Oxidation of a solution of oxalic acid by an acidified solution of $KMnO_4$. $2MnO_4^- + 6H^+ + 5(COOH)_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ Oxalic acid The reaction is very slow at room temp .The reaction is catalyzed by manganese ions(Mn^{2+}) that are not present at start of reaction,hence the rate of reaction is extremely slow..Once reaction starts,Mn^{2+}ions are formed ,the rate of reaction speeds up.	2 2 mark for any 1 eg.
1A-d	**Graphical representation:** **MFR** The performance or design equation is $V / F_{AO} = \tau / C_{AO} = X_A / -r_A$	



1

For constant density system

$V C_{AO} / F_{AO} = \tau = C_{AO} X_A / -r_A = (C_{AO} – C_A) / (-r_A)$

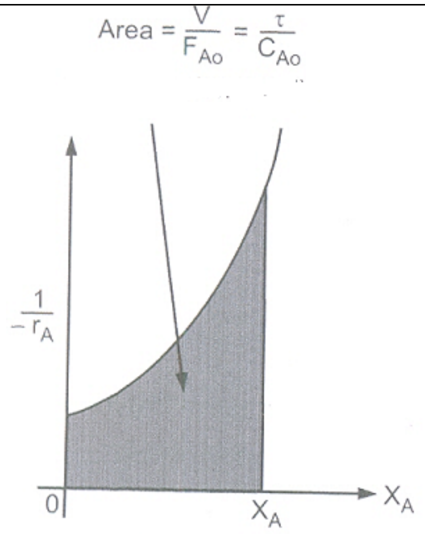
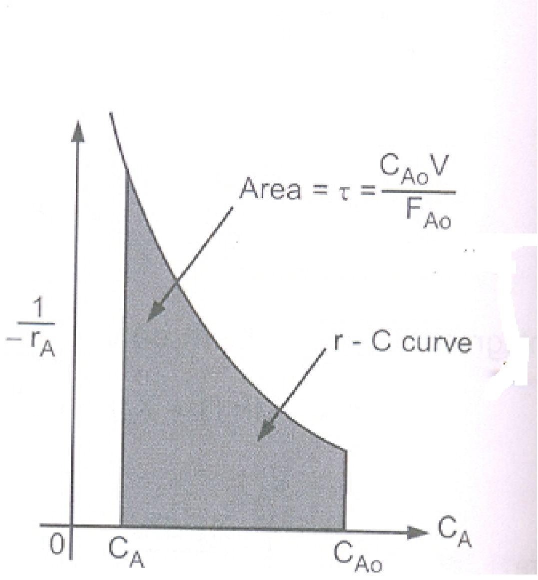


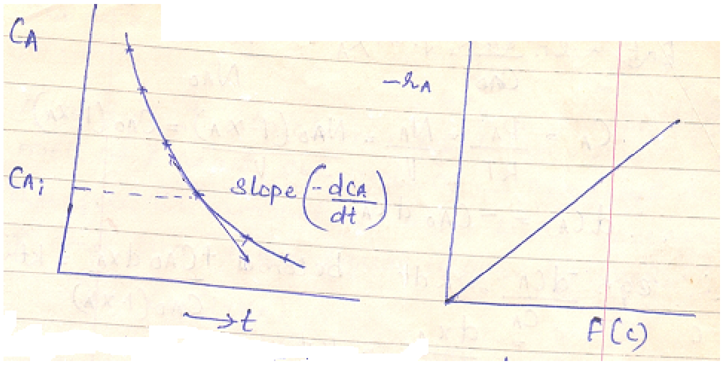
1

PFR

The performance or design equation is

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

	 For constant density system $\frac{V}{F_{A0}} = \int_0^{X_A}\frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}} = \frac{-1}{C_{AO}}\int_{C_{Ao}}^{C_A}\frac{dC_A}{-r_A}$ 	1 1
1B	**Attempt any ONE of the following**	6
1B-a	**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.  	4 2
1B-b	**Given:** $C_{A0} = 1$ mol/l $X_A = 0.80$ when $t = 8$ min. $X_A = 0.90$ when $t = 18$ min **Let us first assume reaction is of zero order.** Therefore the integrated equation for zero order reaction in terms of fractional conversion is $C_{A0}X_A = kt$ Case 1) Where $X_A = 0.80$ when $t = 8$ min.	

$1*0.8 = k*8$ 2

$k = 0.1\ (\text{min})^{-1}(\text{mol} / \text{l})$

Case 2) Where $X_A = 0.90$ when $t = 80$ min.

$1*0.9 = k*18$

$k = 0.05(\text{min})^{-1}(\text{mol} / \text{l})$

Since k values are not same, the reaction is **not of zero order**

Let us now assume reaction is of First order.The integrated equation of first order reaction in terms of fractional conversion is

$$\ln\left\lfloor\frac{1}{1-X_A}\right\rfloor = kt$$

Case 1) Where $X_A = 0.80$ when $t = 8$ min. 2

$$\ln\left\lfloor\frac{1}{1-0.8}\right\rfloor = k*8$$

$k = 0.201\ (\text{min})^{-1}$

Case 2) Where $X_A = 0.90$ when $t = 80$ min.

$$\ln\left\lfloor\frac{1}{1-0.9}\right\rfloor = k*18$$

$k = 0.1279\ (\text{min})^{-1}$

Since k values are not same, the reaction is **not of first order.**

Let us now assume it is of Second order. The integrated equation of second order reaction with respect to A in terms of fractional conversion is

$$\left\lfloor\frac{XA}{1-XA}\right\rfloor = kC_{A0}t$$

Case 1) Where $X_A = 0.80$ when $t = 8$ min. & $C_{A0} = 1$ mol/l

$$\left\lfloor\frac{0.8}{1-0.8}\right\rfloor = k*1*8$$

$k = 0.5\ (\text{mol/l})^{-1}\ (\text{min})^{-1}$

Case 2) Where $X_A = 0.90$ when $t = 18$ min. & $C_{A0} = 1$ mol/l

$$\left\lfloor\frac{0.9}{1-0.9}\right\rfloor = k*1*18$$

$k = 0.5\ (\text{mol/l})^{-1}\ (\text{min})^{-1}$ 2

	since k values are same, reaction is **of second order .**	
2	**Attempt any TWO of the following**	16
2-a	**The given expression** $\mathbf{T=\left(\frac{10KE}{Rln2}\right)^{1/2}}$ ***is wrong. k should not be there in the expression*** $k = ko\, e^{-E/RT}$ $\ln k = \ln ko - (E / RT)$ For 2 different temperatures, this can be written as $\ln k_1 = \ln ko - (E / RT_1)$ …….(1) $\ln k_2 = \ln ko - (E / RT_2)$ …….(2) Equation (2)- equation (1) is $\ln\frac{k_2}{k_1} = \frac{-E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ ………(3) Given $k_2 = 2 k_1$ and $T_2 = T_1 + 10$ Equation (3) becomes $\ln 2 = \frac{-E}{R}\left(\frac{1}{T_{1+10}} - \frac{1}{T_1}\right)$ $\ln 2 = \frac{-E}{R}\left(\frac{T_1 - T_{1+10}}{T_{1*}(T_{1+10})}\right)$ $\ln 2 = \frac{10E}{R\,T_1*(T_{1+10})}$…………(4) Assuming that the difference between T_1 and $T_1 + 10$ is negligible, $T_1 * (T_1 + 10)$ can be written as T_1^2 or simply T^2 Equation 4 can be written as $\ln 2 = \frac{10E}{R\,T^2}$ Therefore $\mathbf{T^2=\left(\frac{10E}{Rln2}\right)}$and $\mathbf{T=\left(\frac{10E}{Rln2}\right)^{1/2}}$ ***If the students have written the basic steps, full mark should be given***	8
2-b	**Comparison of size of MFR and PFR for first order reaction** The performance or design equation for MFR is $V / F_{AO} = \tau / C_{AO} =$ $\tau_m = \left(\frac{C_{A0}V}{F_{A0}}\right)_m = C_{AO} X_A / -r_A$	

	For first order reaction, $-r_A = k\ C_A = KC_{AO}(1-X_A) / (1+\epsilon_A X_A)$ Therefore $\tau_m = \left(\frac{C_{A0}V}{F_{A0}}\right)_m = C_{AO}\ X_A / -r_A = X_A(1+\epsilon_A X_A) / K(1-X_A)$…..(i) For constant volume system $\epsilon_A = 0$ $\tau_m = \left(\frac{C_{A0}V}{F_{A0}}\right)_m = C_{AO}\ X_A / -r_A = X_A / K(1-X_A)$………(ii) The performance or design equation for PFR is $\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$ $\tau_P = \left(\frac{C_{A0}V}{F_{A0}}\right)_P = C_{AO}\int_0^{x_A} \frac{dX_A}{-r_A}$ For first order reaction, $\tau_P = \left(\frac{C_{A0}V}{F_{A0}}\right)_P = C_{AO}\int_0^{x_A} \frac{dX_A}{-r_A} = \int_0^{x_A} \frac{(1+\epsilon AXA)dX_A}{K(1-XA)}$……….(iii) For constant volume system $\epsilon_A = 0$ $\tau_P = \left(\frac{C_{A0}V}{F_{A0}}\right)_P = C_{AO}\int_0^{x_A} \frac{dX_A}{-r_A} = \frac{1}{k}\int_0^{x_A} \frac{dX_A}{(1-XA)} = -\ln(1-X_A) / k$…….(iv) From eqn (i) and (iii), for variable density system $\tau_m / \tau_p = \left(\frac{C_{A0}V}{F_{A0}}\right)_m / \left(\frac{C_{A0}V}{F_{A0}}\right)_p =$ $\{X_A(1+\epsilon_A X_A) / K(1-X_A)\}_m / \{\int_0^{x_A} \frac{(1+\epsilon AXA)dX_A}{K(1-XA)}\}_p$ From eqn (ii) and (iv), for constant density system $\tau_m / \tau_p = \left(\frac{C_{A0}V}{F_{A0}}\right)_m / \left(\frac{C_{A0}V}{F_{A0}}\right)_p = \{X_A / (1-X_A)\}_m / \{-\ln(1-XA)\}_p$ Size of MFR is always greater than PFR	4 4
2-c	**Catalyst poison** They are substances present either in the reactants or produced by the reaction which lowers the activity of the catalyst. **Methods of catalyst Preparation:**	2 mark for definition of catalyst poison

1. Precipitation
2. Gel formation
3. Simple mixing
4. Impregnation method

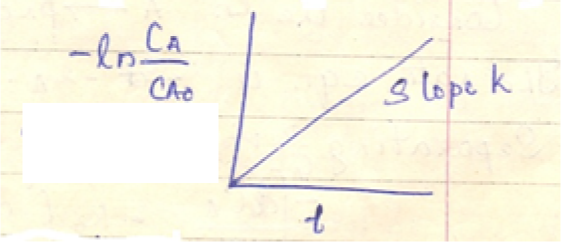
1.Precipitation method :
This method produces catalyst in porous form.It consists of adding a precipitating agent to the solution of the desired component. The precipitation is followed by washing,drying, calcinations & activation(or pretreatment)
Eg. Magnesium oxide catalyst is prepared by this method. 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.
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.

1.5 marks each

	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.***	
3	**Attempt any FOUR of the following**	16
3-a	**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 a given set of reactions).For spontaneous reaction,there should be decrease in Gibb's free energy change . If ΔG^0 is positive ,the reaction cannot take place under these conditions	4
3-b	**Derivation for 1st order reaction in terms of concentration:** Consider the reaction A →R The rate equation is $-r_A = -dC_A / dt = kC_A$….(1) Rearranging $- \frac{dC_A}{C_A} = k\,dt$ Integrating between appropriate limits $- \int_{C_{AO}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$ $-(\ln C_A / C_{A0}) = kt$  	3 1
3-c	$K_p = K_c (RT)^{\Delta n}$	1

	R=0.08206l.atm/mol.K T=300K i) $N_{2(g)}+O_{2(g)} \leftrightarrow 2NO_{(g)}$ $\Delta n=(2-(1+1))=0$ **$K_p/ K_c = 1$**	1.5
	ii) $NH_4Cl_{(s)} \leftrightarrow HCl_{(g)} + NH_{3(g)}$ $\Delta n=(1+1)-0 =2$ $K_p/ K_c = (0.08206 * 300)^2$ = **605.2 (l.atm/mol)^2**	1.5
3-d	**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 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 $\frac{-E}{R}$.	2

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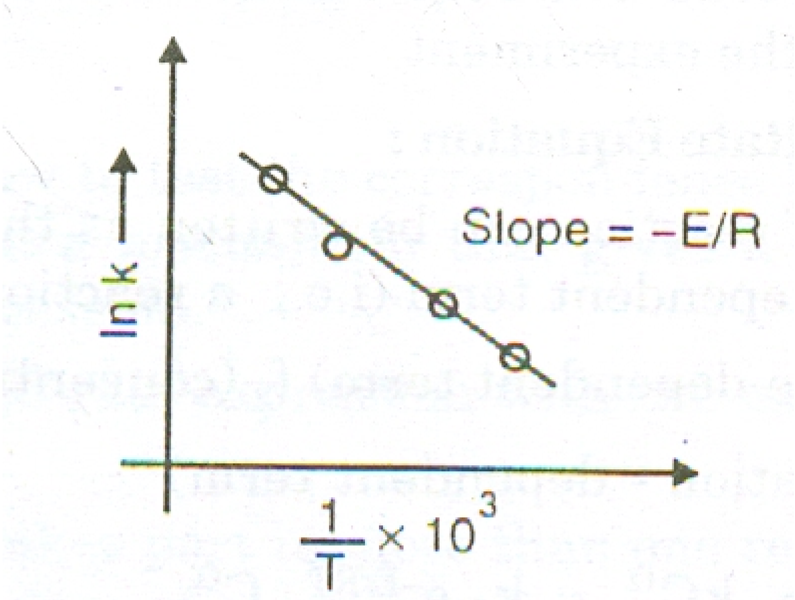
<td> </td>
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<td></td>
<td>Alternatively, if the rate is known at two different temperatures T_1 and T_2, then we can evaluate E with the help of equation
$\ln\frac{k_2}{k_1} = \frac{-E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Lower the value 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.</td>
<td>1</td>
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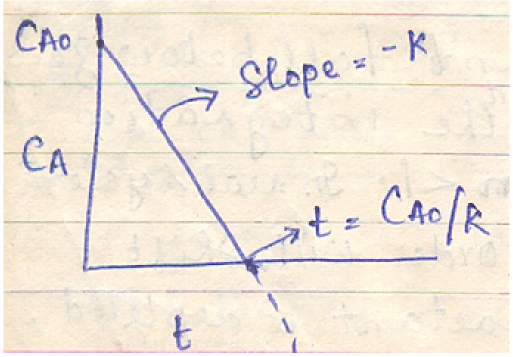
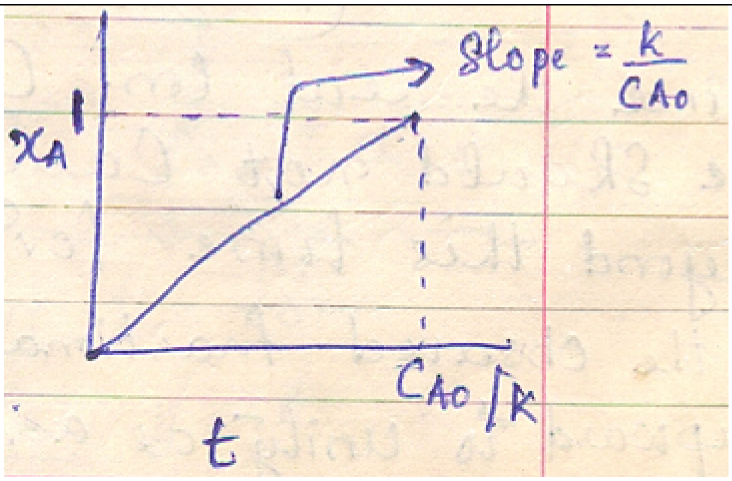
<tr>
<td>3-e</td>
<td>**Difference between fixed bed and fluidized bed reactor:**
<table>
<tr><th></th><th>Fixed bed</th><th>Fluidized bed</th></tr>
<tr><td>1.Flow</td><td>Approximates plug flow.</td><td>Complex.</td></tr>
<tr><td>2.temperature control</td><td>difficult</td><td>Can maintain isothermal conditions</td></tr>
<tr><td>3.size of catalyst</td><td>Cannot use very small size of catalyst</td><td>Can use small size of catalyst</td></tr>
</table>
</td>
<td>1 mark each for any four</td>
</tr>
</table>

	because of plugging and high pressure drop	
4. regeneration of catalyst	difficult	Easily done
5. recovery units	Catalyst loss is not there, so recovery units are not required	Catalyst loss is there, so recovery units are required
6. size	They are small diameter multi tubular reactors	They are large diameter vessels.
7.effective contacting	Easily attained	Effective contacting requires large amount of catalyst .
8.conversion	Highest conversion per unit weight of catalyst	low
9. hot spot formation	Chances are there	No hot spot formation
10. movement of catalyst	Catalyst particles are stationary and gas flows through it.	Catalyst particles are suspended in the gas stream.
11. Suitability	For small commercial units	For large commercial units

4A	**Attempt any THREE of the following**	12

<table>
<tr><td>4A-a</td><td>
<table>
<tr><td>Time,min</td><td>C_{N2O5}</td><td>$k= -\ln(C_A / C_{AO})$</td></tr>
<tr><td>0</td><td>0.16</td><td></td></tr>
<tr><td>1</td><td>0.113</td><td>0.3478</td></tr>
<tr><td>2</td><td>0.08</td><td>0.3465</td></tr>
<tr><td>3</td><td>0.056</td><td>0.349</td></tr>
<tr><td>4</td><td>0.04</td><td>0.3465</td></tr>
</table>
For fist order reaction $-(\ln C_A /C_{A0}) = kt$
Since K values are almost same, reaction is of first order
Value of rate constant is 0.3475 min^{-1}
<i>The problem can also be solved graphically by plotting a graph between $-(\ln C_A /C_{A0})$ (y axis) and t(x axis). slope of the graph gives the value of rate constant k</i>
</td><td>3
1</td></tr>
<tr><td>4A-b</td><td>Desired properties of catalyst:
A catalyst should have
1. Good porous structure or porosity. It should have extended internal surface.
2. Large surface area per unit volume
3. High selectivity or specificity
4. High activity
5. High accessibility
6. Long life time
7. Regenerability
8.Adequate thermal and mechanical strength
9. Low Kindling point</td><td>1 mark each for any 4 points</td></tr>
<tr><td>4A-c</td><td>Integrated form of rate expression for zero order reaction</td><td></td></tr>
</table>

	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 $t < \frac{C_{A0}}{k}$ 	2
	In terms of fractional conversion $C_{A0}\frac{dx_A}{dt} = k$ Integrating between appropriate limits $C_{A0}\int_0^{xA} dx_A = k\int_0^t dt$ $C_{A0} X_A = kt$ for $t < \frac{C_{A0}}{k}$	2
		2

		
4A-d	**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, $\Delta G = 0$ $(r\,\mu_R + s\,\mu_S) - (a\,\mu_A + b\,\mu_B) = 0$ $r(\mu_R^0 + RT\ln p_R) + s(\mu_S^0 + RT\ln p_S) = a(\mu_A^0 + RT\ln p_A) +$ $b(\mu_B^0 + RT\ln p_B)$ $RT\ln\left(\frac{p_R^r\,p_S^s}{p_A^a\,p_B^b}\right) = (a\,\mu_A^0 + b\,\mu_B^0) - (r\,\mu_R^0 + s\,\mu_S^0$ $= -(\Delta G$ product $- \Delta G$ reactant) $= - \Delta G$ 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
4B	**Attempt any ONE of the following**	6
4B-a	$T_1 = 400$ K	

	$T_2 = 500K$ $k_2 = 10 k_1$ (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** (ii) From collision theory: $\ln\frac{k_2}{k_1} = \frac{-E}{R} (\frac{1}{T_2} - \frac{1}{T_1}) + 0.5 \ln (T_1 / T_2)$ $\ln 10 = (-E / 1.987) * (\frac{1}{500} - \frac{1}{400)} + 0.5 \ln(\frac{500}{400})$ E= **8694.5 cal** (iii) $T_1 = 500$ K $T_2 = 600K$ From Arrhenius law $\ln\frac{k_2}{k_1} = \frac{-E}{R} (\frac{1}{T_2} - \frac{1}{T_1})$ $\ln\frac{k_2}{k_1} = (-9137.2 / 1.987) * (\frac{1}{600} - \frac{1}{500)} = 1.533$ $\frac{k_2}{k_1} = 4.63$ From collision theory: $\ln\frac{k_2}{k_1} = \frac{-E}{R} (\frac{1}{T_2} - \frac{1}{T_1}) + 0.5 \ln (T_1 / T_2)$ $\ln\frac{k_2}{k_1} = (-8694.5 / 1.987) * (\frac{1}{600} - \frac{1}{500)} + 0.5 \ln(\frac{600}{500}) = 1.5496$ $\frac{k_2}{k_1} = 4.71$ % change in rate of reaction = (4.71-4.63) / 4.63 = **1.73**	2 2 2
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) 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) 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/dTlnk = ΔH^0/ RT^2 is the Van't Hoff equationwhere ΔH0 is molal enthalpy	2 2 2
5	**Attempt any TWO of the following**	16
5-a	**Integrated rate equation for irreversible Second order reaction A+B → Products** The chemical reaction is A+B → Products The rate law for the reaction can be written as $-r_A = -\frac{dC_A}{dt} = kC_A.C_B$eq.I Let C_{A0} and C_{B0} be initial concentrations of A and B respectively. Let $M = \frac{C_{B0}}{C_{A0}}$ Let C_A and C_B be the concentrations of A and B at any time t. Let $X_A$and X_B be the fractional conversions of A and B respectively. $X_A = \frac{C_{A0} - C_A}{C_{A0}}$ Amount of A reacted = $X_A.C_{A0}$ $X_B = \frac{C_{B0} - C_B}{C_{B0}}$ Amount of B reacted = $X_B.C_{B0}$	1

The amounts of A and B reacted at any time t are equal & given by

1

$$X_A.C_{A0} = X_B.C_{B0} \text{eq.II}$$

$C_A = C_{A0}(1 - X_A)$and $C_B = C_{B0}(1 - X_B)$

Therefore on differentiating $-dC_A = C_{A0}dX_A$

By putting values of C_A , C_B and $-dC_A$Eq.I becomes

$$-r_A = \frac{C_{A0}dX_A}{dt} = kC_{A0}(1 - X_A).C_{B0}(1 - X_B)$$

$-r_A = \frac{C_{A0}dX_A}{dt} = kC_{A0}(1 - X_A)(C_{B0} - C_{B0}.X_B)$eq III

As $X_A.C_{A0} = X_B.C_{B0}$ and $C_{B0} = M.C_{A0}$, eq III becomes

$$\frac{C_{A0}dX_A}{dt} = kC_{A0}(1 - X_A)(C_{B0} - C_{A0}.X_A)$$

$$\frac{C_{A0}dX_A}{dt} = kC_{A0}(1 - X_A)(M.C_{A0} - C_{A0}.X_A)$$

$$\frac{C_{A0}dX_A}{dt} = kC_{A0}(1 - X_A)C_{A0}(M.-X_A)$$

2

$$\frac{C_{A0}dX_A}{dt} = kC_{A0}{}^2(1 - X_A)(M.-X_A)$$

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(M.-X_A) \text{eq IV}$$

Rearranging the Eq.IV,we get

$\frac{dX_A}{(1- X_A)(M.-X_A)} = kC_{A0}dt$ eq.V

Integrating the equation within the limits

At t = 0,$X_A = 0$

At t = t ,$X_A = X_A$

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M.-X_A)} = kC_{A0}\int_0^t dt$$

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M.-X_A)} = kC_{A0}t$$

Breaking the L.H.S.of the above equation into partial fractions & then integrate it

$$\frac{A}{(1-X_A)}+\frac{B}{(M-X_A)}=\frac{1}{(1-X_A)(M-X_A)}$$

$$\frac{A(M-X_A)+B(1-X_A)}{(1-X_A)\quad(M-X_A)}=\frac{1}{(1-X_A)(M-X_A)}$$

$$A(M-X_A)+B(1-X_A)=1$$

Substituting $X_A=1, we\ get A(M-1)=1\ \therefore A=\frac{1}{(M.-1)}$

Substituting $X_A=M, we\ get\ B=-\frac{1}{(M-1)}$

3

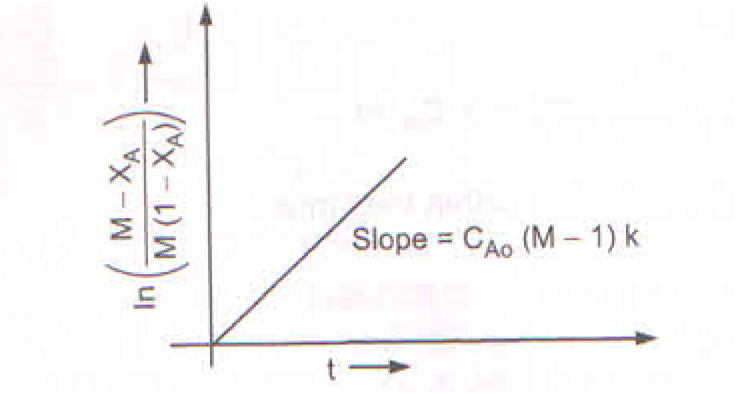
Putting values of A and B,we get

$$\frac{1}{(M-1)}\left[\int_0^{X_A}\frac{dX_A}{(1-X_A)}-\int_0^{X_A}\frac{dX_A}{(M-X_A)}\right]=kC_{A0}t$$

$$\frac{1}{(M-1)}\left[-ln(1-X_A)+ln\frac{(M-X_A)}{M}\right]=kC_{A0}t$$

$ln\left[\frac{(M-X_A)}{M(1-X_A)}\right]=C_{A0}(M-1)kt$ Eq.VI

EqVI is the desired integrated rate equation of irreversible Second order reaction with $C_{A0}\neq C_{B0}$ in terms of conversion.



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5-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

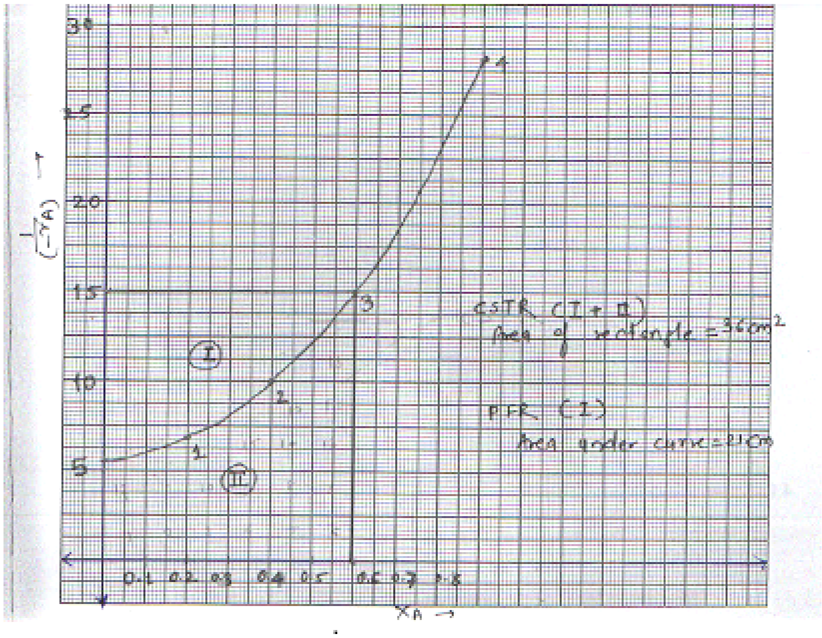
For a mixed flow reactor

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A}$$

<u>For a plug flow reactor</u>

$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} = \int_0^{X_A} \frac{1}{(-r_A)} dX_A$ where $X_A = 0.6$

<u>Construct a plot of</u> $1/(-r_A)$ vs X_A



For a mixed flow reactor refer the graph

$\frac{V}{F_{A0}}$ is the rectangular area upto $X_A = 0.6$

Area of CSTR(I+II) = 36 cm^2

$$\frac{V}{F_{A0}} = Area\ X (Scale\ on\ X - axis) X\ (Scale\ on\ Y - axis)$$

4

	$\frac{V}{F_{A0}}$ = 36 cm^2 X $\frac{5(l.sec/mol)}{2\ cm}$ X $\frac{0.1}{1\ cm}$ $$\frac{V}{F_{A0}} = 9\ (l.sec/mol)$$ V = 9 X F_{A0}= 9 X 10 = 90 lit. Volume of CSTR = **90 lit.** For a plug flow reactor $\frac{V}{F_{A0}}$ is the area under the curve from X_A = 0 to X_A = 0.6 Area under the curve(I) = 21.5 cm^2 $$\frac{V}{F_{A0}} = Area\ X(Scale\ on\ X - axis)X\ (Scale\ on\ Y - axis)$$ $\frac{V}{F_{A0}}$ = 21cm^2 X $\frac{5(l.sec/mol)}{2\ cm}$ X $\frac{0.1}{1\ cm}$ $$\frac{V}{F_{A0}} = 5.25$$ V = 5.25 X F_{A0}=5.25 X 10 = 52.5 lit Volume of PFR = 52.5 lit. Volume of PFR is less than the volume of CSTR for the same onversion.(X_A = 0.6)	2 2
5-c	**Performance equation of PFR in terms of concentration and conversion:** In Plug flow reactor,the composition of fluid varies continuously along a flow path, so rate of reaction also varies. therefore Material balance for any reactant A must be done over a differential element of volume dV of the reactor Taking material balance of a limiting reactant A,over a differential element of volume dV. Material balance equation is (Rate of flow of A to dV) = (Rate of flow of A out from dV) + (Rate of disappearance of A by chemical reaction within dV) +(Rate of accumulation of A within dV)……….eq 1	

For PFR ,the fourth term is zero.Therefore eq.I becomes

Rate of Flow of A To dV = Rate of flow of A out from dV + Rate of disappearance of A by chemical reaction eq.II

For the differential element of volume dV

Input of A, (moles/time) $=F_A$

Output of A, (moles/time) $= F_A + d\,F_A$

Rate of disappearance of A in moles/time

$$(-r_A)dV = \frac{moles\ of\ A\ reacting}{(time)(volume\ of\ fluid)}(volume\ of\ element)$$

Substituting all these values in eq.II

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

As $F_A = F_{A0}(1-X_A)$ and $dF_A = d[F_{A0}(1-X_A)] = -F_{A0}.dX_A$

$$F_A = F_A - F_{A0}.dX_A + (-r_A)dV$$

$F_{A0}.dX_A = (-r_A)dV$ eq.III

Eq.III is the differential form of design equation for a plug flow reactor. For the reactor as a whole,the equation must be integrated . F_{A0} is constant, but $(-r_A)$ depends upon the concentration.

Rearranging the terms & integrating within limits

$$\int_0^v \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$V = F_{A0}\int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

4

As

$$\tau = \frac{V}{v_0} = \frac{V.C_{A0}}{F_{A0}} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{(-r_A)}\ for\ any\ \in_A \qquad eq.IV$$

When $X_{Af} = X_A$

$$\tau = C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)} \qquad eq\ V$$

With the equation V,we can determine the reactor size necessary to achieve a specific conversion X_{Af}.

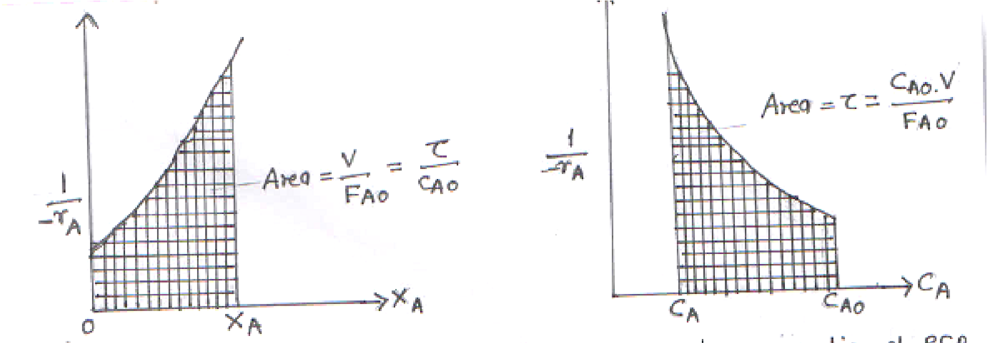
For constant density systems,the performance equation can be expressed in terms of concentration

We have $X_A = \frac{C_{A0} - C_A}{C_{A0}}$ and dX_A = -$\frac{dC_A}{C_{A0}}$ 2

Eq.IV becomes

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = -\frac{1}{C_{A0}}\int_{C_{A0}}^{C_{Af}}\frac{dC_A}{(-r_A)}$$

$$\tau = \frac{V}{v_0} = -\int_{C_{A0}}^{C_{Af}}\frac{dC_A}{(-r_A)} \qquad eq\ VI$$



2

Graphical Representation of Design equation of PFR

6 **Attempt any FOUR of the following** **16**

6-a **Spacetime (τ):**

It is the time required to process one reactor volume of feed measured atspecified condition. 1

Space time = Reactor volume / volumetric flow rate

Mathematical expression: $\boldsymbol{\tau = \frac{V}{v_0}}$

1

	unit: Unitisunitoftime(seconds,minute,etc)	
	Spacevelocity(s) Itisthenumberofreactorvolumeoffeedatspecifiedconditionswhichcanbetreatedinunittime.	1
	Space Velocity = volumetric flow rate / Reactor volume **Equation** $s = \frac{v_0}{V}$ **Unit:** time^{-1}(second^{-1} , min^{-1})	1
6-b	**Entropy Change for an Ideal Gas**: From first law of Thermodynamics,change in internal energy is the difference in heat absorbed by system and work done by that system In differential formdU = dQ –dWEq.I	1
	As work done by the system against external pressure P ,dU = P.dV From Maxwell equation dQ = T.dS Putting values of dU and dQ in Eq.IdU = T.dS- P.dVEq.II The heat capacity at constant volume C_v is given by$C_v = \frac{dU}{dT}$	1
	Therefore $C_v.dT = dU$ Rearranging eq.II we getT.dS = dU + P.dVEq.III The ideal gas equation for one mole of ideal gas is P.V = R.T $P = \frac{R.T}{V}$	1
	Putting values of dU& P in eq.III becomes $T.dS = C_{V.}$ dT+ $\frac{R.T}{V}.dV$ $dS = C_{V.}\frac{dT}{T} + R.\frac{dV}{V}$ Integrating above equation between initial & final states gives $\int_{s_1}^{s_2} dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dV}{V}$	

	$\Delta S = (S_2 - S_1) =$ $C_V.\ln\left(\frac{T_2}{T_1}\right) + R.\,ln\left(\frac{V_2}{V_1}\right) \quad for\ one\ mole$ $For\ n\ moles \quad \Delta S = nC_V.\ln\left(\frac{T_2}{T_1}\right) + nR.\,ln\left(\frac{V_2}{V_1}\right)$	1
6-c	**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 mark each for any 4 points
6-d	**Relation in between C_A & C_{A0}** As the concentration of reactant A is the number of moles of A per unit volume $C_A = \frac{N_A}{V}$ Where C_A is the concentration of reactant A.$N_A$is the number of moles of A unreacted at any time t during the course of reaction. If X_A is the fractional conversion of A ,then$X_A = \frac{moles\ of\ A\ reacted}{initial\ moles\ of\ A}$ N_{A0} = initial moles of A Therefore Moles of A reacted =$N_{A0}\ .\ X_A$	1

	Material Balance of A: A unreacted = A initially – A reacted $N_A = N_{A0} - N_{A0}\,.X_A$ $N_A = N_{A0}(1 - X_A)$ As $C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V}$ EqI For a constant-volume system$V = V_0$ Equation I becomes $C_A = \frac{N_{A0}(1 - X_A)}{V_0}$ $Eq.II$ As $C_A = \frac{N_{A0}}{V_0}$Eq.II becomes$C_A = C_{A0}(1 - X_A)$	1 1 1
6-e	**Relationship between C_A and X_A for constant density batch and flow systems:** These systems includes most liquid phase reactions as well as gas phase reactions carried out at constant temperature and density. For this case C_A and X_A are related as $C_A = C_{A0}(1 - X_A)$ and $N_A = N_{A0}(1 - X_A)$ $\frac{C_A}{C_{A0}} = (1 - X_A)$ and $dC_A = -C_{A0}.dX_A$ $X_A = 1 - \frac{C_A}{C_{A0}}$ and $dX_A = -\frac{dC_A}{C_{A0}}$ These relations are valid for $\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = 0$ For constant density(constant volume systems) there is no change in volume since there is no change in number of moles due to reaction and thus $\varepsilon_A = 0$	1 1 1 1