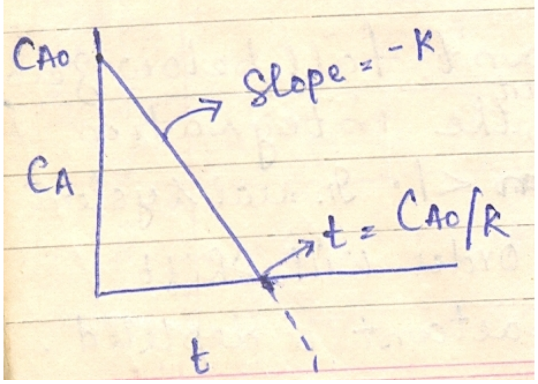
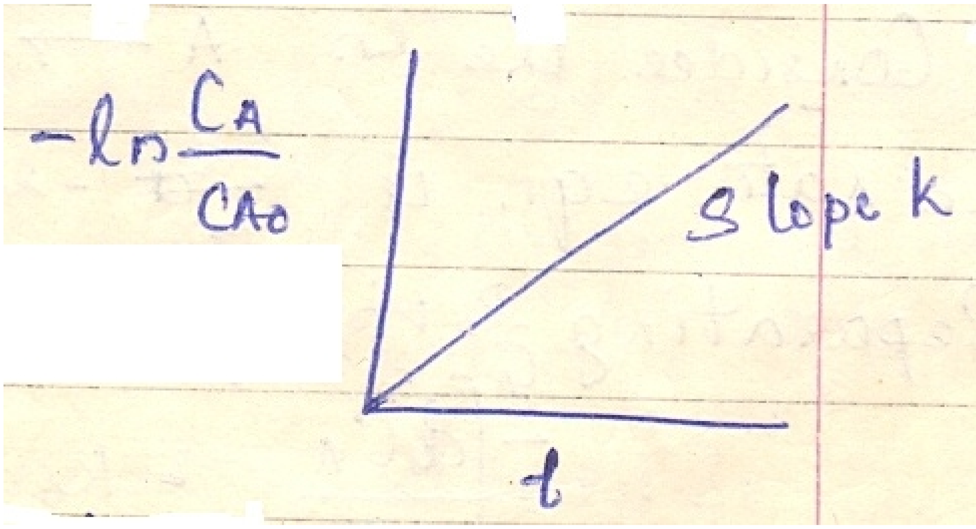
WINTER-14 EXAMINATION

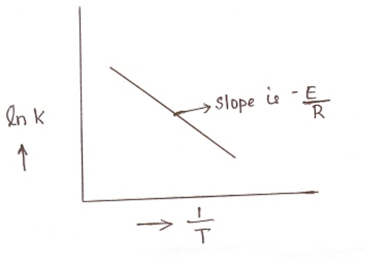
Model Answer

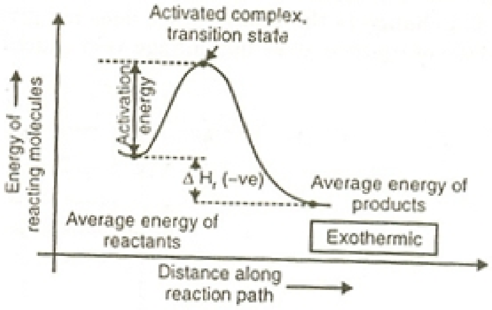
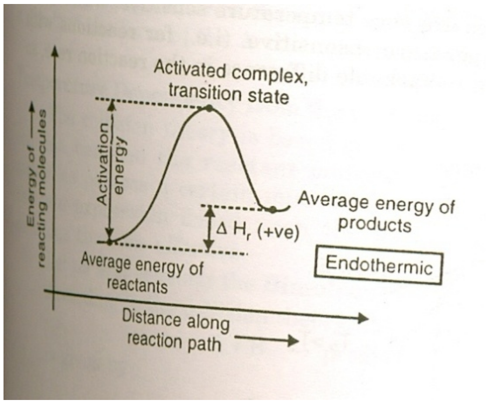
Important Instructions to examiners:

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-a</td><td>
<table>
<tr><th>Sr.No.</th><th>Transition State Theory</th><th>Collision Theory</th></tr>
<tr><td>1</td><td>Prediction of reaction rates is more accurate with experiment.</td><td>Prediction of reaction rates is less accurate with experiment.</td></tr>
<tr><td>2</td><td>The theory is based on statistical mechanics</td><td>The theory is based on kinetic theory of gases.</td></tr>
<tr><td>3</td><td>The theory views that the formation of activated complex is very rapid& decomposition of activated complex is slow.</td><td>The theory views that the formation of activated complex is slow & decomposition of activated complex is very rapid</td></tr>
<tr><td>4</td><td>Temperature Dependency is
$k \propto T.e^{-E/RT}$</td><td>Temperature Dependency is
$k \propto T^{1/2}.e^{-E/RT}$</td></tr>
</table>
</td><td>2 marks each for any two points</td><td>4</td></tr>
<tr><td>1A-b</td><td>Internal energy(U): It is the energy stored in the system by virtue of the configuration and motion of the molecules constituting the system.
Gibbs free energy: It is the energy actually available to do useful work. It predicts the feasibility and equilibrium conditions for chemical reactions at constant temperature and pressure.
Entropy: Entropy(s) is the measure of the total disorder or randomness of the</td><td>1 mark each.</td><td>4</td></tr>
</table>

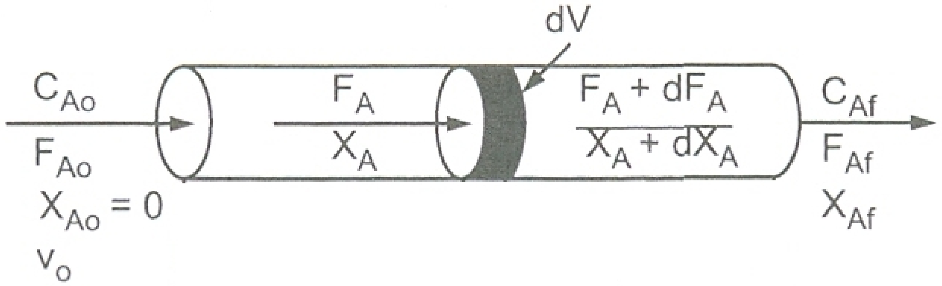
	system or it is a measure of the unavailable energy to perform useful work. **Fugacity:** It is a kind of fictitious pressure used for real gases.ie it is a measure of pressure for real gases.		
1A-c	1) **Plot of concentration Vs time forZero order reaction**.  2) **Plot of concentration Vs time forFirst order reaction**.  	2 2	4
1A-d	**Space time:** It is the time required to process one reactor volume of feed measured at specified condition. **Equation and unit**	1	4

<table>
<tr><td></td><td>$\tau = \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{V}{V_0}$
Unit is unit of time (seconds, minute, etc)
Space velocity
It is the number of reactor volume of feed at specified conditions which can be treated in unit time.
Equation and unit
$\mathbf{S = \frac{1}{\tau} = \frac{F_{A0}}{C_{A0}V} = \frac{V_0}{V}}$
Unit is $time^{-1}$ ($second^{-1}, minute^{-1}$ etc)</td><td>1
1
1</td><td></td></tr>
<tr><td>1B-a</td><td>Assume the reaction is of first order:
The integrated form of equation for first order reaction is $\ln(CA_0 / C_A) = kt$
$K = \ln(CA_0 / C_A) / t$
<table>
<tr><td>t min</td><td>0</td><td>10</td><td>20</td><td>30</td><td>40</td></tr>
<tr><td>C_A mol/lit</td><td>0.86</td><td>0.74</td><td>0.635</td><td>0.546</td><td>0.405</td></tr>
<tr><td>k</td><td>-</td><td>0.01502</td><td>0.01517</td><td>0.01514</td><td>0.0188</td></tr>
</table>
Since the k values are almost same, the reaction is of first order.
Average k value is 0.0160075 minute^{-1}
For first order reaction, $t_{1/2} = \frac{0.693}{k}$ = 43.29 minutes.</td><td>1
2
1
2</td><td>6</td></tr>
<tr><td>1B-b</td><td>Plot of lnK Vs $\frac{1}{T}$
 </td><td>2</td><td>6</td></tr>
</table>

	For exothermic reaction  **For endothermic reaction**  	2 2	
2a	**Temperature dependency of rate constant from transition state theory**: Reactants combine to form unstable intermediates called activated complex which then decompose spontaneously into products. An equilibrium exists between the concentration of reactants and activated complex at all times and the rate of decomposition of the complex is the same for all reactions and is given by kT / h where k is Boltzmann constant and h is Planck constant. Consider the reversible reaction A + B↔AB, k_1 is the rate constant for forward reaction and k_2 is the rate constant for backward reaction	2	8

	According to transition theory, $A + B \underset{k_4}{\overset{k_3}{\leftrightarrow}} AB^* \underset{k_5}{\rightarrow} AB$ $K_c = k_3 / k_4 = C_{AB}*/ C_A.C_B$ $K_5 = kT/h$ $r_{AB,forward}$= (concentration of activated complex) . (rate of decomposition of activated complex) $= C_{AB}* . (kT / h)$ $= (kT / h) . K_c.\ C_A. C_B$ From thermodynamics, $\Delta G = \Delta H - T\Delta S = - RT \ln K_c$ $\ln K_c = - (\Delta G / RT)$ $K_c = e^{-(\Delta G / RT)} = e^{-(\Delta H/ RT) + \Delta S/ R}$ $r_{AB,forward} = (kT / h).C_A. C_B . e^{-(\Delta H/ RT) + \Delta S/ R}$ $= \text{a constant} . T. e^{-(\Delta H/ RT)} C_A. C_B = k C_A. C_B$ where $k = \text{a constant} . T. e^{-(\Delta H/ RT)}$ $e^{\Delta S/ R}$ is less temperature sensitive compared to the other terms so that it can be taken as constant. For forward reaction, $k_1\ \alpha\ T\ e^{-(\Delta H_1 / RT)}$ For backward reaction, $k_2\ \alpha\ T\ e^{-(\Delta H_2 / RT)}$ For relating ΔH and Arrhenius activation energy, analogy from thermodynamics is used. $E = \Delta H - RT$ for liquids and solids $E = \Delta H - (\text{molecularity} - 1) RT$ for gases The difference between E and ΔH is small and of the order RT. Hence transition theory predicts that $K\ \alpha\ T\ e^{-(E/ RT)}$	2 2 2	
2b	**Performance equation of steady state plug flow reactor**: In PFR, the composition of the fluid varies from point to point along the flow		8

path. So the material balance for a reaction component must be made for a differential element of volume dV.



2

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

2

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

$dF_A = - F_{A0}.dX_A$

For the differential volume dV

Input of A in moles/time = F_A

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

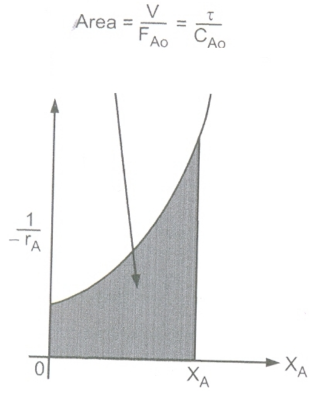
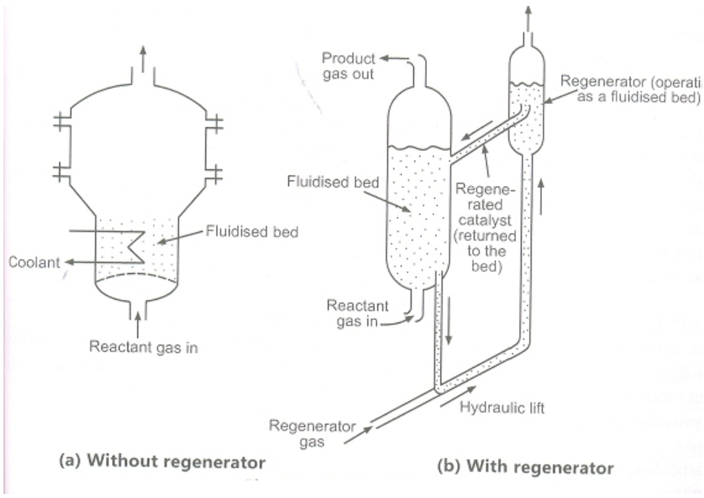
Disappearance of A due to chemical reaction in moles/ time = $(-r_A)$ dV

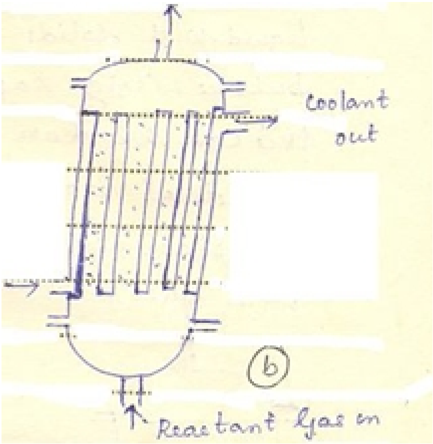
Substituting all the terms in the material balance equation (1)

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

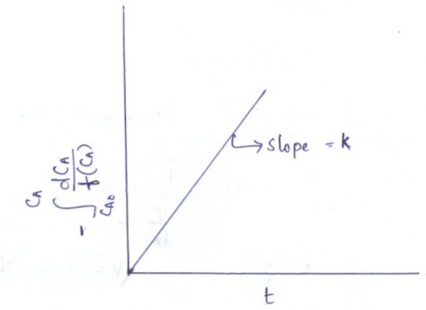
$- dF_A = (-r_A)\,dV$

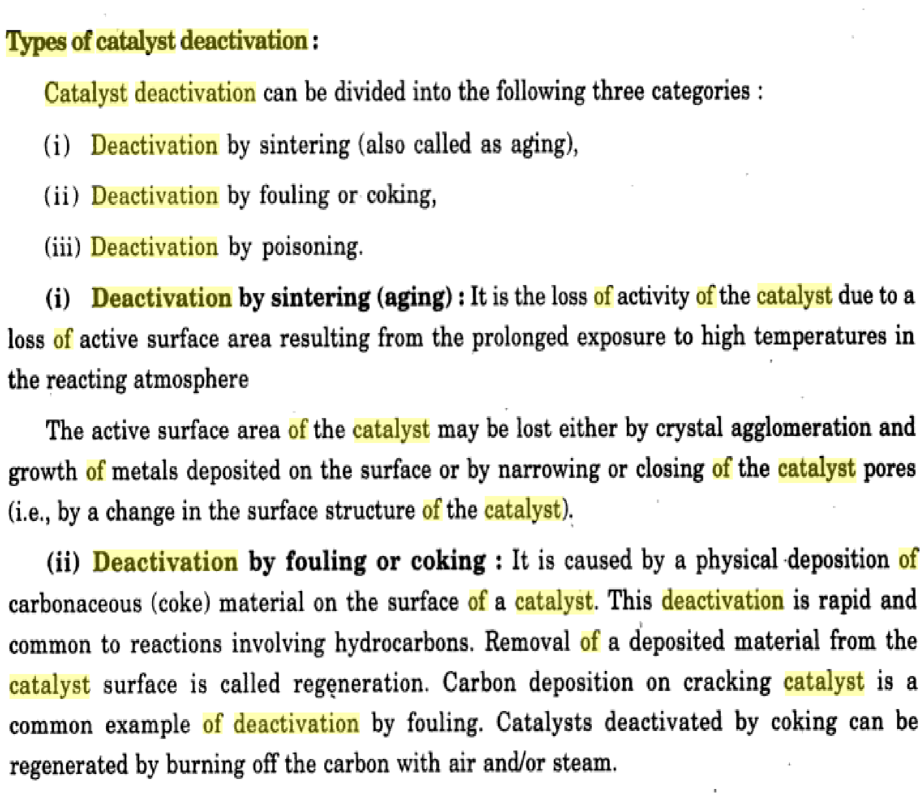
2

	$F_{A0}.dX_A = (-r_A)\,dV$ $$\frac{dV}{F_{A0}} = \frac{dX_A}{-r_A}$$ 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. $\int_0^V \frac{dV}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A}$ $\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$ Where X_A and $(-r_A)$ are evaluated at the exit conditions **Graphical representation:** 	2	
2c	**Fluidised reactor:**  (a) Without regenerator (b) With regenerator	1	8

	Multitubular fixed bed reactor:  **Application of fluidized bed reactor:** 1. Used when frequent regeneration of catalyst is required for reactions with very high heat effects. 2. Used when large quantities of feed are to be handled and good temperature control is required. 3. Used in petroleum and petrochemical industry 4. Used in radioactive waste solidification **Application of multitubular fixed bed reactor:** 1. used to catalyse gas phase reactions 2. Used when high conversion per unit weight of catalyst is required. 3. Used in automobile exhaust purification. 4. Used to treat harmful and toxic substances	1 1 mark for any two application 1 mark for any two application	
3-a	$S_2 - S_1 = nC_p * \ln(T_2 / T_1) + nR * \ln(P_1 / P_2)$ n= 3 mols, P_1=0.2 atm, P_2=2 atm, T_1=300K, T_2=1000K $\Delta S = 3*7*\ln(1000/300)+\{3*1.987*\ln(0.2/2)\}$ ΔS = 11.55 Cal/K	2 1 1	4

3-b	**Steps involved in analysis of kinetic data 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 limitsC_At $-\int(dC_A / f(c)) = k \int dt$ C_{A0} 0 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:	3	4

		1	
3-c	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 $K_c = \{(p_R / RT)^r . (p_S / RT)^s\} / \{ (p_A / RT)^a . (p_B / RT)^b\}$ $= (p_R^r . p_S^s) / (p_A^a . p_B^b) . (1 / RT)^{(r + s + \ldots -(a+b=\ldots))}$ R is the ideal gas constant = 0.0821 L•atm/mol•K 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 **$K_p = K_c \times (RT)^{\Delta n}$**	01 01 01 01	4
3-d	**The rate of a chemical reaction is affected by several factors like**: 1) Concentration of reactants 2) Pressure 3) Temperature	1 /2 mark each for any	4

	4) Catalyst 5) Nature of reactants 6) Orientation of reacting species 7) Surface area 8) Intensity of light 9) Nature of solvent **Unit for rate constant** for 1) First order reaction: (sec)$^{-1}$ 2) Zero order reaction: mol/(lit.sec)	four factors 01 01	
3-e	**Catalyst deactivation:** Catalyst deactivation is a complex phenomenon, but can be defined as the loss of catalytic activity and/or selectivity over time.  **Types of catalyst deactivation :** Catalyst deactivation can be divided into the following three categories : (i) Deactivation by sintering (also called as aging), (ii) Deactivation by fouling or coking, (iii) Deactivation by poisoning. **(i) Deactivation by sintering (aging) :** It is the loss of activity of the catalyst due to a loss of active surface area resulting from the prolonged exposure to high temperatures in the reacting atmosphere The active surface area of the catalyst may be lost either by crystal agglomeration and growth of metals deposited on the surface or by narrowing or closing of the catalyst pores (i.e., by a change in the surface structure of the catalyst). **(ii) Deactivation by fouling or coking :** It is caused by a physical deposition of carbonaceous (coke) material on the surface of a catalyst. This deactivation is rapid and common to reactions involving hydrocarbons. Removal of a deposited material from the catalyst surface is called regeneration. Carbon deposition on cracking catalyst is a common example of deactivation by fouling. Catalysts deactivated by coking can be regenerated by burning off the carbon with air and/or steam.	01 02 01mark for any one	4

4A-a	2A → product **In terms of concentration** $-r_A = -d_{CA}/dt$ $= kC_A^2$ $-d_{CA}/ C_A^2=kdt$ On integration $K=1/t(1/ C_A-1/ C_{A0})$ **In terms of conversion** $-r_A = -d_{CA}/dt$ $= kC_A^2$ $C_A=C_{A0}(1-X_A)$ $d_{CA} = -C_{A0}.d_{XA}$ $- d_{CA} = C_{A0}. d_{XA}$ $C_{A0} (d_{XA} /dt)=k. C_{A0}^2(1-X_A)^2$ On integrating $1/ C_{A0}\{ X_A/(1-X_A)\}= kt$	01 01 01 01	4
4A-b	**Fixed-bed reactors Advantages** 1. Flexible- large variation in operating conditions and contact times is possible 2. Efficient- long residence time enables a near complete reaction 3. Generally low-cost, low-maintenance reactors 4. Little loss or attrition 5. Usually a high ratio of catalyst to reactants 6. Little wear on catalyst and equipment 7. Only practical, economical reactor at very high pressures **Fluidised-bed reactors Advantages** 1. Frequent regeneration of the catalyst possible.	½ mark each for any four ½ mark	4

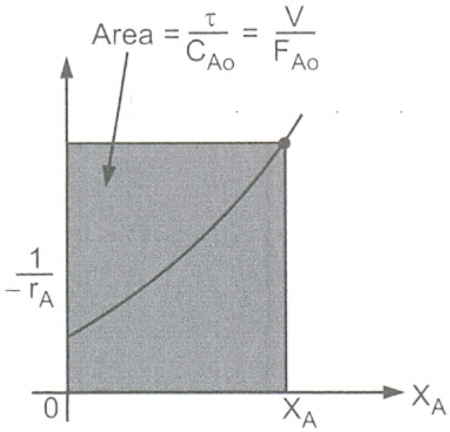
<table>
<tr><td></td><td>2. Rapid mixing of solids in fluid beds means uniform gas composition.
3. Isothermal operation and efficient temperature control is practical.
4. Small-diameter particles in fluid minimize pore diffusional resistance.
5. Improved thermal efficiency because of high heat transfer rates.
6. In the case of highly exothermic, liquid phase reactions, slurry reactors are less complex and less expensive than heat-exchange-tubular systems.</td><td>each for any four</td><td></td></tr>
<tr><td>4A-c</td><td>ε_A =It is the ratio of change in total number of moles of reacion system when reaction is complete to the total number of moles fed to the reactor
OR
It is the fractional change in volume of the system between no conversion and complete conversion of reactant A
Basis : 100 mol of initial reaction mixture
40 mol of A
60 mol of inert
<table>
<tr><td>Moles at no conversion</td><td>Moles after conversion</td></tr>
<tr><td>A=40 mol
Inert=60 mol</td><td>R= 120 mols
Inert=60 mols</td></tr>
<tr><td>100 mols</td><td>180 mols</td></tr>
</table>
ε_A =(180-100)/100=**0.8**</td><td>01
01
01
01</td><td>4</td></tr>
<tr><td>4A-d</td><td>$CO + 0.5O_2 \dashrightarrow CO_2$
$Kp = P_{CO2}/\{P_{CO}*(P_{O2})^{1/2}\}$
$Kp=3.354\ (atm)^{-1/2}$
Total Pressure=P=0.6+0.4+0.2=1.2 atm</td><td>01
01</td><td>4</td></tr>
</table>

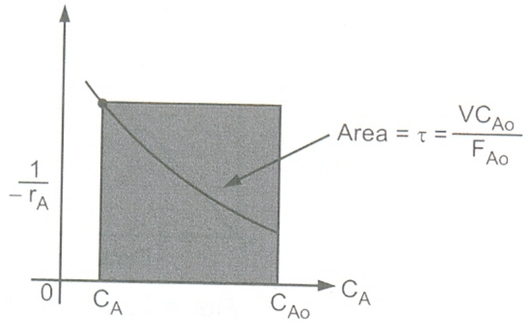
	$Kc=Kp(RT)^{-\Delta n}$	01	
	$\Delta n=1-(1+1/2)= -1/2$		
	$Kc = 3.354\{(0.08206)*(3000)^{1/2}\}$		
	$Kc = 54.64\ mol^{-1/2}.lit^{-1/2}$	01	
4B-a	T_2 =1100 K	01	6
	T_1 = 1000 K		
	$r_2= 20\ r_1$	01	
	$Ln(r_2/r_1)=E/R\{1/T_1-1/T_2\}$	02	
	E=**273973 J/K**	01	
	= 274 KJ/ K = 65477.72 cal/K	01	
4-B-b	Consider the reaction $aA + bB \rightleftarrows rR + sS$		6
	ΔG reaction = ΔG product - Δ G reactant.	1	
	$= (r\,\mu_R + s\,\mu_S) -(a\,\mu_A + b\,\mu_B)$.		
	At equilibrium there is no Gibb's free energy change, $\Delta G = 0$		
	$(r\,\mu_R + s\,\mu_S) -(a\,\mu_A + b\,\mu_B) = 0$	1	
	$r(\mu_R^0 + RT\ln p_R) + s(\mu_S^0 + RT\ln p_S) = a(\mu_A^0 + RT\ln p_A) +$		
	$b(\mu_B^0 + RT\ln p_B)$	1	
	$RT\ln\left(\frac{p_R^r\,p_S^s}{p_A^a\,p_B^b}\right) = (a\,\mu_A^0 + b\,\mu_B^0) - (r\,\mu_R^0 + s\,\mu_S^0$		
	$= -(\Delta G$ product - Δ G reactant)	1	
	$= - \Delta$ G reaction.		
	$\ln\left(\frac{p_R^r\,p_S^s}{p_A^a\,p_B^b}\right) = \frac{-\Delta G\ \text{reaction}}{RT}$	1	
	But $\left(\frac{p_R^r\,p_S^s}{p_A^a\,p_B^b}\right) = K_p$		
	Therefore $\Delta G = - RT\ln K_p$	1	
5-a	**Given:** C_{A0} = 1 mol/l X_A = 0.80 when t = 8 min.		8

	X_A = 0.90 when t = 80 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. $1*0.8 = k*8$ $k = 0.1\ (min)^{-1}(mol / l)$	1	
	Case 2) Where X_A = 0.90 when t = 80 min. $1*0.9 = k*80$ $k = 0.01125\ (min)^{-1}$	1	
	Our assumption is wrong as values of rate constants are not same. The reaction is **not of zero order**	1	
	Let us now assume reaction is of First order. Therefore the integrated equation of first order reaction in terms of fractional conversion is $\ln\left[\frac{1}{1-X_A}\right] = kt$ Case 1) Where X_A = 0.80 when t = 8 min. $\ln\left[\frac{1}{1-0.8}\right] = k*8$ $k = 0.201\ (min)^{-1}$	1	
	Case 2) Where X_A = 0.90 when t = 80 min. $\ln\left[\frac{1}{1-0.9}\right] = k*80$ $k = 0.028\ (min)^{-1}$	1	
	Our assumption is wrong as values of rate constants are not same. The reaction is **not of first order .**	1	
	Let us guess it is of Second order. Therefore the integrated equation of second order reaction wrt A in terms of fractional conversion is $\left[\frac{X_A}{1-X_A}\right] = kC_{A0}t$	1	
	Case 1) Where X_A = 0.80 when t = 8 min. & C_{A0} = 1 mol/l $\left[\frac{0.8}{1-0.8}\right] = k*1*8$ $k = 0.5\ (mol/l)^{-1}\ (min)^{-1}$		
	Case 2) Where X_A = 0.90 when t = 80 min. & C_{A0} = 1 mol/l	1	

	$\left[\frac{0.9}{1-0.9}\right] = k*1*80$ $k = 0.1125\ (mol/l)^{-1}\ (min)^{-1}$ Our assumption is wrong as values of rate constants are not same. The reaction is **not of second order .** ***<u>(Data given in the question is wrong. So if the students have written the correct formula and steps,it should be given due consideration.)</u>***		
5-b	**<u>Performance equation of mixed flow reactor</u>**: Here the composition of the reactants is uniform throughout the reactor. Taking material balance of reactant A over the reactor as a whole, Input of A to reactor = Output of A from reactor + Disappearance of A due to chemical reaction + Accumulation of A within the reactor. For mixed flow reactor at steady state the last term is zero. Input of a to reactor = Output of A from reactor + Disappearance of A due to chemical reaction Let, F_{A0} = Molar feed rate to the reactor V = Volume of reactor C_{A0} = Molar concentration of A in stream entering the reactor (moles/volume) v_0 = Volumetric flow rate(volume/time) X_A = Fractional conversion of A $F_{A0} = C_{A0}.\ v_0$ The molar rate at which A is entering in the reactor = $F_{A0.}\ X_A$ $F_{A0.}\ X_A$ = Moles of A fed / time x Moles of A reacted/ moles of A fed Moles of A reacted/ time = $F_{A0.}\ X_A$ Molar flow rate of A leaving the reactor = F_A Molar flow rate At which A is fed to reactor - Molar rate at which A is consumed = Molar rate at which A leaves the reactor $F_{A0} - F_{A0.}\ X_A = F_A$ Output of A from reactor = $F_A = F_{A0}\ (1 - X_A)$ Rate Disappearance of A due to chemical reaction = $(-r_A)\ .V$ $F_{A0} = F_{A0}\ (1 - X_A) + (-r_A)\ .V$ Rearranging, we get	1 1 1 1 1 1 1	8

	$\frac{V}{F_{A0}} = \frac{X_A}{-r_A}$ $\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{(-r_A)}$ $\boldsymbol{\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{V.C_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}}$ Where X_A and $(-r_A)$ are evaluated at the exit conditions,which are same as conditions prevailing within reactor(ex.composition,temp.) The above equation is the performance equation for a mixed flow reactor.	1	
5-c	**Given:** X_A =0.70 ,t = 13 min For batch reactor with first order chemical reaction $-r_A = k.C_A$ $-\ln(1 - X_A) = kt$ $-\ln(1-0.70) = k * 13$ $k = 0.0926\ min^{-1}$ For Mixed flow reactor : $\tau = \frac{C_{A0}.X_A}{(-r_A)}$ $\tau = \frac{C_{A0}.X_A}{-r_A} = \frac{C_{A0}.X_A}{kC_{A0}(1-X_A)}$ $\tau = \frac{0.70}{0.0926(1-0.7)}$ **= 25.2 min.** **Space velocity = s = 1/ τ = 1/25.2 = 0.03968 min^{-1}** For Plug flow reactor & constant –density systems: $\frac{V}{F_{A0}} = \int_0^{X_A}\frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$ $\tau = C_{A0}\int_0^{X_A}\frac{dX_A}{k.C_{A0.(1-X_A)}}$	1 1 1 1 1 1 1	8

	$$\tau = \int_0^{X_A} \frac{dX_A}{k.(1-X_{A)}}$$ $\tau = \frac{1}{k}$(-ln(1-XA)) = $\frac{1}{0.0926}(-\ln(1-0.7)) = \mathbf{13\ min}$. **Space velocity = s = 1/ $\boldsymbol{\tau}$ = 1/13 = 0.07692 min^{-1}**	1	
6-a	**<u>For a Mixed flow reactor the performance equation</u>** <u>is</u> $\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{V.C_{A0}}{F_{A0}} = \frac{C_{A0}.X_A}{-r_A}$ Eq. A Where τ is the space time ,V is the volume of reactor,v_0 is yhe volumetric flow rate of feed. The graphical representation of the performance equation in terms of fractional conversion is as below  The rectangular area gives the value of $\frac{\tau}{C_{A0}}$. knowing C_{AO}, we can find out τ. **OR** The graphical representation of the performance equation in terms of concentration for constant density system is as below.	1 1	4



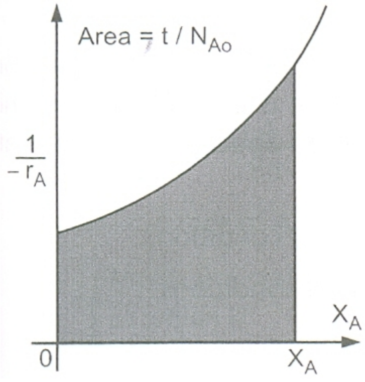
1

The rectangular area gives the value of τ

For a Batch flow reactor: 1mark for any equation B/C/D & 1 mark for the respective graph 1

The performance equation

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A).V} \qquad \text{Eq. B}$$

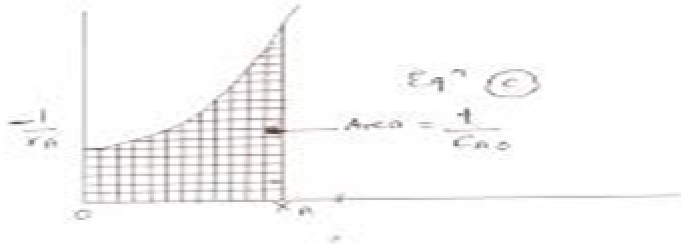


By the graphical representation of above equation ,one can calculate the value of holding time (t) from the value of area under the curve(which gives the value of ratio t/N_{A0}. Knowing N_{A0}, we can find out t.

OR

The performance equation

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)} = -\int_0^{X_A}\frac{dC_A}{-r_A} \qquad \text{Eq. C}$$

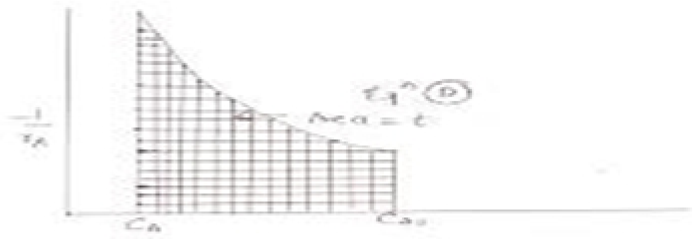


Area is t / C_{A0}. Knowing C_{A0}, we can find out t

OR

The performance equation

$$t = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)} \qquad \text{Eq. D}$$



Area under the curve is t

6-b

Relation between K_p and x_A

Reaction is A↔R

Let

1 mole of A be present initially.

x_A mole of A reacts at equilibrium

P be the total pressure.

1

	A	R	Total moles
Moles present initially	1	--	
Moles reacted / produced at equilibrium	x_A	x_A	

1

4

Moles present at equilibrium	1- x_A	x_A	1
Mole fraction	1- x_A	x_A	
Partial pressure	P(1- x_A)	P x_A	

$$K_p = \frac{Px_A}{P(1-x_A)} = \frac{x_A}{1-x_A}$$ 1

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

$$K_p - K_p\ x_A = x_A$$ 1

$$K_p = x_A\ (1+K_p)$$

$$x_A = \frac{Kp}{1+Kp}$$

6-c **Difference between Molecularity& Order of reaction**(any 4 points) — 1 mark each for any 4 pts — 4

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 exponents of the concentratio terms involved in the rate equation.
2	Molecularity always have an integer value 1,2,3…	Order of reaction can have a fractional value.
3	Molecularity refers only to an elementary reactions	Order of reaction refers to an empirically found rate expression.
4	Molecularity has no meaning for overall reaction specially in complex reactions. Reaction can be unimolecular ,bimolecular etc.	Order of reaction can be one,two ,three & has definite meaning for overall reaction.
5	Molecularity is a theoretical quantity	Order of reaction is entirely experimental value.

6-d	**Integrated equation for First order reaction (variable volume system)** For first order reaction, the rate equation Can be written as $-r_A = \frac{-1}{V}\frac{dN_A}{dt} = kC_A$ ..... ①	1	4
	But $N_A = N_{A0}(1-x_A)$ $dN_A = -N_{A0}\,dx_A$ For Variable Volume System $V = V_0(1+\varepsilon_A x_A)$ — ② and $C_A = \frac{C_{A0}(1-x_A)}{1+\varepsilon_A x_A}$	1	
	Substituting in equation ① $-r_A = \frac{N_{A0}\,dx_A}{V_0\cancel{(1+\varepsilon_A x_A)}\,dt} = \frac{k\,C_{A0}(1-x_A)}{\cancel{1+\varepsilon_A x_A}}$ $\cancel{C_{A0}}\frac{dx_A}{dt} = k\cancel{C_{A0}}(1-x_A)$ $\frac{dx_A}{1-x_A} = k\,dt$. Integrating the above equation, we get $-\ln(1-x_A) = kt$ — ③	1	
	Eqn ② can be written as $V = V_0 + V_0\varepsilon_A x_A$ $V - V_0 = V_0\varepsilon_A x_A$ $\Delta V = V_0\varepsilon_A x_A$. $x_A = \frac{\Delta V}{V_0\varepsilon_A}$ — ④ Substituting x_A from equation ④ into equation ③ $-\ln\left(1 - \frac{\Delta V}{V_0\varepsilon_A}\right) = kt$	1	
6-e	**Difference between Fixed &Fluidised bed reactors**	1 mark each	4

No.	Point	Fixed bed reactor	Fluidised bed reactor	for any	
1	Movement of catalyst	Catalyst particles are stationary and gas flows through it	Catalyst particles are suspended in the gas stream	4 pts.	
2	Nature of flow	Approximates plug flow.	Complex.		
3	Temperature control	difficult	Can maintain isothermal conditions		
4	size of catalyst	Cannot use very small size of catalyst because of plugging and high pressure drop	Can use small size of catalyst		
5	Regeneration of catalyst	difficult	Easily regenerated		
6	Temperature Control	difficult	Can maintain isothermal conditions		
7	Hot spot formation	Chances are there	No hot spot formation		
8	Size of reactor	Small diameter multi-tubular units	Large diameter vessels		
9	Recovery units	Catalyst loss is not there,so recovery units are not required	Catalyst loss is there, so recovery units are necessary.		
10	conversion	Highest conversion per unit weight of catalyst	Low conversion		
11	Applications	Suitable for small commercial units	Suitable for large commercial units		

6-f	**Batch Reactor:**	2 marks	4

<table>
<tr>
<td></td>
<td>The reactants are charged at the beginning into the vessel ,left to react for certaion time period under agitation during which no material is fed or removed from it, and the resultant mixture is withdrawn at a subsequent time.
<table>
<tr><th>Sr. no.</th><th>Advantages</th><th>Disadvantages</th></tr>
<tr><td>1</td><td>Simple in construction & operation</td><td>High labour costs per unit volume of production.</td></tr>
<tr><td>2</td><td>Equipment cost low</td><td>Requires considerable time to empty ,clean out & refill</td></tr>
<tr><td>3</td><td>Gives highest conversion by leaving the reactants for longer periods in reactor.</td><td>Poorer quality control of product</td></tr>
<tr><td>4</td><td>Requires small instrumentation & less supporting equipments</td><td>Large scale production is difficult.</td></tr>
</table>
</td>
<td>for any 2 advantages & 2 marks for any two disadvantages.</td>
<td></td>
</tr>
</table>