



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 1 of 21

**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.







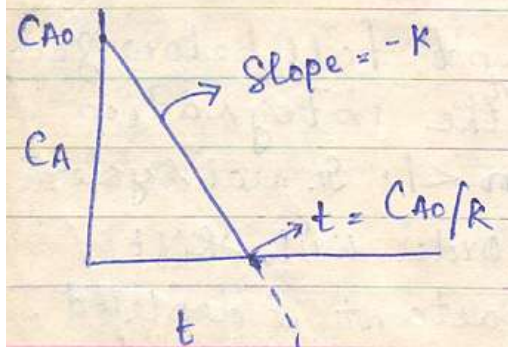
SUMMER-18 EXAMINATION  
Model Answer

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 4 of 21



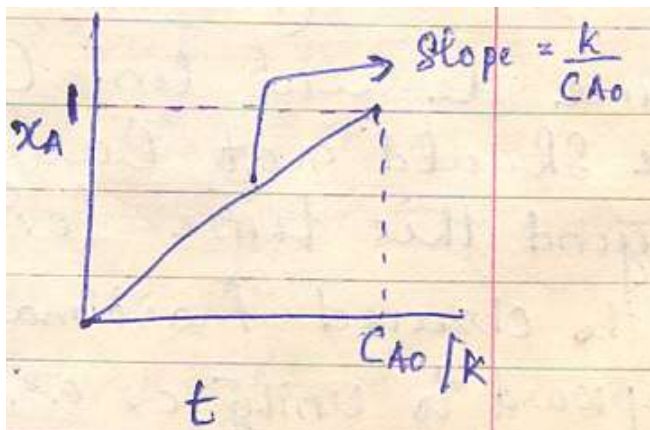
**In terms of fractional conversion**

$$C_{A0} \frac{dx_A}{dt} = k$$

Integrating between appropriate limits

$$C_{A0} \int_0^{x_A} dx_A = k \int_0^t dt$$

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



1

2

1

1B-b

$$T_1 = 500^\circ\text{C} = 773 \text{ K}$$

$$T_2 = 650^\circ\text{C} = 923 \text{ K}$$

$$E = 300 \text{ KJ/mole} = 300 \times 10^3 \text{ J/mole}$$

From Arrhenius law

$$\ln \frac{k_2}{k_1} = \frac{-E}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = (-300 \times 10^3 / 8.314) \times \left( \frac{1}{923} - \frac{1}{773} \right)$$

2



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 5 of 21

	$\ln \frac{k_2}{k_1} = 7.586$ $\frac{k_2}{k_1} = 1970.4$ <p><b>The reaction at 650<sup>0</sup>C is 1970 times faster than the reaction at 500<sup>0</sup>C.</b></p>	2
		2
<b>2</b>	<b>Attempt any TWO of the following</b>	<b>16</b>
2-a	<p><b>Temperature dependency of rate constant from transition state theory:</b> 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 <math>kT/h</math> where <math>k</math> is Boltzmann constant and <math>h</math> is Planck constant. Consider the reversible reaction <math>A + B \leftrightarrow AB</math>, <math>k_1</math> is the rate constant for forward reaction and <math>k_2</math> is the rate constant for backward reaction</p> $A + B \xrightleftharpoons[k_4]{k_3} AB^* \xrightarrow{k_5} AB$ <p><math>K_c = k_3 / k_4 = C_{AB^*} / C_A \cdot C_B</math> <math>K_5 = kT/h</math> <math>r_{AB,forward} = (\text{concentration of activated complex}) \cdot (\text{rate of decomposition of activated complex})</math> <math>= C_{AB^*} \cdot (kT/h)</math> <math>= (kT/h) \cdot K_c \cdot C_A \cdot C_B</math> From thermodynamics, <math>\Delta G = \Delta H - T\Delta S = -RT \ln K_c</math> <math>\ln K_c = -(\Delta G / RT)</math> <math>K_c = e^{-(\Delta G / RT)} = e^{-(\Delta H / RT) + \Delta S / R}</math> <math>r_{AB,forward} = (kT/h) \cdot C_A \cdot C_B \cdot e^{-(\Delta H / RT) + \Delta S / R}</math> <math>= \text{a constant} \cdot T \cdot e^{-(\Delta H / RT)} C_A \cdot C_B = k C_A \cdot C_B</math></p>	2
		3



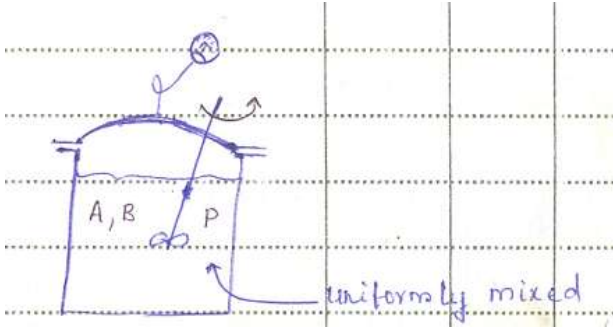
SUMMER-18 EXAMINATION  
Model Answer

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 6 of 21

	<p>where <math>k = \text{a constant} \cdot T \cdot e^{-(\Delta H/RT)}</math></p> <p><math>e^{\Delta S/R}</math> is less temperature sensitive compared to the other terms so that it can be taken as constant.</p> <p>For forward reaction, <math>k_1 \propto T e^{-(\Delta H_1/RT)}</math></p> <p>For backward reaction, <math>k_2 \propto T e^{-(\Delta H_2/RT)}</math></p> <p>For relating <math>\Delta H</math> and Arrhenius activation energy, analogy from thermodynamics is used.</p> <p><math>E = \Delta H - RT</math> for liquids and solids</p> <p><math>E = \Delta H - (\text{molecularity} - 1) RT</math> for gases</p> <p>The difference between <math>E</math> and <math>\Delta H</math> is small and of the order <math>RT</math>. Hence transition theory predicts that <math>K \propto T e^{-(E/RT)}</math></p>	3
2-b	<p><b>Performance equation for constant volume batch reactor with first order kinetics</b></p>  <p>Writing the material balance for any component A.</p> <p>Rate of reactant A in = Rate of reactant A out + Rate of loss of reactant A due to chemical reaction + Rate of accumulation of reactant A within the reactor.</p> <p>In a batch reactor, no fluid enters or leaves the reaction mixture during the reaction.</p> <p>Therefore Rate of reactant A in = Rate of reactant A out = 0</p> <p>Material balance equation then becomes</p>	



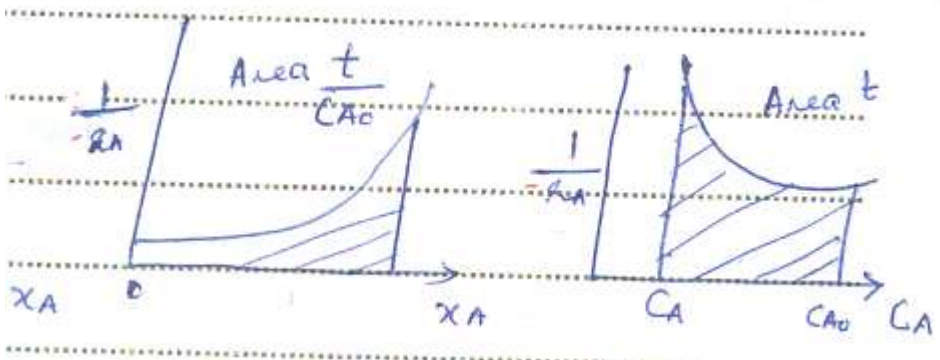
**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 7 of 21

	<p>Rate of loss of reactant A due to chemical reaction = - Rate of accumulation of reactant A within the reactor----- ( 1 )</p> <p>Rate of loss of reactant A due to chemical reaction = <math>-r_A V</math></p> <p>Rate of accumulation of reactant A within the reactor = <math>\frac{dN_A}{dt} = - N_{A0} \frac{dx_A}{dt}</math></p> <p>Substituting in equation ( 1 )</p> $-r_A V = N_{A0} \frac{dx_A}{dt}$ <p>Rearranging and integrating</p> $\int_0^t dt = N_{A0} \int_0^{x_A} \frac{dx_A}{V (-r_A)}$ $t = N_{A0} \int_0^{x_A} \frac{dx_A}{V (-r_A)}$ <p>For constant volume system, the equation becomes</p> $t = \frac{N_{A0}}{V} \int_0^{x_A} \frac{dx_A}{(-r_A)} = C_{A0} \int_0^{x_A} \frac{dx_A}{(-r_A)} = - \int_{C_{A0}}^{C_A} \frac{dC_A}{(-r_A)}$ <p><b>Graphical representation for constant volume batch reactor</b></p> 	<p>2</p> <p>2</p> <p>2</p> <p>2</p>
<p>2-c</p>	<p><b>Methods of catalyst Preparation:</b></p> <ol style="list-style-type: none"> <li>1. Precipitation</li> <li>2. Gel formation</li> <li>3. Simple mixing</li> <li>4. Impregnation method</li> </ol> <p><b>1.Precipitation method :</b></p>	



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 8 of 21

<p>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 &amp; activation(or pretreatment) Eg. Magnesium oxide catalyst is prepared by this method. It is prepared by precipitating <math>MgCO_3</math> from magnesium nitrate solution by adding sodium carbonate. The magnesium carbonate precipitate is washed, dried &amp; calcined to obtain magnesium oxide.</p> <p><b>2. Gel formation:</b> 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.</p> <p><b>3. Simple mixing:</b> 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</p> <p><b>4. Impregnation method:</b> 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.</p> <p><i>Any other appropriate preparation method should also be given due</i></p>	<p>2 marks each for explaining the methods with eg</p>
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**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 9 of 21

<i>consideration</i>		
<b>3</b>	<b>Attempt any FOUR of the following</b>	<b>16</b>
3-a	Number of moles (n) = $10 / 4 = 2.5$ $P_1 = 3 \text{ atm}$ $P_2 = 15 \text{ atm}$ $T = 100^\circ\text{C}$ $\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$ For isothermal operation, $\Delta S = nR \ln \frac{P_1}{P_2}$ $\Delta S = 2.5 \times 1.987 \times \ln (3/15) = -7.994 \text{ cal / K}$	2 2
3-b	$A \rightarrow \text{Products}$ Rate equation is $-r_A = -\frac{dC_A}{dt} = k C_A^n$ Rearranging $\frac{-dC_A}{C_A^n} = k dt$ Integrating between appropriate limits $-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^n} = k \int_0^t dt$ $C_A^{1-n} - C_{A0}^{1-n} = (n-1) kt$ where n is not equal to 1	2 2
3-c	<b>Temperature increase is not desirable for exothermic reaction.</b> Van't Hoff equation is $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$ For exothermic reaction, $\Delta H$ 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.	4



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 10 of 21

3-d	<b>Difference between order and molecularity of reaction.( 4 points)</b>		1 mark each	
	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 have 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.		
3-e	<b>Types of catalyst deactivation</b> 1. Deactivation by Fouling 2. Chemical Deactivation - Poisoning 3. Deactivation by Thermal Degradation and Sintering		1	





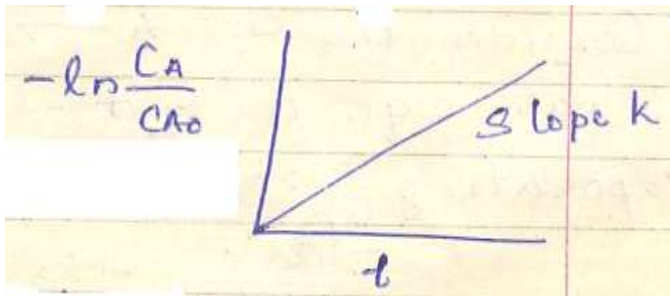
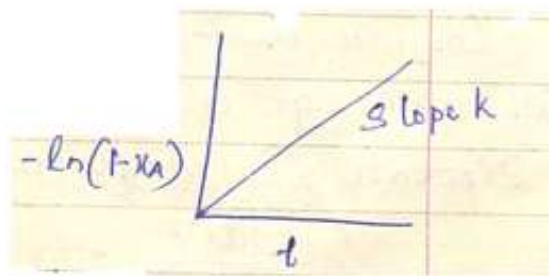
SUMMER-18 EXAMINATION  
Model Answer

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 12 of 21

	<ol style="list-style-type: none"><li>1. Good temperature control</li><li>2. Can use small size catalyst particles</li><li>3. Regeneration is easily done without shut down of the reactor.</li></ol> <p><b>Demerits:</b></p> <ol style="list-style-type: none"><li>1. Effective contacting require large amount of catalyst for high gas conversion</li><li>2. Catalyst loss is there. So recovery units are required.</li></ol>	<p>each for any two points</p> <p>1 mark each</p>
4A-c	<p><b>Graphical representation of integrated rate equation for first order reaction</b></p> <p><b>(i) In terms of concentration</b></p>  <p><b>(i) In terms of conversion</b></p> 	<p>2</p> <p>2</p>
4A-d	<p><b>Relation between Gibb's free energy (<math>\Delta G^0</math>) and equilibrium constant <math>K_p</math></b></p> <p>Consider the reaction <math>aA + bB \rightarrow rR + sS</math></p> <p><math>\Delta G_{\text{reaction}} = \Delta G_{\text{product}} - \Delta G_{\text{reactant}}</math>.</p>	





**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 14 of 21

	<p>From 1 and 2 <math>-RT \ln K = (r\mu_R + s\mu_S) - (a\mu_A + b\mu_B)</math></p> <p>Differentiating with respect to T at constant pressure</p> $d/dT \ln k = -(1/R) \left( (r \frac{\partial}{\partial T} \mu_R/T + s \frac{\partial}{\partial T} \mu_S/T) - (a \frac{\partial}{\partial T} \mu_A/T + b \frac{\partial}{\partial T} \mu_B/T) \right)$ <p>Gibb's Helmholtz equation is <math>a \frac{\partial}{\partial T} (\mu_i/T) = -H_i/RT^2</math></p> <p>ie <math>d/dT \ln k = (1/RT^2) \{ [rH_R + sH_S] - [aH_A + bH_B] \}</math></p> $= (1/RT^2) (\Sigma H^0_{\text{product}} - \Sigma H^0_{\text{reactant}})$ <p><math>d/dT \ln k = \Delta H^0 / RT^2</math> is the Van't Hoff equation where <math>\Delta H^0</math> is molal enthalpy</p>	<p>2</p> <p>2</p>
<b>5</b>	<b>Attempt any TWO of the following</b>	<b>16</b>
5-a	<p><b>Derivation:</b></p> <p><math>2A \rightarrow \text{product}</math></p> <p><b>In terms of concentration</b></p> <p>The rate of reaction is expressed in terms of rate of disappearance of reactant A.</p> $-r_A = -dC_A/dt = kC_A^2$ <p>Rearranging <math>\frac{-dC_A}{C_A^2} = k dt</math></p> <p>Integrating between appropriate limits</p> $-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = k \int_0^t dt$ $-[-C_A^{-1}]_{C_{A0}}^{C_A} = kt$ $\left[ \frac{1}{C_A} - \frac{1}{C_{A0}} \right] = kt$ <p>The above equation is the integrated rate equation for second order reaction in terms of concentration.</p> <p><b>Graphical representation:</b></p>	<p>2</p> <p>3</p>



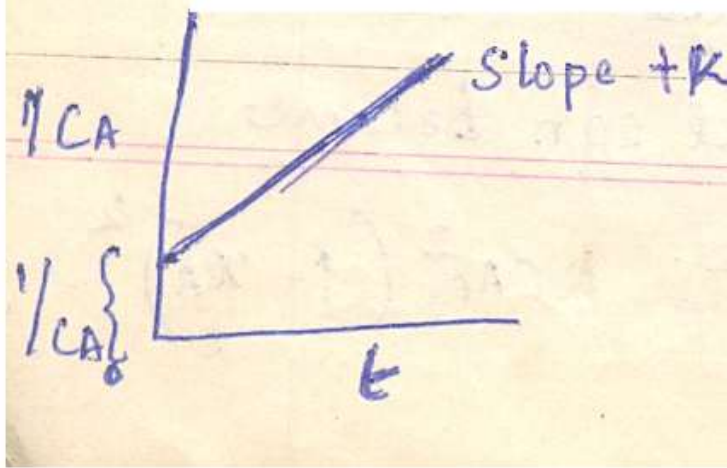
**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 15 of 21



3

The plot of  $\frac{1}{C_A}$  Vs time  $t$  yields a straight line with a slope equal to value of rate constant  $k$  and an intercept equal to  $\frac{1}{C_{A0}}$

5-b

**Given:**

$$X_A = 0.70, t = 13 \text{ min}$$

For batch reactor, in which first order chemical reaction is taking place

$$-r_A = k \cdot C_A$$

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

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

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

**For Plug flow reactor ( constant –density system):**

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

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

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

$$\text{Space time } \tau = \frac{1}{k} (-\ln(1 - X_A)) = \frac{1}{0.0926} (-\ln(1 - 0.7)) = \mathbf{13 \text{ min.}}$$

$$\text{Space velocity } = s = 1/\tau = \mathbf{1/13 = 0.07692 \text{ min}^{-1}}$$

**For Mixed flow reactor :**

2

1

1



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 16 of 21

	$\tau = \frac{C_{A0} \cdot X_A}{(-r_A)}$ $\tau = \frac{C_{A0} \cdot X_A}{-r_A} = \frac{C_{A0} \cdot X_A}{kC_{A0}(1 - X_A)}$ <p><b>Space time <math>\tau = \frac{0.70}{0.0926(1-0.7)} = 25.2 \text{ min.}</math></b></p> <p><b>Space velocity = <math>s = 1/\tau = 1/25.2 = 0.03968 \text{ min}^{-1}</math></b></p>	<p>2</p> <p>1</p> <p>1</p>
5-c	<p><b>Derivation of performance equation for PFR</b></p> <p>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 <math>dV</math>.</p> <div style="text-align: center;"> </div> <p>Taking material balance of reactant A over the reactor,</p> <p>Input of A to reactor = Output of A from reactor + Disappearance of A due to chemical reaction + Accumulation of A within the reactor.</p> <p>For plug flow reactor, the last term is zero.</p> <p>Input of A to reactor = Output of A from reactor + Disappearance of A due to chemical reaction .....(1)</p> <p>Let, <math>F_{A0}</math> = Molar feed rate to the reactor.</p> <p><math>C_{A0}</math> = Molar concentration of A in stream entering the reactor ( moles/volume)</p>	1





**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 17 of 21

<p><math>X_A =</math> Fractional conversion of A <math>F_A = F_{A0} (1 - X_A) = F_{A0} - F_{A0} \cdot X_A</math> <math>dF_A = - F_{A0} \cdot d X_A</math></p> <p>For the differential volume <math>dV</math> Input of A in moles/time = <math>F_A</math> Output of A from reactor in moles/time = <math>F_A + dF_A</math> Disappearance of A due to chemical reaction in moles/ time = <math>(-r_A) dV</math> Substituting all the terms in the material balance equation (1)</p> $F_A = F_A + d F_A + (-r_A) \cdot dV$ $- d F_A = (-r_A) dV$ $F_{A0} \cdot d X_A = (-r_A) dV$ $\frac{dV}{F_{A0}} = \frac{dX_A}{-r_A}$	<p>2</p>
<p>This is the equation accounting for A in the differential section of the reactor of volume <math>dV</math>. For the whole reactor, the equation must be integrated.</p> $\int_0^V \frac{dV}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A}$ $\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}}$ <p>Where <math>X_A</math> and <math>(-r_A)</math> are evaluated at the exit conditions</p> <p><b>For constant volume system :</b></p> $\frac{V}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-r_A} = \frac{\tau}{C_{A0}} = \frac{-1}{C_{A0}} \int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A}$ <p><b>Graphical representation</b></p>	<p>3</p>



SUMMER-18 EXAMINATION  
Model Answer

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 18 of 21

		2
6	Attempt any FOUR of the following	16
6-a	<p><b>Plug flow reactors are not connected in series :</b></p> <p>Assume two PFRs are placed in series as shown below</p> <p>Let <math>X_1</math> &amp; <math>X_2</math> be the fractional conversions of a component A leaving reactors 1 &amp; 2 .</p> <p><math>X_1</math> : conversion of A from first reactor  <math>X_2</math> : overall conversion of A from entire system</p> <p>The performance equation for PFR1 is <math>\frac{V_1}{F_0} = \int_0^{X_1} \frac{dX}{(-r)}</math></p> <p>The performance equation for PFR2 is <math>\frac{V_2}{F_0} = \int_{X_1}^{X_2} \frac{dX}{(-r)}</math></p> <p>Two PFRS in series</p> $\frac{V}{F_0} = \frac{V_1}{F_0} + \frac{V_2}{F_0} = \int_0^{X_1} \frac{dX}{(-r)} + \int_{X_1}^{X_2} \frac{dX}{(-r)} \quad \text{EqI}$ <p>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 <math>V = V_1 + V_2</math> for <math>X_2</math>, then the same conversion (<math>X_2</math>) can be</p>	2



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 19 of 21

	achieved using one PFR of volume Thus it makes no difference if two PFRs are connected in series or one PFR of same reactor volume.	
6-b	<p><b>Relation between <math>K_p</math> and <math>K_c</math></b></p> <p>Consider the reaction <math>aA + bB + \dots \rightarrow rR + sS \dots</math></p> $K_c = (C_R^r \cdot C_S^s) / (C_A^a \cdot C_B^b)$ <p>For ideal gas <math>C_i = p_i / RT</math></p> <p>Therefore <math>K_c = \{ (p_R / RT)^r \cdot (p_S / RT)^s \} / \{ (p_A / RT)^a \cdot (p_B / RT)^b \}</math></p> $= (p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b) \cdot (1 / RT)^{(r+s+\dots-(a+b+\dots))}$ <p>R is the ideal gas constant T the absolute temperature in K P is the pressure in atm</p> <p>ie <math>K_c = K_p \cdot (1 / RT)^{\Delta n}</math> where <math>K_p = (p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b)</math></p> <p><math>\Delta n = (r + s + \dots - (a + b + \dots))</math> is the difference in the number of moles of product and reactant</p> <p><b>Or <math>K_p = K_c \times (RT)^{\Delta n}</math></b></p>	<p>2</p> <p>2</p>
6-c	<p><b>Factors affecting the rate of a chemical reaction :</b></p> <ol style="list-style-type: none"> <li>1. In <b>homogeneous system</b> temperature, pressure and composition are the variables.</li> <li>2. In <b>heterogeneous system</b>, 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.             <ol style="list-style-type: none"> <li>1. rate of heat transfer</li> <li>2. Catalyst</li> <li>3. Nature of reactants</li> <li>4. Surface area available.</li> <li>5. Intensity of light if reaction is light sensitive.</li> </ol> </li> </ol>	<p>1 mark each for any 4 points.</p>
6-d	<b>General procedure for analysis of complete rate equation by integral</b>	



**SUMMER-18 EXAMINATION**  
**Model Answer**

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 20 of 21

**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  $C_{At}$

$$-\int_{C_{A0}}^{C_{At}} (dC_A / f(c)) = k \int_0^t dt$$

$$C_{A0} \quad 0$$

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



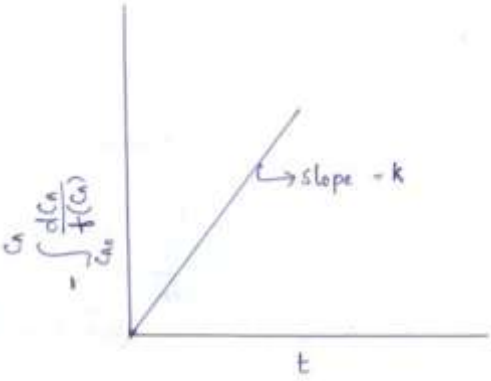
SUMMER-18 EXAMINATION  
Model Answer

Subject Title: Chemical Reaction Engineering

Subject code

17562

page 21 of 21

		1
6-e	<p><b>Batch reactor</b></p> <p><b>Advantages:</b></p> <ol style="list-style-type: none"><li>1. Simple in construction &amp; operation</li><li>2. Low equipment cost</li><li>3. Gives highest conversion by leaving the reactants for longer periods in reactor.</li><li>4. Requires small instrumentation &amp; less supporting equipment.</li></ol> <p><b>Disadvantages:</b></p> <ol style="list-style-type: none"><li>1. High labor costs per unit volume of production.</li><li>2. Requires considerable time to empty, clean out &amp; refill.</li><li>3. Poorer quality control of product.</li><li>4. Large scale production is difficult.</li></ol>	<p>1 mark each for any two points</p> <p>1 mark each for any two points</p>