### MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION

### **SUMMER-13 EXAMINATION**

#### Model Answer

Subject & code: CRE (12206)

### Important instructions to examiners:

- 1. The answers should be examined by keywords 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 given more importance.
- 4. While assessing figures, examiner may give credit for principal components indicated in a 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 answer and model answer.
- 6. In case of some questions credit may be given by judgment of relevant answer based on candidates understanding.

Q	Answer	Mark	Total
No:			marks
1A. a	Enthalpy: Enthalpy(H) is a measure of the total heat content of the	1	4
	substance or system.		
	<b>Expression:</b> $H = U + PV$	1	
	<b>Entropy</b> : Entropy(s) is the measure of the total disorder or randomness	1	
	of the system or it is a measure of the unavailable energy to perform		
	useful work.		
	<b>Expression</b> : $dS = d_{Qreversible} / T$	1	
1A.	Rate law: Rate law is defined as the number of moles of reactant reacted	2	4
b	or product produced in unit volume in unit time.		
	<b>Expression</b> : For component i, $r_i = (1/V) dN_i / dt$ where V is the volume	2	
	of reactor and $\left. dN_i \right/ dt$ is the rate of change of component i		

CRE (12206) Page **1** of **19** 

1A. c	<b>Fractional conversion</b> $\mathbf{x}_{A}$ : Fractional conversion $\mathbf{x}_{A}$ of reactant A is	2	4
	defined as the fraction of A that is converted into product.		
	<b>Equation:</b> $C_A = C_{A0}(1-x_A)$ or $N_A = N_{A0}(1-x_A)$	2	
	Material balance equation for a batch reactor:		4
1A.	Material balance equation for any reactor is	2	
d	(rate of reactant in) = (rate of reactant out) + (rate of reactant loss		
	due to chemical reaction ) +		
	(rate of accumulation of reactant within the reactor)		
	For batch reactor, rate of reactant in $=$ rate of reactant out $=$ 0		
	Therefore material balance equation for a batch reactor is	2	
	Rate of reactant loss due to chemical reaction = -(rate of accumulation		
	of reactant within the reactor)		
1B. a	Relation between K <sub>p</sub> , K <sub>c</sub> and K <sub>y</sub>	3	6
	Consider the reaction $aA + bB + \rightarrow rR + sS$		
	$K_c = (C_R^r \cdot C_S^s) / (C_A^a \cdot C_B^b)$		
	For ideal gas $C_i = p_i / RT$		
	Therefore $K_c = \{\left(\right. p_R \ / \ RT\right)^r$ . ( $p_S \ / \ RT\right)^s\} \ / \ \{\left.\left(\right. p_A \ / \ RT\right)^a$ . ( $p_B \ / \ RT\right)^b\}$		
	$=(p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b) \cdot (1 / RT)^{(r+s+(a+b=))}$		
	ie $K_c = K_p$ . $(1/RT)^{\Delta n}$ where $K_p = (p_R^r \cdot p_S^s)/(p_A^a \cdot p_B^b)$		
	$\Delta n = (r + s + \dots - (a + b + \dots))$ is the		
	difference in the number of moles of product and reactant		
	$p_A = P \cdot y_A$ Where $p_A$ - partial pressure of A, $$ P- total pressure		
	$y_A$ – mole fraction of A.		
	$K_p = (p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b)$	3	
	$= \{ (Py_R)^r . (Py_S)^s \} / \{ (Py_A)^a . (Py_B)^b \}$		
	$= (y_R^r \cdot y_S^s) / (y_A^a \cdot y_B^b) \cdot P^{(r+s+(a+b=))}$		
	$K_p = K_y$ . $P^{\Delta n}$ where $K_y = (y_R^r \cdot y_S^s) / (y_A^a \cdot y_B^b)$		
	$K_c = K_p$ . $(1/RT)^{\Delta n} = K_y$ . $(P/RT)^{\Delta n}$		
1B. b	Activation energy :Activation energy is the minimum energy that the	2	6
	reactants must acquire before reaction takes place to give the product. It		
	can be considered as a potential energy barrier. Only those molecules that		

CRE (12206) Page **2** of **19** 

	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.		
	Graphical representation		
	For exothermic reaction		
		2	
	Activated complex. transition state  Average energy of products  Average energy of reactants  Distance along reaction path		
	Activated complex, transition state  Average energy of products  Average energy of reactants  Distance along	2	
	reaction path		
2.a	Temperature dependency of rate constant from transition state	2	8
	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		

CRE (12206) Page **3** of **19** 

	Boltzmann constant and h is Planck constant		
	Consider the reversible reaction $A + B \leftrightarrow AB$ , $k_1$ is the rate constant for		
	forward reaction and $k_2$ is the rate constant for backward reaction	2	
	$\mathbf{k_3}$		
	According to transition theory, $A + B \leftrightarrow AB^* \rightarrow AB$		
	$\mathrm{k}_4 \qquad \mathrm{k}_5$		
	$K_c = k_3 / k_4 = C_{AB}*/C_A.C_B$		
	$K_5 = kT/h$		
	$r_{AB,forward}$ = (concentration of activated complex) . (rate of		
	decomposition of activated complex)		
	$= C_{AB} * . (kT / h)$		
	$= (kT/h) . K_c . C_A. C_B$		
	From thermodynamics, $\Delta G = \Delta H - T\Delta S = -RT \ln K_c$		
	$ln K_c = - (\Delta G / RT)$		
	$\mathbf{K}_{\mathrm{c}} = \mathrm{e}^{-(\Delta \mathrm{G}/\mathrm{RT})} = \mathrm{e}^{-(\Delta \mathrm{H}/\mathrm{RT}) + \Delta \mathrm{S}/\mathrm{R}}$	2	
	$r_{AB,forward} = (kT / h).C_A.C_B.e^{-(\Delta H/RT) + \Delta S/R}$		
	= a constant . T. $e^{-(\Delta H/RT)}$ $C_A$ . $C_B = K C_A$ . $C_B$		
	$e^{\Delta S/R}$ 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	2	
	$E = \Delta H$ - (molecularity – 1) RT for gases		
	The difference between E and $\Delta H$ is small and of the order RT. Hence		
	transition theory predicts that $\ K \ \alpha \ T \ e^{-(E/RT)}$		
2.b	<b>First order reaction:</b> First order reaction is the reaction whose order of	2	8
	reaction is one.ie the concentration of the reactant is raised to unity in the		
	rate equation.		
	<b>Rate equation:</b> $-r_A = kC_A$	1	

CRE (12206) Page **4** of **19** 

	Derivation:				2	
	Consider the reaction	$A \rightarrow B$				
	The rate equation is -	$-r_A = -dC_A / d$	$t = kC_A(1)$			
			$C_A$	t		
	Separating and integr	rating, -J( dC	$C_A / C_{A)} = k \int d$	t		
			$C_{A0}$	0		
	$-(\ln C_A/C_{A0}) = kt$					
	In terms of conversion	on: $C_A = C_{A0}$	$0(1-x_A)$		2	
	$dC_A = -C_{A0}dx_A$					
	Substituting in (1) as	nd rearrangin	g and integrati	ng		
	x <sub>A</sub> t					
	$\int (dx_A / (1-x_A) = k \int dx_A dx_A / (1-x_A) = k \int dx_A dx_A dx_A dx_A dx_A dx_A dx_A dx_A$	dt				
	$\mathbf{x}_{A0}$ 0					
	$-\ln(1-x_A) = kt$					
	-ln CA CAO OV-ln(1-NA)	1	8 lope k		1	
2.c	$x_{A} = 0.6$					8
	$F_{A0} = 10 \text{ mol/s}$					
	X <sub>A</sub>	-r <sub>A</sub>	1/-r <sub>A</sub>			
	0	0.182	5.49			
	0.2	0.143	6.99		1	
	0.4	0.1	10			
	0.6	0.0667	14.99			

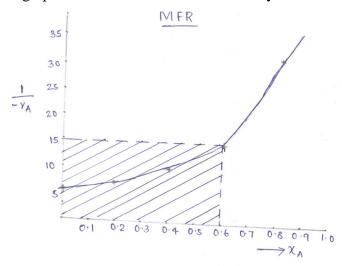
CRE (12206) Page **5** of **19** 

0.8	0.0317	31.55

# For MFR

 $V/\;F_{A0}\;=x_A\,/\,\hbox{-} r_A$ 

Plot a graph with  $x_A$  on x axis and  $1/-r_A$  on y axis.



Area from the graph = 9

$$V/F_{A0}\ =\ 9$$

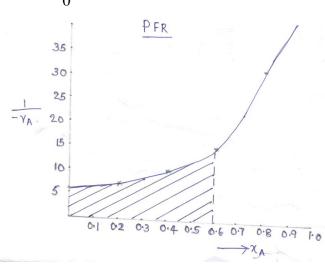
$$V = 9 . 10 = 90$$
litres

## For PFR

 $X_A$ 

$$V/F_{A0} = \int (dx_A / -r_A)$$

0



3

3

CRE (12206) Page **6** of **19** 

	Area under the curve between 0 and $0.6 = 5.315$		
	$V/F_{A0} = 5.315$		
	$V = 5.315 \times 10 = 53.15 \text{ litres}$		
	Volume of MFR required for 60% conversion is greater than that of	1	
	PFR.		
3.a	Integral method of analysis :	3	4
	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 <sub>A</sub>		
	3. Above equation is integrated with appropriate limits		
	$C_{\mathrm{A}}$ t		
	$-\int (dC_A / f(c)) = k \int dt$		
	$C_{A0}$ 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:		

CRE (12206) Page **7** of **19** 

	, s (54)	1	
	Slope = K		
	5 5		
	t		
3.b	$K_1 = 1.10^{-3} \text{ min}^{-1}$		4
	$K_2 = 2.10^{-3} \text{ min}^{-1}$		
	$T_1 = 27^0 c = 300 K$	1	
	$T_2 = 37^0 c = 310 K$		
	R = 1.987 cal / gmole K		
	$\ln (k_1 / k_2) = -(E/R) (1/T_1 - 1/T_2)$	2	
	E = 12809.2 calories	1	
3.c	First law of Thermodynamics :	2	4
	First law of thermodynamics states that energy can neither be created nor		
	be destroyed, it can only be converted from one form to another.		
	Although energy assumes many forms, the total quantity of energy is		
	constant and when energy disappears in one form, it appears		
	simultaneously in other forms.		
	$\Delta U = Q - W$		
	Second law of Thermodynamics :	2	
	Second law of Thermodynamics can be stated in two ways.		
	1. Entropy of an isolated system tends to increase and reaches a		
	maximum value.		
	2. Heat cannot pass from a cold body to a hot body. Mechanical		
	work can be completely converted to heat, but heat cannot be		
	completely converter to work without making some changes		

CRE (12206) Page **8** of **19** 

	either in the system or in the surrounding.		
	$dS = dQ_{reversible} / T$		
3.d	Space time :	1	4
	It is the time required to process one reactor volume of feed measured at		
	specified condition.		
	Unit: unit of time i.e. minute, hour.	1	
	Space velocity: It is the number of reactor volume of feed at specified	1	
	condition which can be treated in unit time.		
	<b>Unit</b> : time <sup>-1</sup> i.e. minute <sup>-1</sup> , hour <sup>-1</sup>	1	
3.e	Regeneration of catalyst: Regaining the activity of poisoned catalyst	1	4
	by different method is known as regeneration of catalyst.		
	Methods for regeneration catalyst :	1 mark	
	1. Volatile poison may be removed from the catalyst surface by	each for	
	passing current of pure gas or liquid or by raising the	any 3	
	temperature.	points	
	2. Coke deposited on the catalyst is removed by roasting the coke		
	by atmospheric oxygen at $550-700^{0}$ c.		
	3. Metallic catalyst like nickel are regenerated by washing with		
	alcohol or acid and other solvents. Irreversibly poisoned catalyst		
	like platinum on silica support, silver and vanadium pentoxide		
	are regenerated by extracting platinum, silver and vanadium from		
	them using acids and alkalies.		
	4. Magnetic methods are also used for regenerating the activity of		
	catalyst.		
	5. Metals concentrate on the surface of cracking catalyst and they		
	can be removed by the abrasion of surface bed.		
	6. Alumino silicate cracking catalyst gets poisoned due to the		
	deposition of metal on them. The poison is converted to a form		
	which is highly volatile or readily soluble in water and the		
	catalyst is treated with aqueous solution of organic acid, alkalies		
	and gases.		

CRE (12206) Page **9** of **19** 

4A.a	$\Delta G = -RT \ln K$	2	4
	Where $\Delta G$ - Gibb's free energy	2	
	R – Universal gas constant		
	T- Temperature in K		
	K- equilibrium constant		
4A.b	Arrhenius theory Collision theory	2 marks	4
	1. $k \alpha e^{-(E/RT)}$ $k \alpha T^{1/2} e^{-(E/RT)}$	each	
	2. Holds good for Holds good for bimolecular		
	unimolecular and reactions but fails with		
	bimolecular unimolecular reactions		
	reactions.		
4A.c	1) Zero order reaction.	2	4
	2) First order reaction.	2	

CRE (12206) Page **10** of **19** 

4A.d	<b>Activity</b> : It is a measure of the accelerating effect that the catalyst has on	2	4
	the rate of given reaction. Activity of catalyst is measured by finding the		
	ratio between the rate constant of a catalysed and uncatalysed reaction.		
	Selectivity: Selectivity or specificity of a catalyst refers to the property	2	
	of catalyst to speed up the main reaction in the presence of several side		
	reactions.		
4B. i	For first order reaction, $-\ln(1-x_A) = kt(1)$	2	6
	First Case:	2	
	$x_{A} = 0.4$		
	t= 5 minutes		
	solving, $k = 0.1021 \text{min}^{-1}$		
	Second Case:	2	
	$x_A = 0.75$		
	Substituting in eqn ( 1), $t = 13.57$ minutes		
	Time required to reach 75% conversion is 13.57 minutes.		
4B.ii	i. CSTR:		
	Diagram :		6
	Uniformly mixed Product	1	
	In CSTR the contents are well stirred and uniform through out.  The exit stream from the reactor has the same composition as the fluid within the reactor.  Advantages:  1. Good temperature control	½ mark each for any two points	

CRE (12206) Page **11** of **19** 

- 2. Possible to operate under isothermal condition even when the reaction is exothermic.
- 3. Low cost of construction.
- 4. Long residence time due to its larger volume.
- 5. Uniform mixing.

### **Disadvantages**:

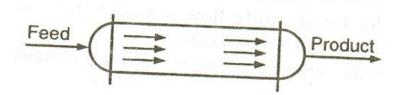
1. Large reactor is required for high conversion.

2. Not suitable for high pressure reaction.

Low area of heat transfer per unit volume and low heat transfer coefficient.

i) **PFR**:

## Diagram:



In PFR, the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind.

### Advantages:

1. Easy to maintain as there are no moving parts.

2. Gives highest conversion per unit volume of reactor.

3. Suitable for high pressure reaction.

4. Rate of heat transfer per unit volume of reaction mixture is high and has high heat transfer coefficient.

**Disadvantages**:

1. Difficult to control temperature within the reactor.

2. Hotspots can be formed for exothermic reactions.

½ mark

½ mark

each for

any two

points

each for

any two

points

½ mark each for

any two

points

CRE (12206) Page **12** of **19** 

5.a	Performance equation of mixed flow reactor:  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.	1	8
	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	1	
	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 = $\ F_{A0.} \ X_A$ $F_{A0.} \ X_A = Moles \ of \ A \ fed \ / \ time \ x \ Moles \ of \ A \ reacted / \ moles \ of \ A \ fed$	1	
	$\begin{array}{llllllllllllllllllllllllllllllllllll$		
	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	
	$\frac{V}{F_{A0}} = \frac{X_A}{-r_A}$		
	$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{(-r_A)}$		
	$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{V.C_{A0}}{F_{A0}} = \frac{C_{A0}}{-r_A}$	2	
	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. Applicable for any value of $\epsilon$ .		
	For first order reaction, $-r_A = kC_A$		

CRE (12206) Page **13** of **19** 

	Therefore $\tau = VC_{10} / F_{10} - C_{10} / VC_{10}$		
	Therefore $\tau = VC_{A0} / F_{A0} = C_{A0} / kC_A$	2	
	From equation (3.22) $-\frac{1}{r_A}$ $\frac{-1}{r_A}$ Area = $\tau$ = From equation (3.22)		
5.b	Catalyst promoters:  A substance which do not act as a catalyst but enhance the efficiency of a catalyst & prolong it's life is called as promoter.  Promoters are present in small amounts & are added during preparation	2	8
	of catalysts.  Ex: Molybdenum(Mo) acts as apromoter in ammonia synthesis by the Haber's process,in which iron is used as a catalyst.	1	
	Accelerators:  Materials that are added to the reactant stream to improve performance of a catalyst are called as accelerators.  They function opposite to poisons.	1	
	<b>Ex</b> : In dehydrogenation of butene to butadiene using Fe as catalyst ,steam is added to butene feed. The added steam to reactor reduces the coke formation & increases the yield of butadiene.	1	
	Inhibitors: A substance which decreases the rate of a reaction(instead of increasing it) is called as an inhibitors or negative catalyst. Inhibitors are useful for reducing the activity of catalyst for an	2	
	undesirable side reaction.  Ex: Silver supported on alumina is an excellent catalyst for oxidation of ethylene to ethylene oxide. However at the same reaction condition, complete oxidation to CO2 & water also occurs, so that the selectivity of ethylene oxide is poor.it has been found that adding halogen compound to the catalyst inhibits the complete oxidation of ethylene & results in satisfactory selectivity.	1	
5.c	Van't Hoff Equation: The van'thoff isotherm: Let us consider the following chemical reaction aA + bB		8

CRE (12206) Page **14** of **19** 

The free energy of mixture of a moles of A & b moles of B in terms of chemical potential(at constant temperature, pressure & composition) is

1

1

1

1

1

G (reactants) =  $a\mu_A + b\mu_B$  and

 $G(products) = r\mu_R + s\mu_S$ 

The free energy ( $\Delta G$ ) accompanying the above reaction at constant temperature & pressure is

 $\Delta G = G(products) - G(reactants)$ 

$$\Delta G = (r\mu_{R+s}\mu_{S}) - (a\mu_{A+b}\mu_{B}) \qquad eq1$$

The chemical potential  $\mu$  of any constituent of a mixture is given by  $\mu=\mu^0+RT$  ln a

 $\mu^0$ = chemical potential of a substance in standard state of unit activity &a is the activity of the substance in mixture under consideration.

On substituting chemical potential in above equation 1,

$$\Delta G = (r\mu^0_{R} + s\mu^0_{S}) - (a\mu^0_{A} + b\mu^0_{B}) + RT(r \ln a_R + s \ln a_S - a \ln a_A - b \ln a_B)$$

As 
$$\Delta G^0 = (r\mu^0_{R} + s\mu^0_{S}) - (a\mu^0_{A} + b\mu^0_{B})$$

$$\Delta G = \Delta G^0 + RT \ln(a_R^r \cdot a_S^s / a_A^a \cdot a_B^b)$$
 eq2

The free energy change accompanying a chemical reaction under equilibrium conditions must be equal to zero.

$$\Delta G = 0$$

Eq 2 becomes

$$0 = \Delta G^0 + \, RT ln(a^r_R \, . \, \, a^s_S \, \, / \, \, a^a_{\,\,A} \, . a^b_{\,\,B})_e \, \qquad e$$
 indicates activity at equilibrium

$$\Delta G^0 = -RT \ln(a_R^r \cdot a_S^s / a_A^a \cdot a_B^b)$$

$$\Delta G^0 = -RT \ln K$$
 eq3

Eq3 relates std. free energy change of the reaction at a specified temp.T to the thermodynamic equilibrium constant.

For gases behaving ideally ,use of partial pressure & so chemical potential of any substance is given by

$$\mu = \mu^0 + RT \ln p$$

Therefore 
$$\Delta G^0 = -RT \ln KpV$$
 an't Hoff isotherm

Van't Hoff isotherm relates Gibb's free energy &equilibrium constant.

The equilibrium constant may increase/ decrease with the temperature. The dependence of temp. of equilibrium constant at constant pressure is quantitatively given by the Van't Hoff isobar which clearly shows that it depends upon astandard enthalpy Change.

$$\frac{dlnK}{dT} = \frac{\Delta H^{\circ}}{RT2}$$

The effect of temperature on equilibrium constant may be determined by differentiation of the Van't Hoff isotherm.

Van't Hoff isotherm is

$$\Delta G^{\circ} = -RT lnK$$

$$lnK = -\Delta G^{\circ}/RT$$

Differentiating with T yields

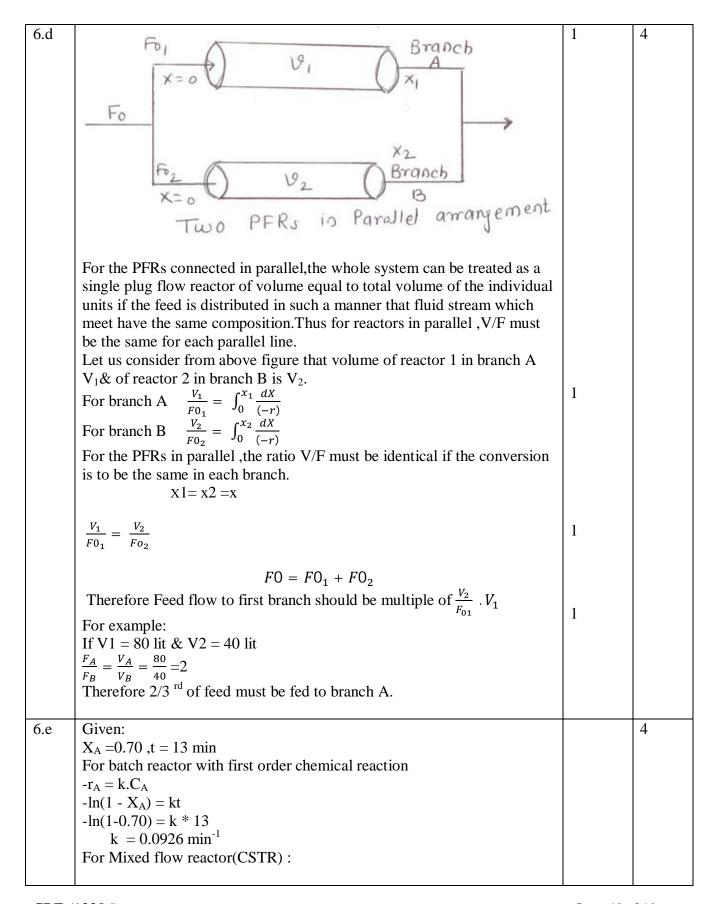
CRE (12206) Page **15** of **19** 

	$dlnK -1 d(\Delta G^{\circ}/T)$		
	$\frac{dT}{dT} = \frac{1}{R} \frac{dT}{dT}$		
	We have $dG = VdP - SdT$		
	At constant pressuredP= 0	1	
	dG = -SdT		
	$d(dG^0) = -\Delta S^0 dT$		
	$\Delta S^0 = -d(dG^0) / dT$		
	$As \Delta G^0 = \Delta H^0 - T\Delta S^0$		
	Substituting value for $\Delta S^0$ , we get		
	$dG^0 = \Delta H^0 + T d(\Delta G^0)/dT$		
	Rearranging we get,		
	$-\Delta H^0 = T d(\Delta G^0)/dT - \Delta G^0$		
	Dividing both the sides by T <sup>2</sup>		
	$-\Delta H^0 / T^2 = T d(\Delta G^0)/dT - \Delta G^0 / T^2$		
	The RHS of above equation is obtained by differentiating $\Delta G^0/T$ wrt T.		
	$\frac{d(\Delta G^{\circ}/T)}{dT} = \frac{T\left(\frac{d(\Delta G^{\circ})}{dT}\right) - \Delta G^{\circ}}{T^{2}}$		
	$\frac{d(\Delta G^{*}/I)}{dT} = \frac{I(dT)}{I}$	1	
	$dT$ $T^2$		
	$d(\Lambda G^{\circ}/T) \qquad \Lambda H^{\circ}$		
	As $\frac{d(\Delta G^{\circ}/T)}{dT} = -\frac{\Delta H^{\circ}}{T^2}$		
	Combining above equations we get		
	$-R\frac{(dlnK)}{dT} = \frac{-\Delta H^{\circ}}{T^{2}}$		
	$u_1$ $I^-$		
	$\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}$		
	$\Delta H^0$ is the standard enthalpy change for a reaction at a constant		
	temperature i.e. the standard heat of reaction. $\Delta H^0 = \Delta H^0_R = (\Sigma \Delta H^0_f) \text{products} - (\Sigma \Delta H^0_f) \text{ reactants}$	1	
	For the homogeneous gaseous phase reaction, Van't Hoff isobar given by	1	
	the above equation takes form as		
	$\frac{d \ lnKp}{dT} = \frac{\Delta H^{\circ}}{RT^{2}}$		
	When $\Delta H^0$ is +ve, d lnKp/dT > zero &Kp(T) is a increasing function.		
	$\Delta H^0$ is -ve, d lnKp/dT < zero &Kp(T) is a decreasing function.		
6.a	Given :t $_{1/2}$ = 240 seconds		4
J	For the first order reaction: $t_{1/2} = 0.693 / k$		
	$k = 0.693 / t_{1/2}$	1	
	k = 0.693/240	1	
	$k = 2.89 * 10-3 s^{-1}$		
	k = 2.89 * 10-3 * 60	1	
	$k = 0.1732 \text{ min}^{-1}$	1	
6.b	Given:		4
0.0	E = 75000 cal/mol		4
	$T_1 = 500 ^{\circ}\text{C} = 773 ^{\circ}\text{K}$		
	11-500 C-775 K		

CRE (12206) Page **16** of **19** 

		1	
	$T_2 = 650 \text{ OC} = 923 ^0\text{K}$ R = 1.987  cal/mol.K		
	Let $k_1$ & $k_2$ be the rate constants at temp $T_1$ & $T_2$ respectively. $\ln (k_2/k_1) = E/R (1/T_1 - 1/T_2)$	2	
	$\ln(k_2/k_1) = 75000/1.987(1/773 - 1/923)$ $\ln(k_2/k_1) = 7.951$		
	$k_2/k_1 = 2838$ $k_2 = 2838 k_1$	2	
	At 650 °C, the decomposition is faster by a factor 2838 than at 500 °C.	2	
	Variation of reaction with temperature at constant pressure for Endothermic reactions:		4
6.c	Endothermic reactions are those chemical reactions where the heats of		
	products are greater than the heats of reactants.  The magnitude of equilibrium constant determines the extent to which a reaction can proceed under given set of conditions. A large value of Kp indicates that the concentration of products in mixture at equilibrium are larger to that of so that reaction favours the formation of products. In this		
	case the extent of reaction is high.  The equation which helps to find out the variation of the equilibrium constant, and hence equilibrium conversion with temperature is	2	
	$Rln\frac{Kp_{2}}{Kp_{1}} = \Delta\alpha ln\frac{T_{2}}{T_{1}} + \frac{\Delta\beta(T_{2}-T_{1})}{2} + \frac{\Delta\gamma}{3}(T_{2}^{2}-T_{1}^{2}) + \left[-\Delta H_{0}^{\circ} + \Delta\alpha T_{0} + \frac{\Delta\beta}{2} \cdot T_{0}^{2} + \frac{\Delta\gamma}{3} \cdot T_{0}^{3}\right] \cdot \left[\frac{1}{T_{2}} - \frac{1}{T_{1}}\right]$	1	
	For endothermic reactions, equilibrium conversion rises with an increase in temperature.  (Kp increases with increase in temperature. As Kp increases, rate of		
	chemical reaction also increases.)	1	
	1		
	1.0 Endothermic		
	↑ / · · · · · · · · · · · · · · · · · ·		
	XA .		
	Temp. →		
	Effect of Temp. on Eglin conversion at con		

CRE (12206) Page **17** of **19** 



CRE (12206) Page **18** of **19** 

$\tau = \frac{C_{A0} \cdot X_A}{(-r_A)}$	1	
	1	
$\tau = \frac{C_{A0} \cdot X_A}{-r_A} = \frac{C_{A0} \cdot X_A}{k C_{A0} (1 - X_A)}$ $\tau = \frac{0.70}{0.0926(1 - 0.7)} = 25.2 \text{ min.}$	1	
Space velocity(s) = $v_0/V = 1/\tau = 1/25.2$ Space velocity =0.39 min <sup>-1</sup>	1	

CRE (12206) Page **19** of **19**