## Subject Name: Chemical Reaction Engineering

Subject Code:
17562
Page 1 of 27

## 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.

Subject Code:

$$
17562
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Page 2 of 27

| Q <br> No. | Sub <br> Q <br> No. |  | Marks |
| :---: | :---: | :--- | :---: |
| 1A |  | Answer | 12 |
| 1A | a | Factors affecting the rate of a chemical reaction : <br> 1. In homogeneous system temperature, pressure and composition are the <br> variables. <br> 2. In heterogeneous system, since more than one phase is involved, material <br> have to move from phase to phase during reaction, hence the rate of mass <br> transfer is important. <br> 3. rate of heat transfer <br> 4. Catalyst <br> 5. Nature of reactants <br> 6. Surface area available. <br> 7. Intensity of light if reaction is light sensitive. | any four <br> factors. |
| 1A | b | Gibb's free energy: <br> Gibb's free energy is the energy actually available to do useful work. It <br> predicts the feasibility and equilibrium conditions for chemical reactions at <br> constant temperature and pressure. <br> Feasibility of a chemical reaction from Gibbs free energy change: <br> At chemical equilibrium $\Delta G^{0}=0 . F o r ~ a ~ c h e m i c a l ~ r e a c t i o n ~ a t ~ e q u i l i b r i u m ~ a t ~ a ~$ <br> given temperature \&pressure, the free energy must be minimum. <br> If $\Delta G^{0}<0$ i.e.it is negative, the reaction can take place spontaneously <br> (reaction is possible under the given set of conditions).For spontaneous | 2 |

\begin{tabular}{|c|c|c|c|}
\hline \& \& \begin{tabular}{l}
reaction, there should be decrease in Gibb's free energy change. \\
If \(\Delta \mathrm{G}^{0}\) is positive ,the reaction cannot take place under the given conditions
\end{tabular} \& \\
\hline 1A \& c \& \begin{tabular}{l}
Definition: \\
Fractional change in volume \(\varepsilon_{A}\) : \\
It is defined as the change in volume of the system between no conversion and complete conversion of reactant A . \\
Fractional conversion \(\mathrm{x}_{\mathrm{A}}\) : \\
Fractional conversion \(\mathrm{x}_{\mathrm{A}}\) of reactant A is defined as the fraction of A that is converted into product. \\
Mathematical expression:
\[
\varepsilon_{\mathrm{A}}=\frac{V_{X A=1-V_{X A=0}}}{V_{X A=0}}
\]
\end{tabular} \& 1.5
1.5

1 <br>

\hline 1A \& d \& | Space time: |
| :--- |
| It is the time required to process one reactor volume of feed measured at specified condition. $\tau=\frac{1}{s}=\frac{C_{A 0 V}}{F_{A 0}}$ |
| Unit |
| 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. $\mathrm{S}=\frac{1}{\tau}=\frac{F_{A 0}}{C_{A O V}}$ |
| Unit |
| Unit is time ${ }^{-1}$ ( second $^{-1}$, minute ${ }^{-1}$ etc) | \& 1

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1
1
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\hline
\end{tabular}

## Subject Name: Chemical Reaction Engineering

Subject Code:
17562
Page 4 of 27

| 1B |  | Attempt any ONE | 6 |
| :---: | :---: | :---: | :---: |
| 1B | a | Differential method of analysis of data <br> 1)Assume a mechanism and from it obtain a rate equation of the form $-r_{A}=\frac{-d C_{A}}{d t}=k f(c)$ <br> 2) From experiment obtain concentration-time data and plot them. <br> 3) Draw a smooth curve through this data. <br> 4) Determine the slope of this curve at suitably selected concentration values. These slopes $\left(\frac{-d C_{A}}{d t}\right)$ are the rates of reaction at these composition. <br> 5) Evaluate $f(c)$ for each composition. <br> 6) Plot $\frac{-d C_{A}}{d t}$ vs $f(c)$ for each composition.If we get a straight line through origin; the rate equation is consistent with the data. If not, then another rate equation should be tested. <br> Merits (any one): <br> 1. It is useful for testing more complicated rate equations. <br> 2. It can be used to evolve or develop the rate equation to fit the data | 4 |

Subject Code:

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17562
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\begin{tabular}{|c|c|c|c|}
\hline \& \& \begin{tabular}{l}
Demerits (any one): \\
1. Differential method is not that much easy, is complicated \& time consuming. \\
2. It is used only when more accurate \&large amount of data are available.
\end{tabular} \& 1 \\
\hline 1B \& b \& \begin{tabular}{l}
Arrhenius equation \\
The temperature dependency of the reaction rate constant \(k\), is given by
\[
\mathrm{k}=\mathrm{k}_{0} e_{R T}^{-E}
\] \\
Where \(\mathrm{k}_{0}\)-frequency factor or pre exponential factor \\
E - activation energy in \(\mathrm{J} / \mathrm{mol}\) or \(\mathrm{cal} / \mathrm{mol}\) \\
R - universal gas constant \\
T - temperature in Kelvin
\[
\begin{aligned}
\& \mathrm{T}_{1}=400 \mathrm{~K} \\
\& \mathrm{~T}_{2}=500 \mathrm{~K} \\
\& \mathrm{k}_{2}=10 \mathrm{k}_{1}
\end{aligned}
\] \\
From Arrhenius law
\[
\ln \frac{k_{2}}{k_{1}}=\frac{-E}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)
\] \\
\(\ln 10=(-\mathrm{E} / 1.987) *\left(\frac{1}{500}-\frac{1}{400}\right)=2.52 * 10^{-4} \mathrm{E}\)
\[
\mathrm{E}=9150.47 \mathrm{cal}
\]
\end{tabular} \& 3

2 <br>
\hline 2 \& \& Attempt any TWO \& 16 <br>

\hline 2 \& a \& | Derivation for temperature dependency of rate constant from collision theory |
| :--- |
| The collision rate of molecules in a gas is found from the kinetic theory of gases. |
| For the bimolecular collision of like molecules A, | \& <br>

\hline
\end{tabular}

$$
\begin{align*}
& \mathrm{Z}_{\mathrm{AA}}=\sigma_{\mathrm{A}}{ }^{2} \mathrm{n}_{\mathrm{A}}{ }^{2} \sqrt{\frac{4 \pi k T}{M_{A}}} \\
& =\sigma_{\mathrm{A}}{ }^{2} \frac{N^{2}}{10^{6}} \sqrt{\frac{4 \pi k T}{M_{A}}} \mathrm{C}_{\mathrm{A}}{ }^{2}  \tag{i}\\
& =\text { number of collisions of A with } \mathrm{A} / \text { sec. } . \mathrm{cm}^{3} \\
& \text { Where } \sigma=\text { diameter of molecule, } \mathrm{cm} \\
& \mathrm{M}=\text { (molecular weight) / } \mathrm{N} \text {, mass of a molecule, gm } \\
& \mathrm{N}=\text { Avogadro's number } \\
& \mathrm{C}_{\mathrm{A}}=\text { concentration of } \mathrm{A}, \mathrm{~mol} / \text { liter } \\
& \mathrm{n}_{\mathrm{A}}=\mathrm{NC}_{\mathrm{A}} / 10^{3} \text {, number of molecules of } \mathrm{A} / \mathrm{cm}^{3} \\
& \mathrm{k}=\text { Boltzmann constant }
\end{align*}
$$

For the bimolecular collision of unlike molecules in a mixture of A and B, kinetic theory gives

$$
\begin{aligned}
\mathrm{Z}_{\mathrm{AB}} & =\left\{\left(\sigma_{\mathrm{A}}+\sigma_{\mathrm{B}}\right) / 2\right\}^{2} \mathrm{n}_{\mathrm{A}} \mathrm{n}_{\mathrm{B}} \sqrt{8 \pi k T\left(\frac{1}{M_{A}}+\frac{1}{M_{B}}\right)} \\
& =\left\{\left(\sigma_{\mathrm{A}}+\sigma_{\mathrm{B}}\right) / 2\right\}^{2} \frac{N^{2}}{10^{6}} \sqrt{8 \pi k T\left(\frac{1}{M_{A}}+\frac{1}{M_{B}}\right)} \mathrm{C}_{\mathrm{A}} \mathrm{C}_{\mathrm{B}} .
\end{aligned}
$$

If every collision between reactant molecules results in the transformation of reactants into product, these expressions give the rate of bimolecular reactions. The actual rate is much lower than that predicted and this indicates that only a small fraction of all collisions result in reaction. This suggests that only those collisions that involve energies in excess of a given minimum energy E lead to reaction. From the Maxwell distribution law of molecular energies the fraction of all bimolecular collisions that involves energies in excess of this minimum energy is given approximately by $e^{-E / R T}$ where $\mathrm{E} \gg \mathrm{RT}$.

Subject Code:

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17562
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Page $\mathbf{7}$ of $\mathbf{2 7}$

\begin{tabular}{|c|c|c|c|}
\hline \& \& \begin{tabular}{l}
Thus the rate of reaction is given by
\[
\begin{align*}
-\mathrm{r}_{\mathrm{A}}= \& -\frac{1}{V} \frac{d N_{A}}{d t}=\mathrm{k} \mathrm{C} \mathrm{C}_{\mathrm{A}} \mathrm{C}_{\mathrm{B}} \ldots \ldots . \text { (iii) } \\
= \& (\text { collision rate, mole } / \text { liter.sec)* (fraction of } \\
\& \quad \text { collision involving energies in excess of E ) } \\
= \& \mathrm{Z}_{\mathrm{AB}} \frac{10^{3}}{N} \mathrm{e}^{-\mathrm{E} / \mathrm{RT}} \\
= \& \left\{\left(\sigma_{\mathrm{A}}+\sigma_{\mathrm{B}}\right) / 2\right\}^{2} \frac{N}{10^{3}} \sqrt{8 \pi k T\left(\frac{1}{M_{A}}+\frac{1}{M_{B}}\right)} \mathrm{e}^{-\mathrm{E} / \mathrm{RT}} \mathrm{C}_{\mathrm{A}} \mathrm{C}_{\mathrm{B}} \ldots \ldots \text { (iv) } \tag{iv}
\end{align*}
\] \\
Comparing iii and iv, \(\quad \mathbf{k} \propto \mathbf{T}^{1 / 2} \mathbf{e}^{-\mathrm{E} / \mathbf{R T}}\)
\end{tabular} \& 2

2 <br>

\hline 2 \& b \& | Data: |
| :--- |
| Reactor is Mixed flow reactor $\mathrm{X}_{\mathrm{A}}=0.5$ |
| Reaction $\mathrm{A} \rightarrow \mathrm{R}$ $-r_{A}=\mathrm{k} C_{A}^{2}$ |
| The performance equation of MFR is $\begin{aligned} & \frac{V}{F_{A 0}}=\frac{X_{A}}{\left(-r_{A}\right)} \\ & \frac{V}{F_{A 0}}=\frac{X_{A}}{\left(\mathrm{k} C_{A}^{2}\right)} \\ & C_{A}=C_{A 0}\left(1-X_{A}\right) \\ & \frac{V}{F_{A 0}}=\frac{X_{A}}{\left(\mathrm{k} C_{A}^{2}\right)}=\frac{.(0.5)}{k \cdot C_{A O}^{2}(1-0.5)^{2}} \\ & \frac{V}{F_{A 0}}=\quad=\frac{2}{k \cdot C_{A O}^{2}} \end{aligned}$ | \& 2 <br>

\hline
\end{tabular}

|  |  | $K=\frac{2 . F_{A 0}}{V C_{A O}^{2}} \quad \ldots .1$ <br> Now the original reactor is replaced by PFR of equal size $\frac{V}{F_{A 0}}=\int_{0}^{X_{A}} \frac{d X_{A}}{-r_{A}}$ <br> But $-r_{A}=\mathrm{k} C_{A}^{2}$ and $C_{A}=C_{A 0}\left(1-X_{A}\right)$ $\frac{V}{F_{A 0}}=\int_{0}^{X_{A}} \frac{d X_{A}}{-r_{A}}=\int_{0}^{X_{A}} \frac{d X_{A}}{K C_{A 0}^{2}\left(1-X_{A}\right)^{2}}=\frac{1}{K C_{A 0}^{2}} \int_{0}^{X_{A}} \frac{d X_{A}}{\left(1-X_{A}\right)^{2}}$ $\frac{V}{F_{A 0}}=\frac{1}{K C_{A 0}^{2}} * \frac{X_{A}}{1-X_{A}}$ <br> Substituting the value of $K$ from equation 1 $\left.\begin{array}{rl} \frac{V}{F_{A 0}}= & \frac{V C_{A O}^{2} X_{A}}{2 F_{A 0} C_{A O}^{2}\left(1-X_{A}\right)} \\ 2=\frac{X_{A}}{\left(1-X_{A}\right)} \end{array}\right) . \quad \begin{aligned} & 2-2 X_{A}=X_{A} ; \quad 2=3 X_{A} ; \end{aligned}$ <br> Conversion in PFR will be $\mathbf{6 6 . 7 \%}$ | $2$ <br> 2 <br> 2 |
| :---: | :---: | :---: | :---: |
| 2 | c | Methods of catalyst Preparation: <br> 1. Precipitation <br> 2. Gel formation <br> 3. Simple mixing <br> 4. Impregnation method <br> 1.Precipitation method : <br> 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 | 2 marks each for explaining the methods with eg |


|  | pretreatment) <br> Eg. Magnesium oxide catalyst is prepared by this method. It is prepared by <br> precipitating $\mathrm{MgCO}_{3}$ from magnesium nitrate solution by adding sodium <br> carbonate.The magnesium carbonate precipitate is washed, dried \& calcined <br> to obtain magnesium oxide. <br> 2.Gel formation: If the precipitate formed in the above method is colloidal, <br> then gel is formed. <br> Eg Catalyst containing silica and alumina are suitable for gel formation <br> because their precipitates are colloidal in nature. <br> 3. Simple mixing: Some porous materials are obtained by mixing the <br> components with water, milling to the desired grain size, drying and <br> calcining. Such materials may be ground and sieved to obtain the particle <br> size. <br> Eg Mixed Mg and Ca oxide catalyst is prepared by this method <br> 4. Impregnation method: <br> This method is used for the preparation of expensive catalysts like platinum, <br> palladium, silver etc. A catalyst carrier provides a means of obtaining a <br> large surface area with a small amount of catalyst. The steps in the <br> preparation of a catalyst impregnated on a carrier include evacuating the <br> carrier, contacting the carrier with the impregnating solution, removing the <br> excess solution, drying, calcining and activation. <br> Eg Nickel catalyst is prepared on alumina by soaking the evacuated alumina <br> particles with nickel nitrate solution, draining to remove the excess solution <br> and heating in an oven to decompose the nitrate to nickel oxide. The final <br> step is activation in which nickel oxide is reduced to nickel. |
| :--- | :--- | :--- |

Subject Code:
17562

|  |  | Any other appropriate preparation method should also be given due consideration |  |
| :---: | :---: | :---: | :---: |
| 3 |  | Attempt any FOUR | 16 |
| 3 | a | $\begin{aligned} & \text { Number of moles }(\mathrm{n})=2 \\ & \mathrm{~V}_{1}=80 \mathrm{l} \\ & \mathrm{~V}_{2}=140 \mathrm{l} \\ & \mathrm{~T}_{1}=50^{\circ} \mathrm{C}=323 \mathrm{~K} \\ & \mathrm{~T}_{2}=200^{\circ} \mathrm{C}=473 \mathrm{~K} \\ & \mathrm{C}_{\mathrm{v}}=7.8 \mathrm{cal} / \mathrm{mol} \mathrm{~K} \\ & \Delta \mathrm{~S}=\mathrm{nC} \ln \frac{T_{2}}{T_{1}}+\mathrm{nRln} \frac{V_{2}}{V_{1}} \\ & \Delta \mathrm{~S}=2 \times 7.8 \times \ln (473 / 323)+2 \times 1.987 \times \ln (140 / 80)=\mathbf{8 . 1 7 4 4} \mathbf{c a l} / \mathbf{K} \\ & \hline \end{aligned}$ | 2 2 |
| 3 | b | Integrated form of rate expression for zero order reaction <br> Rate equation is $-\mathrm{r}_{\mathrm{A}}=-\frac{d C_{A}}{d t}=\mathrm{C}_{\mathrm{A} 0} \frac{d_{x A}}{d t}=\mathrm{k}$ <br> In terms of concentration $-\frac{d C_{A}}{d t}=\mathrm{k}$ <br> Integrating between appropriate limits $\begin{aligned} & \int_{C A_{0}}^{C A}-\mathrm{dCA}=\mathrm{k} \int_{0}^{t} d t \\ & \quad \mathrm{C}_{\mathrm{A} 0}-\mathrm{C}_{\mathrm{A}}=\mathrm{kt} \text { for } \mathrm{t}<\frac{C_{A 0}}{k} \end{aligned}$ | 2 |

Subject Code:

$$
17562
$$

|  |  | In terms of fractional conversion $\mathrm{C}_{\mathrm{A} 0} \frac{d_{x A}}{d t}=\mathrm{k}$ <br> Integrating between appropriate limits $\begin{aligned} & C_{A 0} \int_{0}^{x A} \mathrm{~d}_{\mathrm{xA}}=\mathrm{k} \int_{0}^{t} d t \\ & \quad \mathrm{C}_{\mathrm{A} 0} \mathrm{X}_{\mathrm{A}}=\mathrm{kt} \text { for } \mathrm{t}<\frac{C_{A 0}}{k} \end{aligned}$  | 2 |
| :---: | :---: | :---: | :---: |
| 3 | c | Relation between Gibb's free energy ( $\Delta \mathbf{G}^{\mathbf{0}}$ ) and equilibrium constant $\mathrm{K}_{\mathrm{p}}$ <br> Consider the reaction $\mathrm{aA}+\mathrm{bB} \rightarrow \mathrm{rR}+\mathrm{sS}$ $\begin{aligned} \Delta \mathrm{G} \text { reaction } & =\Delta \mathrm{G} \text { product }-\Delta \mathrm{G} \text { reactant. } \\ & =\left(\mathrm{r} \mu_{\mathrm{R}}+\mathrm{s} \mu_{\mathrm{S}}\right)-\left(\mathrm{a} \mu_{\mathrm{A}}+\mathrm{b} \mu_{\mathrm{B}}\right) . \end{aligned}$ |  |

Subject Code:

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17562
$$

\begin{tabular}{|c|c|c|c|c|c|}
\hline \& \& \multicolumn{3}{|l|}{\begin{tabular}{l}
At equilibrium there is no Gibb's free energy change, \(\Delta \mathrm{G}=0\)
\[
\begin{aligned}
\& \left(\mathrm{r} \mu_{\mathrm{R}}+\mathrm{s} \mu_{\mathrm{S}}\right)-\left(\mathrm{a} \mu_{\mathrm{A}}+\mathrm{b} \mu_{\mathrm{B}}\right)=0 \\
\& \left(\mathrm{r} \mu_{\mathrm{R}}+\mathrm{s} \mu_{\mathrm{S}}\right)=\left(\mathrm{a} \mu_{\mathrm{A}}+\mathrm{b} \mu_{\mathrm{B}}\right)
\end{aligned}
\] \\
But \(\mu_{i}=\mu_{i}^{0}+\) RT \(\ln p_{i}\) \\
Therefore \(\quad \mathrm{r}\left(\mu_{\mathrm{R}}{ }^{0}+\mathrm{RT} \ln p_{\mathrm{R}}\right)+\mathrm{s}\left(\mu_{\mathrm{S}}{ }^{0}+\mathrm{RT} \ln p_{\mathrm{S}}\right)=\mathrm{a}\left(\mu_{\mathrm{A}}{ }^{0}+\mathrm{RT} \ln \mathrm{p}_{\mathrm{A}}\right)+\)
\[
\mathrm{b}\left(\mu_{\mathrm{B}}^{0}+\mathrm{RT} \ln \mathrm{p}_{\mathrm{B}}\right)
\] \\
\(\mathrm{RT} \ln \left(\frac{p_{R}^{r}}{p_{A}^{a}} p_{S}^{s}{ }_{\mathrm{S}}^{b}\right)=\left(\mathrm{a} \mu_{\mathrm{A}}{ }^{0}+\mathrm{b} \mu_{\mathrm{B}}{ }^{0}\right)-\left(\mathrm{r} \mu_{\mathrm{R}}{ }^{0}+\mathrm{s} \mu_{\mathrm{S}}{ }^{0}\right)\) \\
\(=-(\Delta \mathrm{G}\) product \(-\Delta \mathrm{G}\) reactant \()\) \\
\(=-\Delta\) G reaction. \\
\(\ln \left(\frac{p_{R}^{r}}{p_{A}^{a}} \frac{p_{S}^{s}}{p_{B}^{b}}\right)=\frac{-\Delta \mathrm{G} \text { reaction }}{R T}\) \\
But \(\left(\frac{p_{R}^{r}}{p_{A}^{a}} \frac{p_{S}^{s}}{p_{B}^{b}}\right)=\mathrm{K}_{\mathrm{p}}\) \\
Therefore \(\Delta \mathrm{G}=-\mathrm{RT} \ln \mathrm{K}_{\mathrm{p}}\)
\end{tabular}} \& 2

2 <br>

\hline 3 \& d \& | Compa |
| :--- |
| points) |
| Sr no. <br> 1 <br> 2 <br> 3 <br> 4 | \& rison between elementa \& | and non elementary reaction (4 |
| :--- |
| Non-elementary reactions |
| These are multistep reactions. |
| Complex in nature |
| Not identical. |
| Order may be an integer or fractional value. | \& 1 mark each <br>

\hline
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Subject Code:

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17562
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| :--- | :--- | :--- | :--- | :--- | :--- |

## WINTER-18 EXAMINATION

Model Answer
Subject Name: Chemical Reaction Engineering $\quad$ Subject Code: 17562

Page 14 of 27


Subject Code:

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17562
$$



## WINTER-18 EXAMINATION

## Model Answer

Subject Name: Chemical Reaction Engineering
Subject Code:
17562
Page 16 of 27

\begin{tabular}{|c|c|c|c|}
\hline \& \& \begin{tabular}{l}
\[
t_{1 / 2}=\left(\frac{2^{n-1}-1}{k^{\prime}(n-1)}\right) C_{A_{0}}^{1-n}
\] \\
Where \(\mathrm{t}_{1 / 2}=\) half life period \\
\(\mathrm{C}_{\mathrm{A}} \mathrm{O}=\) Initial concentration of reactant A \\
\(\mathrm{n}=\) Order of reaction, \(\quad \mathrm{k}^{\prime}=\) Rate constant of reaction.
\end{tabular} \& 1

1 <br>

\hline 4A \& d \& | Relation between $K_{p}$ and $K_{y}$ (derivation) |
| :--- |
| Consider the reaction $\mathrm{aA}+\mathrm{bB} \rightarrow \mathrm{rR}+\mathrm{sS}$ $\mathrm{K}_{\mathrm{p}}=\left(\mathrm{p}_{\mathrm{R}}{ }^{\mathrm{r}} \cdot \mathrm{p}_{\mathrm{S}}{ }^{\mathrm{s}}\right) /\left(\mathrm{p}_{\mathrm{A}}{ }^{\mathrm{a}} \cdot \mathrm{p}_{\mathrm{B}}{ }^{\mathrm{b}}\right)$ |
| But $\mathrm{p}_{\mathrm{A}}=\mathrm{P} . \mathrm{y}_{\mathrm{A}}$ Where $\mathrm{p}_{\mathrm{A}}-$ partial pressure of A, P - total pressure $y_{A}$ - mole fraction of $A$. $\begin{aligned} \mathrm{K}_{\mathrm{p}} & =\left(\mathrm{p}_{\mathrm{R}}{ }^{\mathrm{r}} \cdot \mathrm{p}_{S}{ }^{\mathrm{s}}\right) /\left(\mathrm{p}_{A}{ }^{\mathrm{a}} \cdot \mathrm{p}_{\mathrm{B}}{ }^{\mathrm{b}}\right) \\ & =\left\{\left(\mathrm{Py}_{\mathrm{R}}\right)^{\mathrm{r}} \cdot\left(\mathrm{Py}_{S}\right)^{\mathrm{s}}\right\} /\left\{\left(\mathrm{Py}_{A}\right)^{\mathrm{a}} \cdot\left(\mathrm{Py}_{\mathrm{B}}\right)^{\mathrm{b}}\right\} \\ & =\left(\mathrm{y}_{\mathrm{R}}{ }^{\mathrm{r}} \cdot \mathrm{yS}_{\mathrm{s}}^{\mathrm{s}}\right) /\left(\mathrm{y}_{\mathrm{A}}{ }^{\mathrm{a}} \cdot \mathrm{y}_{\mathrm{B}}{ }^{\mathrm{b}}\right) \cdot \mathrm{P}^{(\mathrm{r}+\mathrm{s}+\ldots)-(\mathrm{a}+\mathrm{b}+\ldots))} \end{aligned}$ |
| $K_{p}=K_{y} \cdot P^{\Delta n} \quad$ where $K_{y}=\left(y_{R}{ }^{r} \cdot y_{s}{ }^{s}\right) /\left(y_{A}{ }^{a} \cdot y_{B}{ }^{b}\right)$ and |
| $\Delta \mathrm{n}=(\mathrm{r}+\mathrm{s}+\ldots)-(\mathrm{a}+\mathrm{b}+\ldots))$ is the difference in the number of moles of product and reactant | \& 2

2 <br>
\hline 4B \& \& Attempt any ONE \& 6 <br>

\hline 4B \& a \& | Types of intermediates in non- chain reaction: |
| :--- |
| 1. Free radicals. Free atoms or larger fragments of stable molecules which contain one or more unpaired electrons are called free radicals. The unpaired electron is designated by a dot in the chemical symbol for the substance. |
| Eg. $C \dot{H}_{3}$ |
| $\mathrm{C}_{2} \dot{H}_{5}$ |
| 2. Ions and polar substances. Electrically charged atoms, molecules or fragments of molecules such as $\mathrm{Na}^{+}, \mathrm{OH}^{-}, \mathrm{NH}^{+}$are called ions. They | \& | 1.5 marks |
| :--- |
| for each |
| point | <br>

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Subject Code:

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17562
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|  |  | may act as intermediates in reaction. <br> 3. Molecules: Consider the consecutive reaction $\mathrm{A} \rightarrow \mathrm{R} \rightarrow \mathrm{~S}$ <br> This is a multiple reaction. If the product R is highly reactive, its concentration in the reaction mixture can become too small to measure. In such a situation, R is not observed and can be considered to be a reactive intermediate. <br> 4. Transition complexes. The collision between reactant molecules result in a wide distribution of energies among the individual molecules. This can result in strained bonds, unstable form of molecules or unstable association of molecules which can then either decompose to give products or by further collision return to molecules in the normal state. Such unstable forms are called transition complexes. |  |
| :---: | :---: | :---: | :---: |
| 4B | b | Relation between conversion and equilibrium constant for second order reversible reaction <br> Reaction is $\mathrm{A}+\mathrm{B} \leftrightarrow \mathrm{R}+\mathrm{S}$ <br> Let 1 mole of $A$ and 1 mole of $B$ is present initially. $\mathrm{x}_{\mathrm{A}}$ mole of A reacts at equilibrium <br> $P$ is the total pressure. <br> When 1 mole of A reacts, 1mole of B also reacts. Then 1 mole of R and 1 mole of S is produced | 2 |

Subject Code:


Subject Code:

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17562
$$

Page 19 of 27

| 5 | a | Given: $\begin{aligned} & \mathrm{C}_{\mathrm{A} 0}=1 \mathrm{~mol} / \mathrm{l} \\ & \mathrm{X}_{\mathrm{A}}=0.80 \text { when } \mathrm{t}=8 \mathrm{~min} . \\ & \mathrm{X}_{\mathrm{A}}=0.90 \text { when } \mathrm{t}=18 \mathrm{~min} \end{aligned}$ <br> Let us first assume reaction is of zero order. The integrated equation for zero order reaction in terms of fractional conversion is $\mathrm{C}_{\mathrm{A} 0} \mathrm{X}_{\mathrm{A}}=\mathrm{kt}$ <br> Case 1) Where $X_{A}=0.80$ when $t=8 \mathrm{~min}$. $\begin{aligned} 1 * 0.8= & \mathrm{k}^{*} 8 \\ & \mathrm{k}=0.1(\mathrm{~min})^{-1}(\mathrm{~mol} / \mathrm{l}) \end{aligned}$ <br> Case 2) Where $X_{A}=0.90$ when $t=18 \mathrm{~min}$. $\begin{aligned} 1 * 0.9= & \mathrm{k}^{*} 18 \\ \mathrm{k} & =0.05(\mathrm{~min})^{-1}(\mathrm{~mol} / \mathrm{l}) \end{aligned}$ <br> Since k values are not same, the reaction is not of zero order <br> Let us now assume reaction is of First order. The integrated equation for first order reaction in terms of fractional conversion is $\ln \left\lfloor\frac{1}{1-X_{A}}\right\rfloor=\mathrm{kt}$ <br> Case 1) Where $X_{A}=0.80$ when $t=8 \mathrm{~min}$. $\begin{aligned} & \ln \left\lfloor\frac{1}{1-0.8}\right\rfloor=\mathrm{k}^{*} 8 \\ & \mathrm{k}=0.201(\mathrm{~min})^{-1} \end{aligned}$ <br> Case 2) Where $X_{A}=0.90$ when $t=80 \mathrm{~min}$. $\begin{aligned} & \ln \left\lfloor\frac{1}{1-0.9}\right\rfloor=\mathrm{k}^{*} 18 \\ & \mathrm{k}=0.1279(\mathrm{~min})^{-1} \end{aligned}$ <br> Since k values are not same, the reaction is not of first order. | 2 |
| :---: | :---: | :---: | :---: |


|  |  | Let us now assume it is of Second order. The integrated equation for second order reaction with respect to A in terms of fractional conversion is $\frac{X_{A}}{1-X_{A}}=\mathrm{k} C_{A O} \mathrm{t}$ <br> Case 1) Where $\mathrm{X}_{\mathrm{A}}=0.80$ when $\mathrm{t}=8 \mathrm{~min} . \& \mathrm{C}_{\mathrm{A} 0}=1 \mathrm{~mol} / \mathrm{l}$ $\frac{0.8}{1-0.8}=\mathrm{k} * 1 * 8$ $\mathrm{k}=0.5(\mathrm{~mol} / \mathrm{l})^{-1}(\mathrm{~min})^{-1}$ <br> Case 2) Where $X_{A}=0.90$ when $t=18 \mathrm{~min} . \quad \& C_{A 0}=1 \mathrm{~mol} / \mathrm{l}$ $\frac{0.9}{1-0.9}=\mathrm{k} * 1 * 18$ $\mathrm{k}=0.5(\mathrm{~mol} / \mathrm{l})^{-1}(\mathrm{~min})^{-1}$ <br> since $k$ values are same, reaction is of second order . <br> Rate of the reaction is $-\mathrm{r}_{\mathrm{A}}=\mathrm{kC}_{\mathrm{A}}{ }^{2}=0.5 \mathrm{C}_{\mathrm{A}}{ }^{2}(\mathrm{~mol} / \mathrm{I}$ minute $)$ | , |
| :---: | :---: | :---: | :---: |
| 5 | b | Derivation of performance equation / design equation of mixed flow reactor: <br> In MFR, the composition of the reactants is uniform throughout the reactor. <br> Taking material balance of reactant A over the reactor as a whole, <br> Rate of input of A to the reactor $=$ Rate of output of A from the reactor <br> + Rate of disappearance of A due to chemical reaction + Rate of accumulation of A within the reactor. <br> For mixed flow reactor at steady state the last term is zero. Therefore the material balance equation becomes <br> Rate of input of A to the reactor $=$ Rate of output of A from the reactor + <br> Rate of disappearance of A due to chemical reaction $\qquad$ <br> Let, $\quad \mathrm{F}_{\mathrm{A} 0}=$ Molar feed rate to the reactor <br> $\mathrm{V}=$ Volume of reactor |  |



## WINTER-18 EXAMINATION

Model Answer

## Subject Name: Chemical Reaction Engineering

Subject Code:
17562
Page 22 of 27

|  |  | fractional conversion is as below <br> The graphical representation of the performance equation in terms of concentration for constant density system is as below. | 2 |
| :---: | :---: | :---: | :---: |
| 5 | c | Comparison of MFR and PFR <br> 1) For any given duty \& for all positive reaction orders, size of MFR is always larger than that of PFR. The volume ratio Vm / Vp increases with reaction order. <br> 2) For low values of conversion, reactor size is only slightly affected by type of flow. As conversion approaches zero, volume / size ratio of | 1 mark each |


|  |  | these reactors approaches unity. The size ratio increases very rapidly at high values of conversion. <br> 3) Design of reactor is affected by density variation during reaction. Expansion (density decrease) during reaction increases the volume ratio, but decreases, the effectiveness of CSTR with respect to PFR. Density increase during reaction has the opposite effect. <br> 4) The performance equation for MFR is $\tau_{m} \cdot C_{A 0}^{n-1}=\left(\frac{C_{A 0} V}{F_{A 0}}\right)_{m}=\frac{X_{A}\left(1+\varepsilon_{A} \cdot X_{A}\right)^{n}}{k\left(1-X_{A}\right)^{n}}$ <br> For PFR $\tau_{p} \cdot C_{A 0}^{n-1}=\left(\frac{C_{A 0 . .}^{n} \cdot V}{F_{A 0}}\right)_{p}=\frac{1}{K} \int_{0}^{X A} \frac{(1+\varepsilon A X A)^{n}}{\left(1-X_{A}\right)^{n}} \cdot d X_{A}$ <br> 5) For a given space time, conversion in a PFR is higher than in MFR. <br> 6) It is possible to operate MFR under isothermal conditions whereas with PFR it is difficult. <br> 7) MFR has long residence time compared to PFR. <br> 8) MFR is not suitable for high pressure reactions whereas PFR is suitable. |  |
| :---: | :---: | :---: | :---: |
| 6 |  | Attempt any FOUR | 16 |
| 6 | a | Method of feeding when PFR's are connected in parallel Consider PFRs are connected as shown in the figure. |  |

Subject Code:
17562
Page 24 of 27


| 6 | b | Temperature increase is not desirable for exothermic reaction. <br> Van't Hoff equation is $\frac{d l n K}{d T}=\frac{\Delta H}{R T^{2}}$ <br> For exothermic reaction, $\Delta \mathrm{H}$ is negative. When temperature is increased, dT is positive; the overall equation is negative, which means $\ln \mathrm{K}$ is negative. When $\ln \mathrm{K}$ is negative, the value of K is low which denotes lower concentration of products. Therefore temperature increase is not desirable for exothermic reaction. |  |  | 4 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 6 | c | Difference between order and molecularity of reaction. (4 points) |  |  | 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 $1,2,3 \ldots$ | 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 |  |

Subject Code:

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17562
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\begin{tabular}{|c|c|c|c|}
\hline \& \& \begin{tabular}{|l|l|l} 
\& \& order reactions \\
\hline 5 \& \begin{tabular}{l} 
Molecularity is a theoretical \\
quantity
\end{tabular} \& \begin{tabular}{l} 
Order of reaction is entirely \\
an experimental value.
\end{tabular} \\
\hline
\end{tabular} \& \\
\hline 6 \& d \& \begin{tabular}{l}
Graph of concentration term with time \\
(i) For first order reversible reaction \\
Slope \(=k_{1}(M+1) /\left(M+X_{A e}\right)\) where \(M=C_{B o} / C_{A o}\) \\
(ii) For first order irreversible reaction
\end{tabular} \& 1

1 <br>
\hline
\end{tabular}

## Model Answer

Subject Code:
17562
Page 27 of 27

|  |  | Slope is k | 1 |
| :---: | :---: | :---: | :---: |
| 6 | e | Relation between $\mathrm{C}_{\mathrm{A}}$ and $\mathrm{X}_{\mathrm{A}}$ <br> i) Constant volume System $\mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\mathrm{A} 0}\left(1-\mathrm{X}_{\mathrm{A}}\right)$ <br> ii) Variable volume system $\frac{c_{\mathrm{A}}}{c_{\mathrm{AO}}}=\frac{\left(1-x_{\mathrm{A}}\right)}{\left(1+\varepsilon_{\mathrm{A}} x_{\mathrm{A}}\right)}$ | 2 |

