MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION

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SUMMER-19 EXAMINATION Model Answer

Subject title: Chemical Reaction Engineering

Subject code

17562

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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.





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Q No.		Answer	Marking
			scheme
1	a	Attempt any THREE of the following	12
1a	i	Factors affecting the rate of a chemical reaction :	1 mark each
		1. In homogeneous system temperature, pressure and composition are the	for any four
		variables.	factors.
		2. In heterogeneous system, since more than one phase is involved, material	
		have to move from phase to phase during reaction, hence the rate of mass	
		transfer is important.	
		3. rate of heat transfer	
		4. Catalyst	
		5. Nature of reactants	
		6. Surface area available.	
		7. Intensity of light if reaction is light sensitive.	
1a	ii	Definition:	1 mark each
		1) Internal energy (U): It is the energy stored in the system by virtue of the	
		configuration and motion of the molecules constituting the system.	
		2) Gibb's free energy:	
		Gibb's free energy is the energy actually available to do useful work. It	
		predicts the feasibility and equilibrium conditions for chemical reactions at	
		constant temperature and pressure.	
		3) Entropy: Entropy(s) is the measure of the total disorder or randomness of	
		the system or it is a measure of the unavailable energy to perform useful work.	
		4) Fugacity: It is a kind of fictitious pressure used for real gases.ie it is a	
		measure of pressure for real gases.	

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1a	iii	Space time:	
		It is the time required to process one reactor volume of feed measured at	1
		specified condition.	
		$\tau = \frac{1}{s} = \frac{C_{A0V}}{F_{A0}}$	
		Unit	
		Unit is unit of time (seconds, minute, etc)	1
		Space velocity	
		It is the number of reactor volume of feed at specified conditions which can be	1
		treated in unit time.	1
		$\mathbf{S} = \frac{1}{\tau} = \frac{F_{A0}}{C_{A0V}}$	
		Unit	1
		Unit is $time^{-1}$ ($second^{-1}$, $minute^{-1}$ etc)	
1a	iv	Types of catalyst deactivation:	4
		Poisons are substances present either in the reactants or produced by the	
		reaction which lowers the activity of a catalyst.	
		1. Deactivation by fouling:- Rapid deactivation caused by physically	
		depositing a substance which blocks the active sites of the catalyst.	
		2. Chemical Deactivation - Poisoning by reversible or irreversible	
		chemisorption of substances on the active sites of the catalyst.	
		3. Deactivation by Thermal Degradation and Sintering: Deactivation caused	
		by a change in the surface structure of the catalyst due to prolonged exposure	
		of the catalyst to high temperature for a long time.	
1	b	Attempt any ONE of the following	06
1b	i	General procedure for analysis of complete rate equation by integral	1 mark for
		method	each point



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The pr	ocedure for integral method of analysi	s is as follows :			
1.	In a constant volume system, the rate	e expression for the disap	pearance		
	of reactant A will be of the following	form			
	$-\mathbf{r}_{\mathrm{A}} = -\mathrm{d}\mathbf{C}_{\mathrm{A}} / \mathrm{d}\mathbf{t} = \mathrm{k}\mathbf{f}(\mathbf{c})$				
2.	Rate equation is rearranged as $-dC_A$	f(c) = kdt			
	f(c) involves the concentration of ma	terials which may be exp	ressed in		
	terms of C _A				
3.	Above equation is integrated with app	propriate limits			
	C _A t				
	$-\int (dC_A / f(c)) = k \int dt$				
	C _{A0} 0				
4.	The concentration function is prop	portional to time, so a	plot of		
	concentration vs time gives a straigh	t line of slope k for this p	oarticular		
	rate equation.				
5.	From experiment, determine the num	erical value for the above	e integral		
	and plot these at the corresponding tin	ne.			
6.	If the data fall on a reasonable strai	ght line, then it may say	that the		
	particular rate equation being tested	satisfactorily fits the da	ta. If the		
	data are being fitted by a curve, the	rate equation and mecha	nism are		
	rejected and another rate equation is t	ried.			
Graph:					



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		5 Jos K		
1b	ii	$T_1 = 400 \text{ K}$		
		$T_2 = 500K$		
		$k_2 = 10 k_1$		
		From Arrhenius law		
		$\ln \frac{k_2}{k_1} = \frac{-E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$		2
		$\ln 10 = (-E / 1.987) * (\frac{1}{500} - \frac{1}{400}) = 2.52 * 10^{-4}E$		2
		E = 9137.2 cal		2
2		Attempt any TWO of the following		16
2	a	Arrhenius law		
		The temperature dependence of the reaction rate constant k, is give	en by	
		k αe_{RT}^{-E}		
		$\mathbf{k} = \mathbf{k}_0 \boldsymbol{e}_{RT}^{-E}$		4
		Where k_0 - frequency factor or pre exponential factor		
		E - activation energy in J/ mol or cal/ mol		
		R – universal gas constant		
		T – temperature in Kelvin		
		The activation energy is determined experimentally by carrying ou	it the	



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		$t = CAO \int_0^{X_A} \frac{dX_A}{\text{k. CA0 (1 - XA)}}$	
		$-\ln(1 - X_A) = kt$	2
		$-\ln(1-0.70) = k * 13$	
		$k = 0.0926 \text{ min}^{-1}$	
		For Plug flow reactor (constant –density system):	
		$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{\tau}{c_{A0}}$ $\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{\tau}{c_{A0}}$	
		$\tau = \int_{0}^{X_{A}} \frac{dX_{A}}{k \cdot (1 - X_{A})}$	2
		Space time $\tau = \frac{1}{k}(-\ln(1-X_A)) = \frac{1}{0.0926}(-\ln(1-0.7)) = 13 \text{ min.}$ Space velocity = s = 1/ τ = 1/13 = 0.07692 min ⁻¹	1
		For MFR	
		$\frac{V}{F_{A0}} = = \frac{\tau}{C_{A0}} = \frac{X_A}{-r_A}$	
		Space time $\tau = C_{AO} \frac{X_A}{-r_A} = C_{AO} \frac{X_A}{kC_{AO}(1-X_A)} = \frac{X_A}{K(1-X_A)}$ $\frac{0.7}{0.0926(1-0.7)} = 25.2 \text{min}$	2
		Space velocity $s = 1/\tau = 0.039 \text{ min}^{-1}$	1
2	c	Diagram of	
		Fluidized bed reactor	



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Subject title: Chemical Reaction Engineering Subject code 17562 Page 8 of 23 2 marks for diagram and Product 2 marks for gas out Regenerator (operating as a fluidised bed) labeling Fluidised bed Regen rated catalyst returned to the bed) Reactant gas in. Hydraulic lift Regenerator gas Multitubular fixed bed reactor: Product gas 2 marks for diagram and 2 marks for Coolant out labeling Tubes packed with catalyst Coolant in Reactant gas in 3 Attempt any FOUR of the following 16 **Characteristics of chemical equilibrium:** 1 mark each 3 a (i). It is the state when the rate of forward reaction is equal to the rate of for any 4

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		backward reaction.				
		(ii) At cl	hemical equilibrium, the net change i	n the concentration of reactants		
		and products will be zero.				
		(iii)Catal	lysts have no effect on the equilibrium	point.		
		(iv Cha	nges in the concentrations of eith	er the products or reactants,		
		temperature, volume, or pressure can offset the equilibrium point.				
		(v)The equilibrium state can only be reached if the chemical reaction takes				
		place in a closed system.				
3	b	Differen	ce between order and molecularity of	of reaction.(4 points)	1 mark each	
		Sr.No.	Molecularity	Order of reaction	for any 4	
		1	Molecularity is the number of	Order of reaction is the sum	points	
			molecules, atoms or ions in a	of exponents of the		
			chemical reaction.	concentration terms		
				involved in the rate		
				equation.		
		2	Molecularity always have an	Order of reaction can have a		
			integer value 1,2,3	fractional value.		
		3	Shows the elementary mechanism	Shows the kinetic		
			or separate steps of a complicated	dependence of the rate on		
			process	the concentration of the		
				reactants.		
		4	Depending upon the value of	Depending upon the value		
			molecularity, reaction can be	of order, the reactions are		
				termed as first order, second		



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	unimolecular ,bimolecular etc.	order reactions		
	5 Molecularity is a theoretical quantity	Order of reaction is en an experimental value	tirely	
3 c	Relation between C _A & C _{A0}			
	Consider the reaction $A \rightarrow R$			
	Let			
	N_{A0} represent the number of moles of A pre-	esent initially $(t = 0)$.		
	N_A represent the number of moles of A pres	sent at time t.		
	X_A be the fractional conversion of A at times the transformed terms of A at the transformation of	ne t		2
	Moles of A reacted at any time $t = N_{A0} X_A$			
	At time t, moles of A present $N_A = N_{A0}$ -	N _{A0} X _A		
	Divide throughout by V, $(N_A / V) = (N_{A0})$	/ V) - $(N_{A0} X_A / V)$		
	But concentration = moles $/ 1$			
	Therefore $C_A = C_{A0}$	$- C_{A0} X_A;$		2
	$\mathbf{C}_{\mathbf{A}} = \mathbf{C}_{\mathbf{A}0} \left(1 \cdot \mathbf{X}_{\mathbf{A}} \right)$			
3 d	Batch reaction/reactor:			
	Advantages :			
	1.Simple in construction & operation			
	2. Low equipment cost			
	3. Gives highest conversion by leaving t	he reactants for longer pe	riods in	¹∕₂ mark
	reactor.			each
	4. Requires small instrumentation & less su	pporting equipment.		
	Disadvantages:			

Page 11 of 23 ¹ ⁄2 mark each
¹ ∕2 mark each
each
1 mark each
for any 4
points
e
1
f
12
4
).



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	$C_{A0} X_A = kt \text{ for } t < \frac{C_{A0}}{k}$	
	XA XA CAO IX	
4a ii	Rate of a reaction: It is defined as change in the moles of any reactant /	1
	product of the reaction per unit time per unit volume of reacting fluid.	
	Rate constant : Rate constant of a chemical reaction is a measure of the rate of	1
	the reaction when all the reactants are at unit concentration.	
	Unit of rate constant for	
	First order reaction	
	General equation for unit of rate constant is time ⁻¹ (concentration) ¹⁻ⁿ	
	Assume that concentration is given in mole/ liter and time in seconds	
	For first order reaction n=1	
	Therefore unit of rate constant is minute ⁻¹	1
	Second order reaction:	
	For second order reaction n=2	
	Therefore unit of rate constant is minute ⁻¹ (mole/liter) ⁻¹ = liter/(mole*minute)	1
4a iii	Derivation for entropy change of an ideal gas for a constant volume	
	process.:	

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	From first law of thermodynamics, $dU = dQ - dW$	
	$dQ = dU + dW \dots(i)$	
	But $dQ = TdS$ (ii)	
	dW = PdV(iii)	
	For ideal gas $dU = n C_v dT$ (iv)	
	Substituting ii,iii and iv in i	
	$TdS = n C_v dT + PdV$	
	$dS = \frac{n CvdT}{T} + \frac{PdV}{T}$	2
	For ideal gas $P = \frac{nRT}{V}$	
	Substituting dS = $\frac{n CvdT}{T} + \frac{nRdV}{V}$	
	Integrating between limits	
	$\int_{S_1}^{S_2} dS = nC_v \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$	
	$\Delta S = nC_{v} \ln \frac{T_{2}}{T_{1}} + nR \ln \frac{V_{2}}{V_{1}} \dots \dots (v)$	
	For constant volume process , $v_1 = v_2$ and the equation becomes	
	$\Delta \mathbf{S} = \mathbf{n} \mathbf{C}_{\mathbf{v}} \ln \frac{T_2}{T_1}$	2
4a iv	1. Catalyst:	
	Any substance which alters the speed of a chemical reaction without itself	1 mark each
	undergoing any chemical change is known as catalyst.	
	2.Promoters	
	They are substances which do not act as catalyst but enhances the efficiency	
	and life of the catalyst. It is a substance added during the preparation of a	
	catalyst which improves the activity or selectivity or stabilizes the catalytic	
	agent so as to increase its life.	

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Subject title: Chemical Reaction Engineering Subject code 17562 Page 14 of 23 **3.Inhibitors** It is the substance which decreases the performance of the catalyst. It lessens activity, stability or selectivity of a catalyst. It is useful for reducing the activity of a catalyst for an undesirable side reaction. **3.**Catalyst poison They are substances present either in the reactants or produced by the reaction which lowers the activity of the catalyst. **4**b Attempt any ONE of the following **06** For first order reaction, $-\ln(1-x_A) = kt$ 4b i When $x_A = 0.5$ - $\ln(1-0.5) = kt_1$ $t_1 = \frac{0.693}{k} - (1)$ 3 When $x_A = 0.75$ - $\ln(1-0.75) = kt_2$ $t_2 = \frac{1.386}{k} - (2)$ From equation (1) and (2) $t_2 = 2 t_1$ 3 Therefore the time required for 75% conversion is double the time required for 50% conversion. Relation between Gibb's free energy (ΔG^0) and equilibrium constant K_p 4b ii Consider the reaction $aA + bB \rightarrow rR + sS$ ΔG reaction = ΔG product - ΔG reactant. 2 = $(r \mu_R + s \mu_S) - (a \mu_A + b \mu_B)$. At equilibrium there is no Gibb's free energy change, $\Delta G = 0$ $(r \mu_R + s \mu_S) - (a \mu_A + b \mu_B) = 0$ $(r \mu_R + s \mu_S) = (a \mu_A + b \mu_B)$ But $\mu_i = \mu_i^0 + RT \ln p_i$ Therefore $r(\mu_R^0 + RT \ln p_R) + s(\mu_S^0 + RT \ln p_S) = a(\mu_A^0 + RT \ln p_A) + c(\mu_B^0 +$

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		b($\mu_B^0 + RT \ln p_B$)	2
		RT ln $\left(\frac{p_R^r}{p_A^p}\frac{p_S^s}{p_B^p}\right) = (a \mu_A^0 + b \mu_B^0) - (r \mu_R^0 + s \mu_S^0)$	
		= - (ΔG product - ΔG reactant)	
		$= -\Delta G$ reaction.	
		$\ln\left(\frac{p_R^r}{p_A^r}\frac{p_S^s}{p_B^s}\right) = \frac{-\Delta G \text{ reaction}}{RT} \qquad \text{But}\left(\frac{p_R^r}{p_A^r}\frac{p_S^s}{p_B^s}\right) = K_p$	
		Therefore $\Delta G = -RT \ln K_p$	2
5	I	Attempt any TWO of the following	16
5	a	Performance equation of ideal batch reactor:	
		In batch reactor, the composition is uniform throughout reaction zone at any	
		instant of time.	
		Taking material balance of the limiting reactant A over the whole reactor	
		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.	
		In a batch reactor, no fluid enters or leaves the reaction mixture during the	
		reaction. Therefore Rate of reactant A in = Rate of reactant A out = 0	1
		Material balance equation then becomes	
		Rate of loss of reactant A due to chemical reaction = - Rate of accumulation	
		of reactant A within the reactor(1)	
		Rate of loss of reactant A due to chemical reaction = $-r_A V$	3
		Rate of accumulation of reactant A within the reactor $= \frac{dN_A}{dt} = -N_{A0}\frac{dX_A}{dt}$	
		Substituting in equation (1)	
		$-\mathbf{r}_{\mathrm{A}}\mathbf{V} = \mathbf{N}_{\mathrm{A}0}\frac{dX_{\mathrm{A}}}{dt}$	
		Rearranging and integrating	

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			-
		$\int_{0}^{t} dt = N_{A0} \int_{0}^{x_A} \frac{dx_A}{v(-r_A)}$ t = $N_{A0} \int_{0}^{x_A} \frac{dx_A}{v(-r_A)}$ (2) Equation (2) is the design equation for batch reactor, which indicates the time needed to achieve a conversion X_A . For either isothermal or non-isothermal operation, the terms rate $-r_A$ & volume V are retained under the integral sign because they both may change as the reaction proceeds. The set of the set of	2
5	h	Integrated Rate Equation For second order reaction	
5		Integrated Nate Equation For Second Order reaction.	
		(i) Definition: When the rate of reaction is directly proportional to the square	2
		of concentration of one reactant, it is called as second order reaction.	۷.
		(ii) Expression:	
		$2A \rightarrow \text{product}$	
		In terms of concentration	
		Rate equation is $-r_A = -d_{CA}/dt = kC_A^2$	
		Rearranging $-d_{CA}/C_{A}^{2}=kdt$	

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		(iv) Example:Saponification of an ester	
		$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$	2
5	c	Types of reactors used in industry:	
		Based upon mode of operation, the reactors are classified as	
		1) Batch reactors: Reactants added at beginning into reactor, left to react for	
		certain time & products are withdrawn at a subsequent time.	3
		2) Continuous reactors: Feeding of reactants, chemical reaction & removal of	
		product occur simultaneously,	
		3) Semi batch reactor: One of the reactant added initially& the other is	
		continuously added to a reactor over a certain time under agitation.	
		Reactors like packed bed reactors, fluidized bed reactors are also used in	
		industry.	
		Application	
		1) Batch reactor (Any one): These are used when relatively small amount of	1 mark
		material are to be treated. Also to produce different products using same	each
		reactor, for testing new products etc.	
		2) Semi batch reactors (Any one): When good control of reaction is required,	
		also used for liquid phase reactions & 2-phase reactions where gas is	
		continuously bubbled through the pool of liquid in reactor.	
		3) Continuous reactors(Any one): Used for higher production rates with	
		short reaction times, for producing high quality products, for carrying out	
		reactions when rate of reaction is high.	
		4) Packed (fixed) bed reactor: Used when high conversion rate per catalyst	
		weight is required.	
		5) Fluidized bed reactor (Any one): Used when good temperature control is	



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			stoichiometric			
			coefficient of that			
			species.			
		4	For these reactions,	Order may be an integer or fractional		
			order must be an	value.		
			integer			
		5	If $2A \rightarrow R$, the rate law	For non-elementary reaction		
			is $-r_A = kC_A^2$	$2B \rightarrow S$, the rate law may be		
				$-r_{\rm B} = {\rm k}C_{\rm B}^{\alpha}$		
				Where $\propto \neq 2$		
		6	Fx CaHaOH +	Fy $H_2 + Br_2 \rightarrow 2HBr$		
			$CH_2COOH \rightarrow$			
			$CH_2COOC_2H_5 + H_2O$			
6	C	Method	s of catalyst Prenaration	•		
0	C	1 Preci	nitation	•		
		2 Gel	formation			2
		3. Simr	ble mixing			-
		4. Impre	egnation method			
		1.Preci	pitation method :			
		This me	thod produces catalyst in p	oorous form.It consists of adding a		
		precipit	ating agent to the solution	of the desired component. The precipita	tion	2
		is followed by washing, drying, calcinations & activation (or pretreatment)				_
		Eg. Magnesium oxide catalyst is prepared by this method. It is prepared by				
		precipitating MgCO ₃ from magnesium nitrate solution by adding sodium				
		carbona	te.The magnesium carbona	te precipitate is washed, dried & calcine	ed to	





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		obtain magnesium oxide.		
6	d	Definition:	1 mark each	
		(i)Thermodynamics: It is the branch of science which deals with all forms of		
		energy and the inter conversion of the different forms of energy. OR		
		It is the branch of science which deals with the relations between heat and		
		other forms of energy accompanying physical and chemical processes.		
		(ii)Enthalpy: It is a measure of the total heat content of the system OR It is		
		the total energy possessed by the system .It is the sum of the internal energy		
		and the flow energy.		
		(iii) Chemical Potential: It is defined as the change in free energy of a		
		substance when one mole of it is added to such a large quantity of the system		
		that there is no appreciable change in overall composition of the system at		
		constant temperature & pressure		
		(iv) Chemical Kinetics:		
		It is the study of the rates at which chemical reactions occur and effect of		
		parameters like temperature, pressure and concentrations of reactant on the		
		rate of reaction.		
6	e	Relation between Kp and K _c (Derivation)		
		Consider the reaction $aA + bB + \dots \rightarrow rR + sS \dots$		
		$K_{c} = (C_{R}^{r} \cdot C_{S}^{s}) / (C_{A}^{a} \cdot C_{B}^{b})$		
		For ideal gas $C_i = p_i / RT$		
		Where R is the ideal gas constant	2	
		T the absolute temperature in K		
		P is the pressure in atm		
		Therefore $K_c = \{(p_R / RT)^r . (p_S / RT)^s\} / \{(p_A / RT)^a . (p_B / RT)^b\}$		

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		$= (p_{R}^{r} . p_{S}^{s}) / (p_{A}^{a} . p_{B}^{b}) . (1 / RT)^{(r+s+(a+b=))}$	
		Ie $K_c = K_p$. $(1 / RT)^{\Delta n}$ where $K_p = (p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b)$	
		And $\Delta n = (r + s + (a + b +))$ is the difference in the number of moles of	
		product and reactant	2
		Or $\mathbf{K}_{\mathbf{p}} = \mathbf{K}_{\mathbf{c}} \times (\mathbf{RT}) \Delta^{\mathbf{n}}$	
6	f	Types of intermediates in non- chain reaction: 1. Free radicals. Free atoms or larger fragments of stable molecules which	1 mark each
		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. $C\dot{H}_3$	
		$C_2\dot{H_5}$	
		2. Ions and polar substances. Electrically charged atoms, molecules or	
		fragments of molecules such as Na^+ , OH^- , $NH4^+$ are called ions. They may	
		act as intermediates in reaction.	
		3. Molecules: Consider the consecutive reaction	
		$A \rightarrow R \rightarrow S$	
		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.	
		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.	