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[Time : 3 Hours

[Total Marks : 100

Please check whether you have got the right question paper.

N.B. : 1. All Questions are compulsory.

2. Figures to the right indicate full marks.

3. Use of log-table/nonprogrammable calculator is allowed.

4. Answers for the same question as far as possible should be written together.

1.	(A)	Select the correct option and complete the following sentences. (any twelve)		12
	(i)	Homogeneous		
	(ii)	Ideal solution		
	(iii)	Negative slope		
	(iv)	Initiation		
	(v)	Parallel		
	(vi)	Critical solution temperature		
	(vii)	4		
	(viii)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$		
	(ix)	Tetrahedral		
	(x)	Silicon occurs in free state in nature.		
	(xi)	Decreases		
	(xii)	+1		
	(xiii)	no $\alpha$ -H atom		
	(xiv)	$\text{sp}^2$ - $\text{sp}^2$		
	(xv)	$\text{CH}_3\text{COCl}$		
	(xvi)	$>\text{C}=\text{C}-\text{N}<$		
	(xvii)	no $\alpha$ -H atom		
	(xviii)	Acetaldehyde		
	(B)	State whether the following statements are true or false. (any three)		3
	(i)	False		
	(ii)	False		
	(iii)	True		
	(iv)	True		
	(v)	True		
	(vi)	False		
	(C)	Match the column. (any five)		5
	(i)	Temperature coefficient	(c)	$\frac{k_{(T+10)}}{k_T}$

	(ii)	Raoult's law	(e)	$x_2 = \frac{p^0 - p}{p^0}$
	(iii)	NH <sub>3</sub>	(c)	Tetrahedral
	(iv)	Nitric oxide	(d)	Odd electron molecule
	(v)	Acetal	(f)	$\begin{array}{c} \text{OC}_2\text{H}_5 \\   \\ \text{CH}_3\text{-C} \\   \\ \text{H} \\   \\ \text{OC}_2\text{H}_5 \end{array}$
	(vi)	Diethyl malonate	(d)	H <sub>3</sub> C <sub>2</sub> OOC-CH <sub>2</sub> -COOC <sub>2</sub> H <sub>5</sub>
2. Attempt any four of the following. <span style="float: right;">20</span>				
(A)	<p>Nernst distribution law states that when a solute X distributes itself between two immiscible solvents A and B at equilibrium at a constant temperature and X is in the same molecular condition in both the solvents, then the ratio concentration of X in the two solvents is constant.</p> $K = \frac{C_1}{C_2}$ <p>Applications-</p> <ol style="list-style-type: none"> <li>Solvent extraction</li> <li>Investigation of association, dissociation, or complex formation of solute molecules.</li> <li>Liquid-liquid chromatography</li> <li>Determination of equilibrium constant</li> <li>Confirmatory test for halide ions.</li> </ol>			
(B)	<p>Raoult's law states that the vapour pressure of any solvent is equal to its mole fraction in the solution <math>X_A</math> multiplied by the vapour pressure <math>P_A^0</math> of the pure solvent. <math>P_A = X_A P_A^0</math></p> <p>Diagram and explanation of positive and negative deviations.</p>			
(C)	<p><math>P_{\text{Benzene}} = 0.40</math>  <math>P_{\text{toluene}} = 1.0 - 0.40 = 0.60</math>.</p> <p>Partial pressure of Benzene, <math>P_A = X_A P_A^0</math></p> <p>(i) <math>P_{\text{Benzene}} = 2.453 \times 10^4 \text{ Nm}^{-1} \times 0.40 = 9.812 \times 10^3 \text{ N m}^{-1}</math></p> <p><math>P_{\text{toluene}} = 7.864 \times 10^3 \text{ Nm}^{-1} \times 0.60 = 4.718 \times 10^3 \text{ N m}^{-1}</math></p> <p>(ii) <math>P_{\text{total}} = 9.812 \times 10^3 \text{ N m}^{-1} + 4.718 \times 10^3 \text{ N m}^{-1} = 14.530 \text{ N m}^{-1}</math></p> <p>(iii) Mole fraction of benzene in the vapour above the solution:</p> $p_{\text{benzene}} = x'_{\text{A}} \cdot P_{\text{total}}$ $x'_{\text{benzene}} = \frac{p_{\text{benzene}}}{P_{\text{total}}} = \frac{9.812 \times 10^3 \text{ N m}^{-1}}{14.530 \times 10^3 \text{ N m}^{-1}} = 0.675$			

(D)	<p><b>Collision theory:</b> The assumptions of collision theory are :-</p> <ol style="list-style-type: none"> <li>Molecules are treated as rigid spheres which describe only translational motion.</li> <li>For a reaction to take place molecules should collide each other.</li> <li>During collision only exchange of energy takes place. No gain or loss of energy. I.e, elastic collision.</li> <li>Only those molecules which possess a certain minimum energy will react on collision. Such collisions are effective collision and the energy, activation energy.</li> </ol> <p><b>Drawbacks:</b></p> <ol style="list-style-type: none"> <li>Collision theory fails in reactions involving large complex molecules.</li> <li>It cannot give a quantitative interpretation of the rate of unimolecular reactions.</li> <li>Only effective collisions which can raise the reactant molecules to activation energy level can form product.</li> </ol>	
(E)	<p>i. The minimum energy that the reactant molecules must acquire to undergo chemical reaction and form product is called energy of activation.</p> <p><b>Method 1.</b> The chemical reaction is carried out at different temperatures and the corresponding rate constants are determined. A graph of <math>\log k</math> against <math>1/T</math> is plotted. <math>E_a</math> is evaluated from the slope of the straight line plot. <math>E_a = \text{slope} \cdot 2.303R</math>.</p> <p><b>Method II</b></p> <p>The chemical reaction is carried out at two temperatures <math>T_1</math> and <math>T_2</math>. the rate constants <math>k_1</math> and <math>k_2</math> are determined. <math>\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]</math>      <math>E_a = \frac{2.303RT_1T_2 \log \frac{k_2}{k_1}}{T_2 - T_1}</math></p>	
(F)	$E_a = \frac{2.303RT_1T_2 \log \frac{k_2}{k_1}}{T_2 - T_1} = \frac{2.303 \times 8.314 \times 289 \times 333 \times \log \frac{6.71}{5.0320} \times 10^{-2}}{333 - 289} = 88.757 \times 10^3 \text{ J mol}^{-1}$	
3.	Attempt any <b>four</b> of the following.	
(A)	<p>Among <math>\text{BF}_3</math> &amp; <math>\text{BCl}_3</math> who is strong lewis acid? Explain.</p> <p><b>Ans.:-</b></p> <ul style="list-style-type: none"> <li><math>\text{BCl}_3</math> is strong lewis acid - <b>1M</b></li> <li>Explanation - Boron trihalide act as lewis acid as they have <math>6e^-</math>s in the valence shell of Boron atom. To complete octate they readily accept <math>2e^-</math>s. -<b>2M</b></li> <li>As with the decrease in electron density on boron atom from <math>\text{BI}_3</math>, the tendency of boron to accept <math>e^-</math> pair donated by lewis base increase. - <b>2M</b></li> </ul>	20
(B)	<p>Draw structure of tetraborane? How many terminal and bridge bonds are in its structure? Calculate the total no. of <math>e^-</math>s involved in it.</p> <p><b>Ans.:-</b></p> <ul style="list-style-type: none"> <li>structure of tetraborane - <b>2M</b></li> <li>6 terminal B-H bonds - <b>1M</b></li> <li>4 bridge B-H-B bonds - <b>1M</b></li> <li>6 terminal B-H bonds - <math>6 \times 2 = 12 e^-</math>s</li> <li>1 B-B bond - <math>1 \times 2 = 2 e^-</math>s</li> <li>4 bridge B-H-B bonds - <math>4 \times 2 = 8 e^-</math>s</li> </ul> <p style="text-align: center;"><b>22 <math>e^-</math>s - 1M</b></p>	

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(C)	What is silica? Why is it inert? Ans.:- <ul style="list-style-type: none"><li>• Silica is silicon dioxide – <math>\text{SiO}_2</math> - 1M</li><li>• In <math>\text{SiO}_2</math> structure all bonds are <math>\sigma</math> covalent bonds. <math>\pi</math> bonds are absent in the structure as 3p orbital of silicon atom and 2p orbital of oxygen atom have appreciable difference in their energy. - 2½M</li><li>• The giant structure of <math>\text{SiO}_2</math> is very stable and great amount of energy is required to break Si-O bonds hence it is inert. - 1½M</li></ul>	
(D)	Explain Zone refining technique for purification of germanium. Ans.:- <ul style="list-style-type: none"><li>• Diagram - 2½M</li><li>• Technique - 2½M</li></ul>	
(E)	Find O.S. of nitrogen in $\text{N}_2\text{O}$ and $\text{N}_2\text{O}_5$ and explain their structures. Ans.:- <ul style="list-style-type: none"><li>• Formula O.S. of Nitrogen <math>\text{N}_2\text{O}</math> +1 - 1M <math>\text{N}_2\text{O}_5</math> +5 - 1M</li><li>• Structure :- <math>\text{N}_2\text{O}</math> – linear, its structure can be represented as a resonance hybrid.</li><li>• Resonance hybrid structure - 1½M</li><li>• Structure of <math>\text{N}_2\text{O}_5</math> - 1½M</li></ul>	
(F)	Explain synthesis of ammonia by Bosch-Haber process. Ans.:- <ul style="list-style-type: none"><li>• Reaction- <math>\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3</math> - 1M</li><li>• Name of catalyst - 1M</li><li>• Synthesis - 3M</li></ul>	
4.	Attempt any four of the following.	
(A)	i) Benzyl alcohol ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ) on treatment with PCC (Pyridinium Chlorochromate) in presence of $\text{CH}_2\text{Cl}_2$ gives Benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ )- chemical equation- 1½ M 1-Phenylethanol ( $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ ) on treatment with PCC (Pyridinium Chlorochromate) in presence of $\text{CH}_2\text{Cl}_2$ gives Acetophenone ( $\text{C}_6\text{H}_5\text{COCH}_3$ )- chemical equation- 1½ M ii) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CHO}$ (3-phenyl-2-propenal) ↓ i) $\text{LiAlH}_4$ , dry ether, ii) $\text{H}_2\text{O}$ , $\text{HCl}$ $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ (3-phenyl-1-propanol) When a phenyl group is attached to $\beta$ -C-atom of $\alpha,\beta$ -unsaturated aldehyde, then $\text{LiAlH}_4$ reduces the $\text{C}=\text{C}$ bond also. - 2 M	20
(B)	i) a) Protonation - Discussion and Chemical equation - 1½ M b) Nucleophilic addition - Discussion and Chemical equation - 1½ M ii) Grignard reagent ( $\text{R}-\text{Mg}-\text{X}$ ) reacts with formaldehyde ( $\text{CH}_2=\text{O}$ ) in presence of dry ether gives addition product ( $\text{R}-\text{CH}_2-\text{O}-\text{Mg}-\text{X}$ ) which on further hydrolysis in presence of acid gives primary alcohol ( $\text{R}-\text{CH}_2-\text{OH}$ )- Chemical equation- 2M	

(C)	<p>i) 2-butanone from acetyl acetone-Synthesis- <span style="float: right;">2½M</span>  <math>\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3</math> to <math>\text{CH}_3\text{-CO-CH(Na)-CO-CH}_3</math>  <math>\text{CH}_3\text{-CO-CH(Na)-CO-CH}_3</math> to <math>\text{CH}_3\text{-CO-CH(CH}_3\text{)-CO-CH}_3</math> (using <math>\text{CH}_3\text{Cl}</math>)  <math>\text{CH}_3\text{-CO-CH(CH}_3\text{)-CO-CH}_3</math> to <math>\text{CH}_3\text{-CO-CH}_2\text{-CH}_3</math>            (i) conc. <math>\text{KOH}</math> (1 mole), ii) <math>\text{HCl}</math>)</p> <p>ii) succinic acid from ethyl acetoacetate- Synthesis- <span style="float: right;">2½M</span>  <math>\text{CH}_3\text{-CO-CH}_2\text{-COOC}_2\text{H}_5</math> to <math>\text{CH}_3\text{-CO-CH(Na)-COOC}_2\text{H}_5</math>  <math>\text{CH}_3\text{-CO-CH(Na)-COOC}_2\text{H}_5</math> to <math>\text{CH}_3\text{-CO-CH(CH}_2\text{COOC}_2\text{H}_5\text{)-COOC}_2\text{H}_5</math>            (using <math>\text{Cl-CH}_2\text{-COOC}_2\text{H}_5</math>)  <math>\text{CH}_3\text{-CO-CH(CH}_2\text{COOC}_2\text{H}_5\text{)-COOC}_2\text{H}_5</math> to <math>(\text{CH}_2\text{COOCH})_2</math>            (i) conc. <math>\text{KOH}</math>, ii) <math>\text{HCl}</math>)</p>	
(D)	<p>i) Rosenmund reduction:-            Defination / Explanation- <span style="float: right;">1M</span>            Any one example - <span style="float: right;">1M</span>            Role of <math>\text{BaSO}_4</math> - <span style="float: right;">1M</span></p> <p>ii) i) Benzaldehyde cynohydrin:  <math>\text{C}_6\text{H}_5\text{CHO} + \text{HCN} \rightarrow \text{C}_6\text{H}_5\text{CH(OH)CN}</math> - <span style="float: right;">1M</span></p> <p>ii) Benzaldehyde phenyl hydrazine  <math display="block">\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{-NH-NH}_2 \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{CH=N-NH-C}_6\text{H}_5</math> <span style="float: right;">1M</span></p>	
(E)	<p>i) Mechanism of base catalyzed enolisation:-            Step 1:- Removal of proton from <math>\alpha</math>- C-atom of carbonyl compound to give carbanion in presence of a base- reaction- <span style="float: right;">1½M</span>            Step 2:- Transfer of proton to 'O' of the enolate ion by the conjugate base - reaction- <span style="float: right;">1½M</span></p> <p>ii) reduction of 2-butenal by using <math>\text{NaBH}_4</math>:- <span style="float: right;">2M</span>  <math>\text{CH}_3\text{-CH=CH-CHO} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}</math> (i) <math>\text{NaBH}_4</math>, <math>\text{CH}_3\text{OH}</math>, ii) <math>\text{H}_2\text{O}</math>, <math>\Delta</math>)  <math>\text{NaBH}_4</math> is less reactive, reduces <math>\text{C=O}</math> of aldehyde, does not reduce <math>\text{C=C}</math> in alkene</p>	
(F)	<p>Mechanism of Claisen-Schmidt reaction:- <span style="float: right;">5M</span>            Step 1:- Formation of carbanion, Step 2:- Nucleophilic addition of carbanion,            Step 3:- proton abstraction            All three steps with chemical equations.</p>	
5.	Attempt any four of the following.	20
(A)	<p>A reaction in which a series of steps involving reactive intermediates is called chain reaction. The steps involved are ,</p> <p>i) Chain initiation – reactive intermediates like ions and free radicals are formed.</p> $\text{Br}_2 \xrightarrow{k_1} 2 \text{ Br atoms}$ <p>ii) Chain propagation- <math>\text{Br} + \text{H}_2 \xrightarrow{k_2} \text{HBr} + \text{H atom}</math>  <math>\text{H} + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br atoms}</math></p>	

	ii) Chain inhibition - $H + HBr \xrightarrow{k_4} H_2 + Br$ atom iii) Chain termination - $Br + Br \xrightarrow{k_5} Br_2$	
(B)	$\log_{10} \frac{n^*}{n} = \frac{-E_a}{20303 \times R \times T}$ <p> <math>T = 560 \text{ K}</math>  <math>n = 5 \times 10^{30} \text{ cm}^{-3} \text{ s}^{-1}</math>  <math>R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}</math>  <math>E_a = 1.76 \times 10^5 \text{ J mol}^{-1}</math>            Therefore <math>\log_{10}(n^*)/(5 \times 10^{30}) = \frac{-1.76 \times 10^5}{20303 \times 8.314 \times 560}</math> </p> <p>The number of XY molecules, <math>n^* = 1.945 \times 10^{14} \text{ cm}^{-3} \text{ s}^{-1}</math></p>	
(C)	<p>Formation of trihalides &amp; pentahalides of nitrogen family.</p> <p><b>Ans.:-</b></p> <ul style="list-style-type: none"> <li>All the elements of nitrogen family form two series of halides trihalides <math>MX_3</math> and pentahalides <math>MX_5</math>. - ½M</li> <li>Trihalides- 3M</li> <li>The trihalides are mainly covalent with the exception of <math>BiF_3</math>. The ionic character trihalides increases down the group. Like hydrides the trihalides have a pyramidal structure.</li> <li>All the trihalides except <math>NX_3</math> can be easily hydrolysed by water.  <math>MX_3 + H_2O \rightarrow MOCl + HCl</math></li> <li>The inability of nitrogen to hydrolysed is due to the absence of vacant d-orbital in nitrogen.</li> <li>The trihalides of P, As, Sb acts as Lewis acids &amp; combine with Lewis bases.  <math>PF_3 + F_2 \rightarrow PF_5</math></li> <li>Pentahalides- Except nitrogen other elements of this group form pentahalides. Nitrogen can not form pentahalides because it can't expand its covalency due to non-availability of d-orbital in the valency shell. - 1½M</li> </ul>	
(D)	<p>Czochralski technique of Si.</p> <p><b>Ans.:-</b></p> <ul style="list-style-type: none"> <li>Diagram - 2M</li> <li>Description - 3M</li> </ul>	
(E)	<p>i) Gattermann - Koch formylation :-</p> <p>Explanation:- 1M</p> <p>Any one example:- 1M</p> <p><math>CO + HCl \rightarrow + HCOCl</math> (CO first reacts with HCl (gas) to form the intermediate compound HCOCl which react with the Ar-HC to give an Ar-aldehyde.) 1M</p> <p>ii) active methylene compounds:-</p> <p>Compounds in which a methylene group (<math>-CH_2-</math>) is attached to two electron withdrawing groups like <math>&gt; C=O</math>, <math>-C \equiv N</math>, <math>-NO_2</math> etc.</p> <p>Carbon acids:- The <math>-H</math> atoms of the methylene group (<math>-CH_2-</math>) can be removed as protons in presence of a strong base (due to electron withdrawing inductive effect of electron withdrawing groups), hence they behave as C-acids.</p>	

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	<p>(F) Mechanism of Benzoin condensation:- Step 1:- Attack of Nucleophile, cyanide ion, Step 2:- Nucleophilic addition of carbanion, Step 3:- Elimination of cyanide ion. All three steps with chemical equations.</p>	5M
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