

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) Solution is a _____ mixture of two or more non-reacting substances.
(a) homogeneous (b) simple (c) heterogeneous
 - (ii) By fractional distillation constituents of _____ can be separated.
(a) non ideal solution (b) ideal solution (c) any mixture
 - (iii) The plot of $\log k$ versus T^{-1} is linear with a _____ slope.
(a) positive (b) negative (c) zero
 - (iv) In a chain reaction, the reactive intermediates like atoms or free radicals are produced in chain _____ step.
(a) termination (b) inhibition (c) initiation
 - (v) Chlorination of toluene is an example of _____ reaction.
(a) consecutive (b) parallel (c) reversible
 - (vi) The temperature at which two conjugate solutions merge into one another to form a single layer is called _____.
(a) distillation temperature (b) critical solution temperature
(c) evaporation temperature.
 - (vii) In diborane molecule, number of terminal B-H bonds are _____.
(a) 2 (b) 4 (c) 6
 - (viii) Molecular formula of borax is _____.
(a) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (b) $\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (c) $\text{Na}_2\text{B}_4\text{O}_6 \cdot 10\text{H}_2\text{O}$
 - (ix) Silicon tetrachloride has _____ structure.
(a) triangular (b) octahedral (c) tetrahedral
 - (x) _____ is the incorrect statement.
(a) Silicon is extensively used as a semiconductor
(b) Silicon occurs in free state in nature
(c) SiO_2 is inert
 - (xi) Thermal stability of hydrides _____ gradually from NH_3 to BiH_3 .
(a) increases (b) decreases (c) remains same
 - (xii) In nitrous oxide, oxidation state of nitrogen is _____.
(a) +1 (b) +2 (c) +3
 - (xiii) The aldehyde used in the Knoevenagel reaction has _____.
(a) α -H atom (b) α - and β -H atom (c) no α -H atom
 - (xiv) The hybridisation of 'C' and 'O' in the $>\text{C}=\text{O}$ group is _____.
(a) $\text{sp}^3\text{-sp}^3$ (b) $\text{sp}^2\text{-sp}^2$ (c) $\text{sp}^3\text{-sp}^2$

- (xv) Friedel Craft acylation of benzene can be carried out by using _____.
 (a) CH_3COCl (b) CH_3COOH (c) CH_3OCH_3
- (xvi) The general structure of enamine is _____.
 (a) $>\text{C}=\text{C}=\text{N}-$ (b) $>\text{C}=\overset{\text{N}}{\underset{\text{N}}{\text{C}}}-$ (c) $>\text{C}=\overset{\text{N}}{\underset{\text{N}}{\text{C}}}-$
- (xvii) The aldehyde used in the Cannizzaro reaction has _____.
 (a) α -H atom (b) α - and β -H atom (c) no α -H atom
- (xviii) _____ may be prepared by the action of one mole of CH_3MgI on ethyl formate followed by hydrolysis of addition product.
 (a) Methanol (b) Acetaldehyde (c) Isopropyl alcohol

(B) State whether the following statements are true or false. (any **three**)

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- For the study of distribution ratio, the two solvents must be miscible with each other.
- Ideal solutions obey Dalton's law.
- BH_3 does not exist in free form.
- In silicon dioxide each silicon atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms.
- If a compound contains both aldehyde and ketonic group, then the aldehyde is considered as the parent compound.
- Ketones are usually more reactive towards nucleophilic reagent than aldehydes.

(C) Match the column. (any **five**)

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| (i) Temperature coefficient | (a) Odd electron molecule |
| (ii) Raoult's law | (b) Tetrahedral |
| (iii) NH_3 | (c) $\frac{k_{(T+10)}}{k_T}$ |
| (iv) Nitric oxide | (d) $\text{H}_5\text{C}_2\text{OOC}-\text{CH}_2-\text{COOC}_2\text{H}_5$ |
| (v) Acetal | (e) $x_2 = \frac{p^0 - p}{p^0}$ |
| (vi) Diethyl malonate | (f) $\begin{array}{c} \text{OC}_2\text{H}_5 \\ \\ \text{CH}_3-\text{C} \\ \\ \text{H} \\ \\ \text{OC}_2\text{H}_5 \end{array}$ |
| | (g) $K = \frac{C_1}{C_2}$ |
| | (h) Square planar |
| | (i) $\begin{array}{c} \text{CH}_2-\text{COOC}_2\text{H}_5 \\ \\ \text{CH}_2-\text{COOC}_2\text{H}_5 \end{array}$ |

2. Attempt any **four** of the following. **20**
- (A) State and explain Nernst's distribution law. What are its important applications?
- (B) State Raoult's law. With the help of suitable diagrams explain positive and negative deviations from Raoult's law.
- (C) The vapour pressures of pure benzene and toluene at 40°C are $2.453 \times 10^4 \text{ Nm}^{-2}$ and $7.864 \times 10^3 \text{ Nm}^{-2}$ respectively. Mole fraction of benzene in the solution is 0.40. Assume that the solution is an ideal one. Calculate
- the partial pressure of benzene and toluene
 - the total vapour pressure of the solution and
 - the mole fraction of benzene in the vapour above the solution.
- (D) State the important assumptions of the collision theory of reaction rates. What are the drawbacks of this theory?
- (E) What is meant by 'energy of activation' in kinetic studies? How it is determined experimentally?
- (F) For the reaction, $\text{C}_2\text{H}_5\text{I} + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{I}^-$, the rate constants were found to be 5.03×10^{-2} at 289 K and 6.71 at 333K. Calculate the energy of activation for the reaction. [$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]
3. Attempt any **four** of the following. **20**
- (A) Among BF_3 and BCl_3 , who is strong Lewis acid ? Explain.
- (B) Draw a structure of tetraborane. How many terminal and bridge bonds are in its structure ? Calculate total number of electrons involved in it.
- (C) What is silica ? Why is it inert ?
- (D) Explain zone refining technique for the purification of germanium.
- (E) Find oxidation state of nitrogen in N_2O and N_2O_5 and explain their structures.
- (F) Explain synthesis of ammonia by Bosh - Haber process.
4. Attempt any **four** of the following.
- (A) i) Give preparation of benzaldehyde and acetophenone by oxidation of alcohol by using PCC. **3**
- ii) Discuss the reduction of 3-phenyl-2-propenal by using LiAlH_4 . **2**
- (B) i) Explain general mechanism of acid catalyzed nucleophilic addition to carbonyl compound. **3**
- ii) How is primary alcohol obtained from Grignard reagent? **2**
- (C) Give preparation of: **5**
- i) 2-butanone from acetyl acetone
- ii) succinic acid from ethyl acetoacetate.
- (D) i) Write a note on Rosenmund reduction. **3**
- ii) How benzaldehyde cynohydrin and benzaldehyde phenyl hydrazone are obtained from benzaldehyde? **2**
- (E) i) Give the mechanism of base catalyzed enolisation. **3**
- ii) Discuss the reduction of 2-butenal by using NaBH_4 . **2**
- (F) Explain the mechanism of Claisen-Schmidt reaction. **5**

5. Attempt any **four** of the following.

- (A) What are the important steps involved in a chain reaction? Explain the steps involved in the reaction between hydrogen and bromine. **5**
- (B) At 560 K, at a concentration of 1 mol dm^{-3} , the number of XY molecules colliding per cm^3 per second is 5×10^{30} . If the activation energy of the reaction, $2\text{XY} \rightarrow \text{X}_2 + \text{Y}_2$ is $1.76 \times 10^5 \text{ J mol}^{-1}$, calculate the number of XY molecules reacting per cm^3 per second. [$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$] **5**
- (C) Write a note on formation of trihalides and pentahalides of the elements of nitrogen family. **5**
- (D) With suitable diagram, explain Czochralski pulling technique for purification of silicon. **5**
- (E) i) Write a note on Gattermann – Koch formylation. **3**
 ii) What are active methylene compounds? Why are they considered as carbon acids? **2**
- (F) Explain the mechanism of benzoin condensation. **5**

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