

## CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

- Note : 1) Attempt question one and fourteen other questions.  
2) Log table is enclosed.

1. Attempt any three of the following :

- A) Assign structure to the molecule containing nitrogen 6  
Mol. wt. 71 ( $m/z$  71  $M^+$ )  
IR (neat) : 2941 – 2857, 2247, 1460  $cm^{-1}$ .  
UV : no  $\lambda$  max above 200 nm.  
PMR :  $\delta$  4.22 (2H, s); 3.49 (3H, s)
- B) Deduce the structure of the molecule having mol. formula  $C_6H_{10}O$  6  
IR (neat) : 1715  $cm^{-1}$   
PMR :  $\delta$  1.6 (2H, quintet) 1.7 (4H, quintet) 2.25 (4H, triplet)
- C) Metallic iron at room temperature shows six fingered hyperfine structure, while  $FeSO_4 \cdot 7H_2O$  shows quadrupole doublet. Explain the above behaviour. 6
- D) The EPR spectrum of bis-salicylaldimine Cu (II) with isotopically pure  $Cu^{63}$  shows eleven lines as against fifteen lines expected. Comment on this observation. 6
- E) Sketch schematically the normal modes of vibration of  $CO_2$  molecule. Indicate which are active in Infrared and which are Raman active. 6
- F) State and explain the differences between the phenomena of fluorescence and phosphorescence. 6

2. Prepare a table of microstates and obtain term symbols for the ground state of P atom. 13

3. Consider the following variational wave-functions for the particle in a one-dimensional box  $0 \leq x \leq 1$  where A, B, C ..... are parameters. 13

i)  $Ax$

ii)  $B(1-x)$

iii)  $Cx(1-x) + Dx(1-x)^2$

iv)  $Ex(1-x) + Fx(1-x)^2 + Gx^2(1-x)$

v)  $Hx^2 + I(1-x)^2$   $H, I \neq 0$ .

vi)  $Jx(1-x)^2 + Kx^2(1-x)$

Identify the invalid ones from the list. Arrange the valid one in the order of increasing energy.

4. Make qualitative sketches of 13
- a)  $\psi_4$  and  $\psi_4^2$  for one dimensional Harmonic oscillator.
- b)  $\psi_2$  and  $\psi_2^2$  for one dimensional particle in a box.

5. A) Write down briefly and clearly, the assumptions of the Hückel theory. 5

- B) Obtain the eigenvalues for cyclopropenyl radical within Hückel theory.  $\left( \triangle \right)$  8

6. A) Show that the entropy of mixing of two ideal gases, both at the same temperature and pressure, per mole of the mixture is given by

$$\Delta S = -R (X_1 \ln X_1 + X_2 \ln X_2)$$

- B) Estimate the equilibrium constant for the isomerization of n-butane [ $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$ ] to isobutane [ $(\text{CH}_3)_3\text{CH}$ ] at 25°C and 1 atm. pressure from the following data under the same conditions 7

n-butane	:	$\Delta H_{\text{formation}}^0$	=	-124.6 kJ/mole
		$S^0$	=	309.74 J/°K/mole
iso-butane	:	$\Delta H_{\text{formation}}^0$	=	-131.46 kJ/mole
		$S^0$	=	294.35 J/°K/mole

7. A) Assuming the Maxwell Boltzmann distribution law for energy, show that the total energy of one mole of an ideal gas at temperature Y is given by 8

$$E = RT^2 \left[ \frac{\partial \ln Q}{\partial T} \right]_V$$

Where Q is the appropriate partition function

- B) Calculate the rotational partition function for one mole of gaseous  $^{16}\text{O}_2$  at 25° C and 1 atm. pressure.

Given : 5

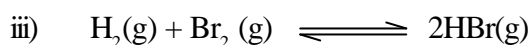
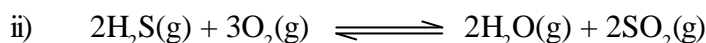
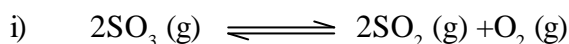
Bond length  $^{16}\text{O}_2$  : 1.21 Å.

8. A) With the help of a schematic diagram show 'vibrational coarse structure' of an electronic absorption band for a diatomic molecule. 7

- B) The electronic absorption spectrum of gaseous  $\text{O}_2$  at room temperature exhibits vibrational structure having the convergence limit at 56876  $\text{cm}^{-1}$ . The oxygen molecule in the corresponding excited state dissociates into one atom in the ground state and the other atom in an excited state with energy 15875  $\text{cm}^{-1}$ . Estimate the dissociation energy (in kJ/mole) of molecular  $\text{O}_2$  in the ground electronic state. 6

9. A) What are the two equilibrium constants  $K_c$  and  $K_p$  ? Derive the relation between the two. Under what condition is  $K_c = K_p$  ? 7

B) Calculate the ratio of  $K_p$  to  $K_c$  at 300 K for the following reactions : 6

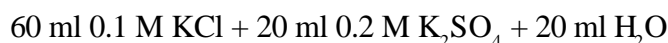


10. A) Write down the Gibbs-Duhem equation. Explain the terms therein. Describe briefly how this equation can be used to evaluate the activity coefficient of urea dissolved in water. 8

B) What is meant by ideal and non-ideal solutions ? Show with the help of neat diagrams the variation of enthalpy-free-energy and entropy of mixing for ideal solutions. What happens for non-ideal solutions? 5

11. A) Define mean ionic activity coefficient. Briefly describe one method of determination of mean ionic activity coefficients of ions in aqueous solutions. 9

B) Calculate the ionic strength of the following solution : 4



12. A) The quantum efficiency for the formation of the compound X from compound Y with 313 nm light is 0.21. How many molecules of Y per second are destroyed when the sample is irradiated with a 50 Watt, 313 nm source under conditions of total absorption ? 8

B) Explain the Harpoon mechanism for the reaction between ions. 5

13. A) Eyring showed that the rate constant  $k_R$  of a reaction is given by the expression : 13

$$k_R = \frac{k \cdot T}{h} K_{eq}^\ddagger$$

Formulate the rate constant in terms of

$$\Delta G^\ddagger, \Delta S^\ddagger \quad \text{and} \quad \Delta H^\ddagger$$

14. A) Explain the phenomenon of superconductivity. Name any two superconductors and their uses. 7

B) A sample of silicon is doped with  $10^{21}$  boron atoms /  $\text{m}^3$ . 6

i) Will the resultant material be a metal, n-or p-type semiconductor ?

ii) How will the electrical conductivity of doped material vary with temperature ?

15. A) How will the density be affected by the introduction of  
 i) Schottky defects and  
 ii) Frenkel defects in an ideal crystal  
 Draw a schematic diagram 7
- B) Explain the reactions involved in Wagner's experiment between silver and sulphur. 6
16. A) Explain with suitable examples how the chemical and spectral interferences in flame spectrometric analysis are eliminated. 7
- B) List the advantages and disadvantages of a potentiometric titration relative to a titration with chemical indicators. 6
17. A) Explain the cold vapour method for the estimation of mercury at ppb level. 7
- B) Define the following terms (only three) 6
- i) voltammograms  
 ii) mercury film electrode  
 iii) Nernst diffusion layer  
 iv) hanging mercury electrode
18. A) What are coronands, cryptands and pedants ? 6
- B) Calcium oxalate dihydrate was heated from room temperature to 900°C. Draw a schematic (TGA) thermogram and label various steps in it. 7
19. A) With the help of molecular orbital (MO) diagram explain the high spin nature of  $[\text{FeF}_6]^{3-}$  and low spin nature of  $[\text{CO}(\text{NH}_3)_6]^{3+}$ . 6
- B) Explain briefly Nephelauxetic series. 7
20. A) Explain the role of haemoglobin as transporter of oxygen. 6
- B) Write a short note on neutron activation analysis. 7
21. A) With the help of orbital diagram, discuss the structure of nickel tetracarbonyl. 7
- B) Explain why gadolinium salts do not show maximum magnetic moment. 6

22. A) Give one example of each of the following types of isomers. 6
- i) ionization isomers
  - ii) linkage isomers
  - iii) coordination isomers

B) Explain the difference between kinetic inertness (or lability) and thermodynamics stability (or instability). 7

23. A) Give IUPAC nomenclature for the following 8
- i)  $\text{Na}_3 [\text{Ag} (\text{S}_2\text{O}_3)_2]$
  - ii)  $\text{K}_3 [\text{Fe}(\text{CN})_5 \text{NO}]$
  - iii)  $[\text{CuCl}_2 (\text{CH}_3\text{NH}_2)_2]$
  - iv)  $(\text{COCl} (\text{NH}_3)_5 ]^{2+}$

B) Write a note on the chemistry of thallium in the (+1) oxidation state. 5

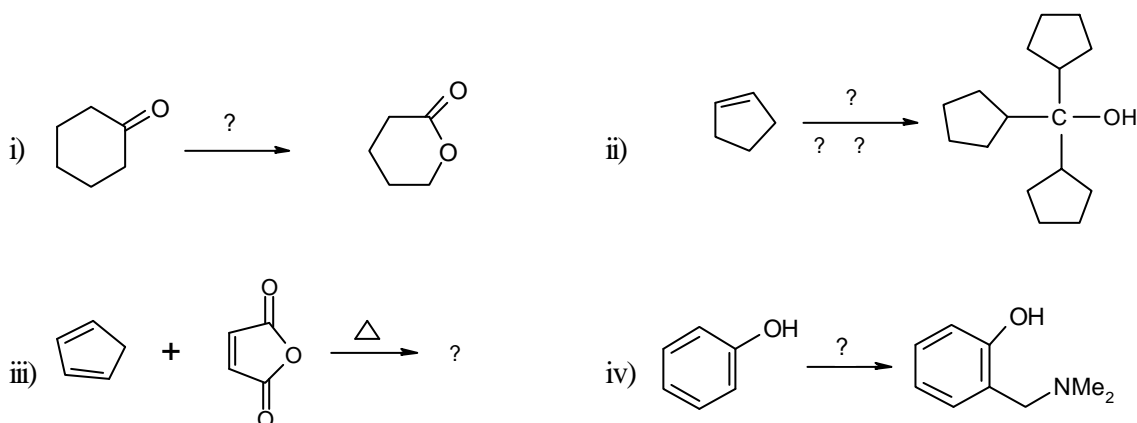
24. A) Give a method for the preparation of  $\text{Et}_3\text{Al}$  and explain its use as a catalyst for the polymerisation of  $\text{C}_2\text{H}_4$ . 5

B) Give a method for the production of hydrazine and hydrazine sulphate. What are the practical difficulties involved in these ? Mention their uses. 8

25. A) Give a method for the preparation of lead tetra-acetate. Draw its structure and mention its uses. 9

B) Oxide of carbon is gaseous while oxide of silicon is solid – Comment 4

26. Complete the following. Name the reaction involved. 13



27. A) Estimate  $\delta$  m OMe and  $\delta$  p Cl from the following data :  
 pKa of benzoic acid, meta-methoxybenzoic acid and p-chlorobenzoic acid are 4.20, 3.08 and 3.99 respectively. 3

B) Give sign of Hammett sigma constants for the following substituents : 2



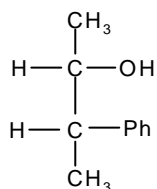
C) Account for the rho values observed for following reactions : 4

i) Nitration of substituted benzene - 7.29

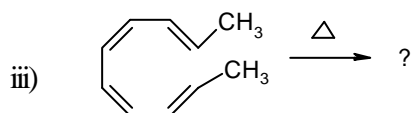
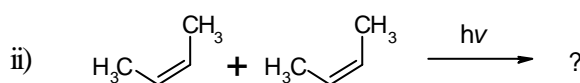
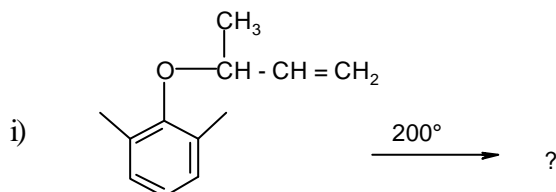
ii)  $\text{Ph}_3\text{C}^+ + \text{H}_2\text{O} \longrightarrow \text{Ph}_3\text{C} - \text{OH}$  3.97

iii)  $\text{PhCH}_2\text{Cl} + \text{EtOH} \longrightarrow \text{PhCH}_2\text{OEt}$  - 5.1

D) Convert the given Fischer projection formula into Sawhorse and Newman Projection 4

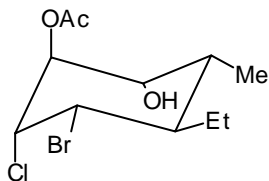


28. Predict the product and its stereochemistry (if any) for the following reactions. Indicate for each reaction (i) type of pericyclic reaction (ii) necessary selection rule. 13



29. A) In the given conformation

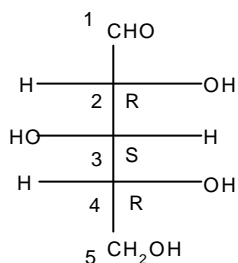
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- i) Identify and equatorial groups
- ii) Indicate geometrical relationship (cis or trans) of
  - a) OAc and OH
  - b) OAc and Cl
  - c) OAc and Br
  - d) OH and Me
  - e) Me and Et

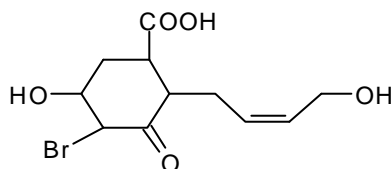
B) One stereoisomer of aldopentose along with configuration of chiral centres is given below. Draw any three stereoisomers and give configuration of each centre.

6



30. Predict the product when following molecule reacts separately with each of the given reagents. Explain your answer.

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Reagents :

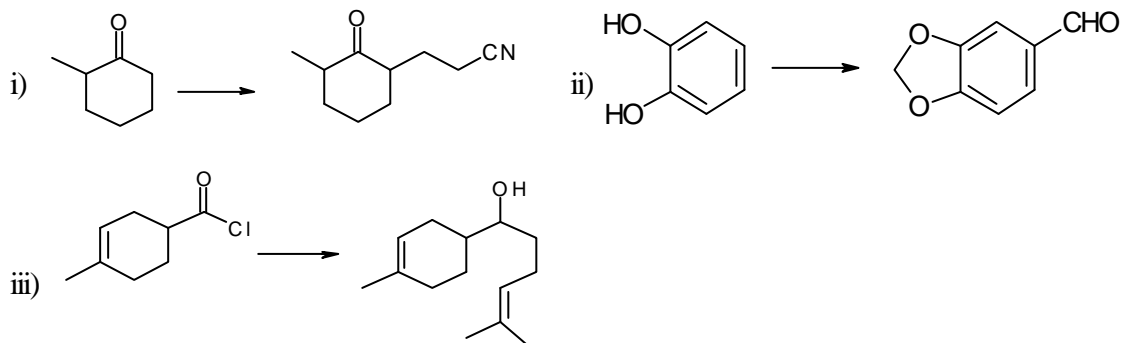
DCC : active  $\text{MnO}_2$ ;

Sharpless oxidation reagents

$\text{NaBH}_4$ ; TBTH;  $\text{CH}_2\text{N}_2$

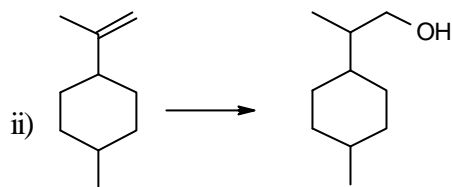
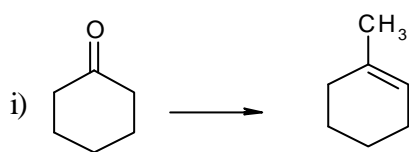
31 A) Indicate the reagents for the following conversions, which may involve more than one step.

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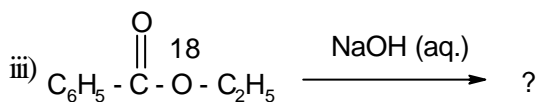
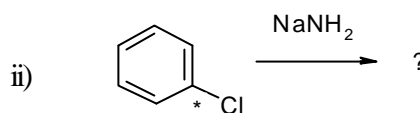
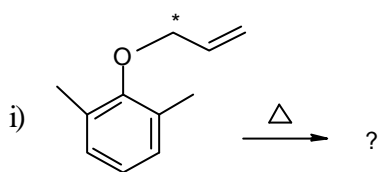
B) Indicate the reagents for the following

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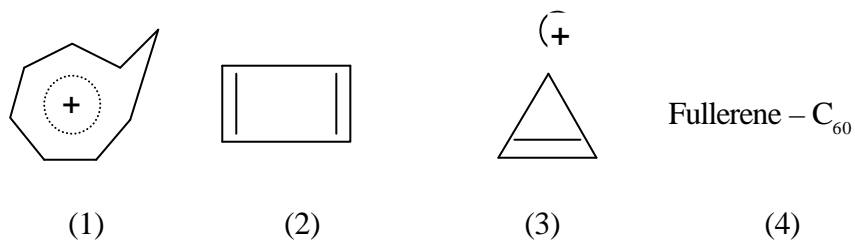
32. A) Trace the position of label in the product. Explain your answer.

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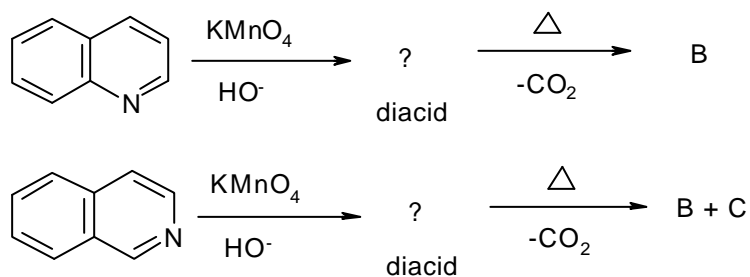
B) Classify following systems into aromatic, antiaromatic, pseudoaromatic and homoaromatic giving reasons.

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33. A) There are three isomeric pyridine carboxylic acids A, B, and C. Complete following reactions and identify A, B and C.

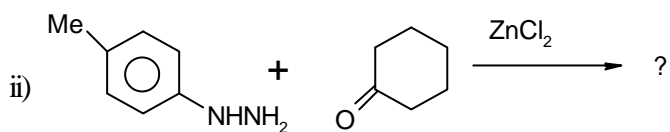
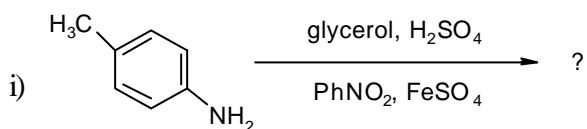
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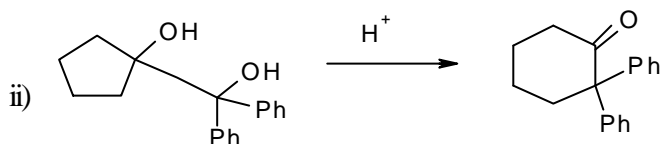
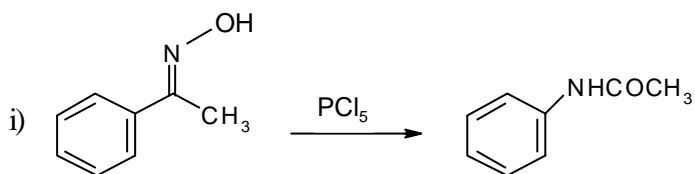
B) Complete the following

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34. A) Propose mechanisms for the following

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