CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours Maximum Marks : 200

Note : Question one is compulsory. Attempt any fourteen other questions from the remaining.

1. Attempt any three of the following :-

a) Draw the schematic energy diagram and show ESR hyperfine splitting for an electron interacting with two non-equivalent protons. 6

b) The Mossbauer spectrum of $Na[Fe(CN)_6]$ consists of a single line, while that of a $Na_2Fe(CN)_3NO$ shows a doublet. Explain the above observation. 6

c) The carbon IS XPS spectrum of $(CH_3)_3C^+ {}^-SbF_6$ in the soild state shows two well resolved doublets with relative intensities 1:3, with the lower signal occuring at lower kinetic energy. Assign these two signals. 6

d) Predict the structure of the compound C_4H_9Br which shows NMR signals at δ 1.04 (*d*, 6H); 1.95 (*m*, 1H) and 3.3 (*d*, 2H). Assign the signals. 6

e) Derive the structure of a ketone, $C_5H_{10}O$ which shows ions at m/z 86, 71 and 43. Assign possible structure to these ions. 6

2. Prove that 13

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta Cp$$

3. a) The freezing point of an abnormal blood sample is –0.402°C. Calculate its osmotic pressure at 37°C. K_f = 1.86; R = 82 cc atm/mol. K. 7

b) In a two-component liquid-solid system, a eutectic point exists. Draw the phase diagram for benzene-napthalene system and show the eutectic point. 6

4. Show that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ 13

and $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$

5. Given that 13

$$\hat{L}^2 = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\right]$$

and $\hat{L}_z = --i\hbar\frac{\partial}{\partial\phi}$, prove that

$\hat{L}^2$ and $\hat{L}_z$ commute

6. a) Obtain the expression for electron density for H_2 within VB and MO frameworks. 7

b) Write down clearly and explicitly the assumptions of the Huckel theory. 6

7. Write down the microstates and derive term symbols for the $2s^1 2p^2$ configuration of an atom. 13

8. Solutions of potassium trioxalatocobaltate (III) are rapidly reduced by iron (II) sulphate in dilute solution.

$$Fe^{2+} + [Co(C_2O_4)_3]^{3-} \rightarrow Fe^{3+} + Co^{2+} + 3C_2O_4^{2-}$$

rate = $k[Fe^{2+}]\ [Co(C_2O_4)^{3-}_3]$

Determine the half-life of the reaction at 320 K, if the initial concentrations of both the reactants are equal to 10^{-3} mol/dm^3.

(k at 320 k = 9.8 x 10^2 dm^3/mol.s) 13

9. a) On a tungsten surface, the decompositions of phosphine is first order at low pressures, but at high pressures, it becomes zeroeth order. Explain these observations on the basis of the Langmuir isotherm. 7

b) Sketch a molecular weight distribution curve for a polymer sample and label $\overline{M_n}$ and $\overline{M_w}$. 6

10. a) Draw the band structure diagrams of metals, semiconductors and insulators. On the basis of these diagrams, discuss the difference in the electrical conductivity of metals, semiconductors and insulators. 8

b) Pure silicon is doped with equal concentrations of phosphorous and boron. Will the resultant semiconductor be n– or p– type ? Comment. 5

11. State all the possible types of defects that can be present in crystalline solids. Explain any two of them with one example each. Draw suitable diagrams wherever necessary. 13

12. a) An ion M (II) forms the complexes $[M(H_2O)_6]^{2+}$, $[MBr_6]^{-4}$ and $[M(en)_3]^{2+}$. The colours of the complexes, though not necessarily in order are green, red and blue. Match the complex with the appropriate colour and explain. 8

b) Account for the fact that *4f* elements have weaker tendency to form complexes as compared to elements of 3d transition series. 5

13. a) Outline the steps involved in the synthesis of borazine ($B_3N_3H_6$) from dibrane and ammonia. 6

b) Explain the structure of ClF_3 molecule and comment about the type of hybridization involved in it. 7

14. a) The complex Co $(en)_2$ Cl_2 (where en = ethylenediamine), is a low spin one. Calculate its 'spin only' magnetic moment and draw the structures of all the isomers of the complex. 9

b) Account for the fact that electronic spectra of lanthanides exhibit characteristic sharp bands. 4

15. a) Outline briefly the principle of Nondrastic Neutron Activation Analysis (NNAA). 5

Complete the following nuclear reactions :

(i) $^{31}_{15}P + ^{1}_{0}n = ^{30}_{15}P + ...$

(ii) $^{16}_{8}O + ... = ^{14}_{7}N + ^{4}_{2}He$

(iii) $^{32}_{16}S + ^{1}_{0}n = ^{32}_{15}P + ...$

(iv) $^{2}_{1}H + \gamma = ^{1}_{0}n + ...$ 8

16. a) For the same ligand, the value of Δ in octahedral complexes of Co^{3+}, Rh^{3+} and Ir^{3+} are approximately in the ratio 2 : 3 : 4. Explain the above behaviour. 8

b) $K_3[CoF_6]$ has μ eff = 4.9 B.M. Calculate the crystal field stabilisation energy in Δ scale)ignore pairing energy). 5

17. a) Give IUPAC nomenclature for the following compounds :

i) $[Co(en)_2.Cl_2]\ H_2O$

ii) $K_4[Co\ (CN)_6]$

iii) $[Co(NH_3)_4Br_2]\ Zn\ Cl_3$. 6

b) The infrared spectrum of $[Fe_2(CO)_9]$ shows bands at 2100 cm^{-1}, 2000 cm^{-1} and 1800 cm^{-1}. Explain the observed spectrum and write the molecular structure. 7

18. a) Give a block diagram of a DTA apparatus and explain in brief the working of different constituent units. 7

b) Comment briefly on three types of interferences which affect the results in atomic absorption spectrophotometric analysis. 6

19. a) Outline the advantages of amperometric titrations. 4

b) In an ion-selective double addition method, the potential of a 25 ml solution containing unknown amount of Cu(II) was 247.2 mV. After first addition of 5.0 ml aliquot of 2.0 x 10^{-3} M Cu (II) solution the potential was 261.8 mV. After the second addition of 5.0 ml aliquot, the potential was 271.9 mV. Calculate the concentration of Cu (II) in unknown solution.

r	CV/Cs Vs	$r = \frac{\Delta E_2}{\Delta E_1}$
1.690	1.787	
1.695	1.840	

Where r is the ratio and Cs and C at Vs and V are the concentrations and volumes of standard and unknown solutions respectively. 9

20. a) Explain the ferromagnetic behaviour of iron metal on the basis of Weiss theory. 8

b) Given E° of the half-cell reactions,

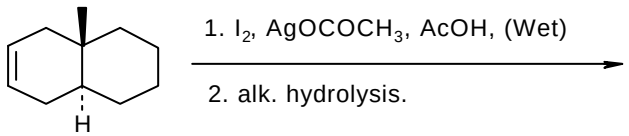
	E° (V)
i) $CuS + 2\bar{e} \rightarrow Cu + S^{2-}$	–0.54
ii) $Cu^{2+} + 2\bar{e} \rightarrow Cu$	+ 0.34

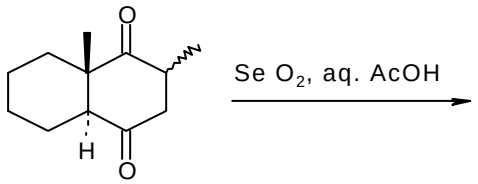
Calculate the solubility product (Ksp) of CuS at 25°C. 5

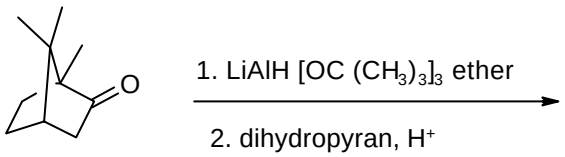
21. a) Though manganese in MnO contains five unpaired electrons it shows antiferromagnetic behaviour at low temperature. Explain this on the basis of magnetic structure. 7

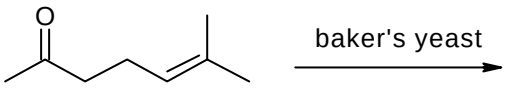
b) List the symmetry elements of the following molecules and name the point groups to which they belong : NO_2 (bent), CH_2, Cl, CCl_3H. 6

22. Complete the following by inserting structures at appropriate places :

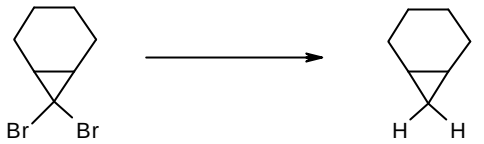
a) 

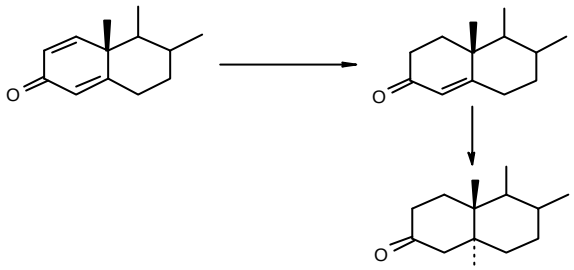
b) 

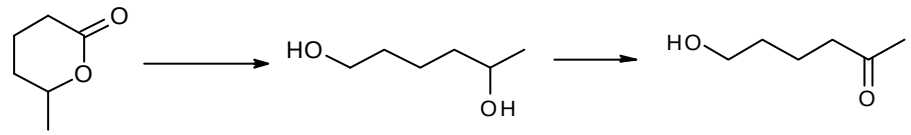
c) 

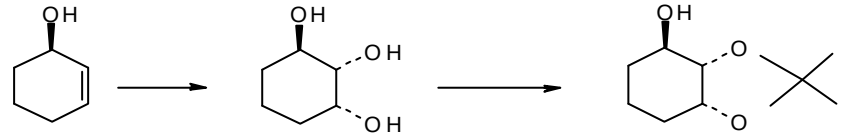
d) 

23. Indicate the reagents for the following conversions :

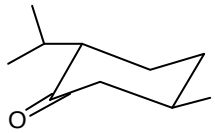
a) 

b) 

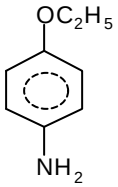
c) 

d) 

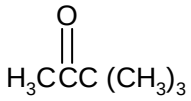
24. A) Match the following 6

a) 

i) peaks at 3350, 3470 cm^{+1}

b) 

ii) ion at m/z 85

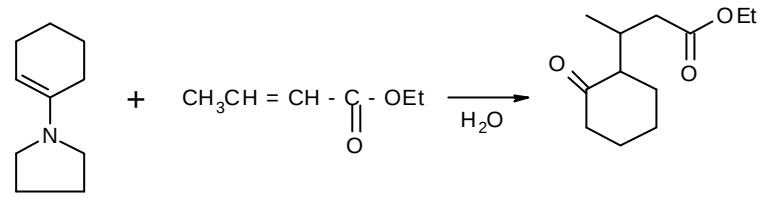
c) 

iii) +ve Cotton effect

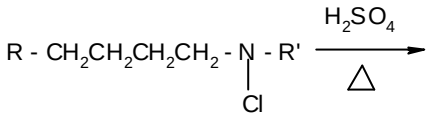
Ans. (a) (b) (c)

B) A compound $C_5H_8O_2$ shows characteristic IR peak at 1810 cm^{-1}. Its H NMR has singlets at 1.1 and 2.2 ppm with peak ratios of 3 : 1. Propose a structure for the compound. Indicate briefly your reasons. 7

25. a) Give a plausible mechanism for the following reaction. 6



b) Complete the following

i) 

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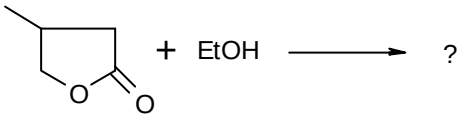
ii) 

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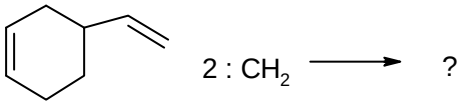
iii) 

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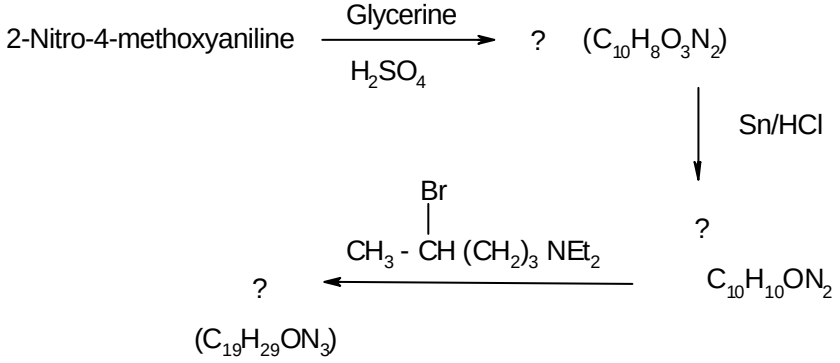
26. a) Predict the products in the following reactions : 7

i) Pyridine - N - oxide $\xrightarrow{\text{Nitration}}$?

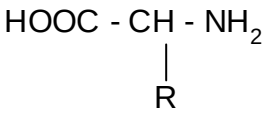
ii) Furan + Ac_2O + BF_3 etherate $\xrightarrow{O°}$?

iii) Furfural (Furan-2-carboxaldehyde) $\xrightarrow[\text{aq. NaOH}]{\text{con.}}$? + ?

b) Complete the following 6



27. a) A pentapeptide on hydrolysis gives two moles each of valine (A) and alanine (B) and one mole of leucine (C). Calculate the molecular weight of the pentapeptide.



A R = $CHMe_2$

B R = CH_3

C R = CH_2 - $CHMe_2$

b) The above pentapeptide on reaction with 2,4–dinitrofluorobenzene gives a derivative which on hydrolysis gives N-2, 4-dinitrophenyl leucine. Indicate the six different structures of the pentapeptide. 6

c) Partial hydrolysis of above pentapeptide gave the following di–and tri–peptides :

Val–Ala; Leu – Val;

Val–Ala–Val; Ala–Val–Ala

Deduce the structure of the pentapeptide.

28. Match the Hammett ρ values for the following reactions :

a) ArCOOH ionization in H_2O at 25°	(i) –3.974
b) Benzoylation of $ArNH_2$ in C_6H_6 at 25°	(ii) +0.374
c) Ar–OH ionization in H_2O at 25°	(iii) –2.69
d) Ionization of Ar_3CCl in SO_2 at 0°	(iv) –5.920
e) Decomposition of ArCOCOAr in acetophenone at 80°	(v) +2.00
f) Nitration of Ar-H in Ac_2O at 18°	(vi) 1.00

Ans a) b) c)

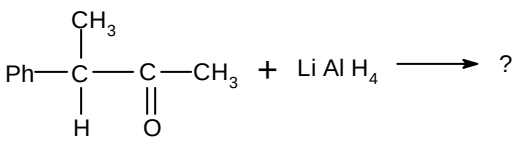
d) e) f)

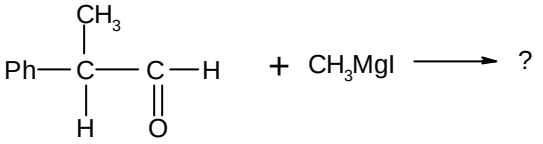
29. a) Draw two chair conformations for each of the following compounds. Arrange these in decreasing order of stability. Given ΔF for CH_3, OH, $CHMe_2$ and COOH are 1.8, 0.7, 2.1 and 1.3 kcal/mole respectively.

i) cis 2–methylcyclohexanol

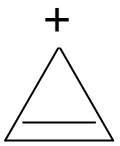
ii) trans 3–isopropylcyclohexane carboxylicacid 9

b) Use Cram's rule to predict the major product in the following reactions 4

i) 

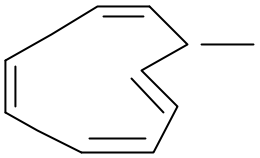
ii) 

30. a) Identify giving reasons the aromatic systems among the following :



(i)

(ii)



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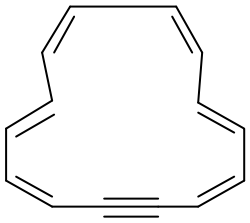

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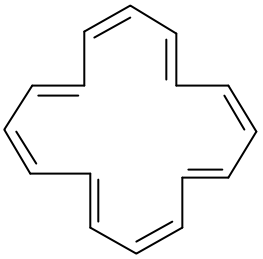

(v)