

- N.B.** 1) All questions are **compulsory**.
 2) Figures to the **right** indicate **full** marks.
 3) **Use** of logarithmic table/non programmable calculator is allowed.

Q.1 Select the most appropriate choice for the following:

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- A)** The primary salt effect is represented by
 a) $\ln K = \ln K_0 + 2.02Z_A Z_B I$
 b) $\ln K = Z_A Z_B \sqrt{I}$
 c) $\ln K = Z_A Z_B I$
 d) $\ln K = \ln K_0 + 1.02Z_A Z_B \sqrt{I}$
- B)** The eigen functions are orthogonal when
 a) $\int \psi_n^* \psi_m d\tau = 0$
 b) $\int \psi_n^* \psi_m d\tau = 1$
 c) $\int \psi_n^* \psi_m d\tau = 2$
 d) $\int \psi_n^* \psi_m d\tau = 3$
- C)** The third law of thermodynamics states that in the limit $T \rightarrow 0$
 a) $\Delta G = 0$ b) $\Delta = 0$ c) $\Delta = 0$ d) $\Delta S = 0$
- D)** Reduced phase rule equation for a two components system becomes
 a) $F = 4 - P$ b) $F = 3 - P$ c) $P = F - 3$ d) $P = F - 4$
- E)** The Debye – Falkenhagen effect is
 a) Conductance under high potential gradient
 b) Conductance under high resistance
 c) Conductance under high A.C. frequencies
 d) Conductance under high high D.C. frequencies
- F)** sp^3d hybridization occurs in PCl_5 but not in PH_5 . This could be because
 a) Cl^- is more reactive than H^-
 b) Cl has d orbital but H does not
 c) Cl atom is larger than H atom
 d) Due to the higher electronegativity of Cl, the 'd' orbital of phosphorous expands
- G)** The point groups for the molecules H_3^+ , H_3 , H_2O , $BeCl_2$, respectively are,
 a) D_{3h} , $D_{\infty h}$, C_{2v} , $D_{\infty h}$
 b) D_{3h} , C_{3v} , C_{2v} , $C_{\infty v}$,
 c) $C_{\infty h}$, C_{4v} , C_{3v} , D_{3h} ,
 d) $C_{\infty v}$, C_{2v} , C_{2v} , $C_{\infty v}$,
- H)** The lone pair of electrons becomes an inert pair of electrons in the following order for NH_3 , AsH_3 , SbH_3 , BiH_3
 a) $NH_3 > AsH_3 > SbH_3 > BiH_3$
 b) $NH_3 > BiH_3 > SbH_3 > AsH_3$
 c) $NH_3 > SbH_3 > BiH_3 > AsH_3$
 d) $NH_3 > BiH_3 > AsH_3 > SbH_3$

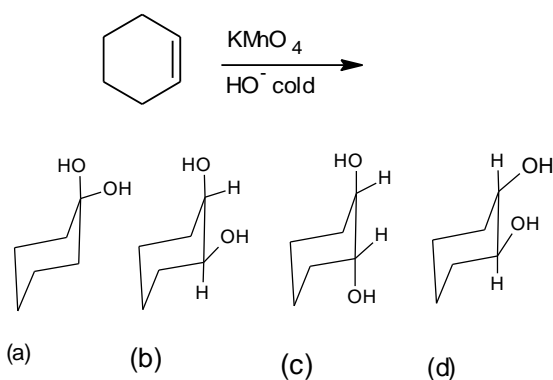
I) In case of Mg^{2+} and Ca^{2+} , the former

- a) is found concentrated in the inside of an animal cell
- b) is found concentrated in the outside of an animal cell
- c) is not found in animal cell
- d) is found in plant cells

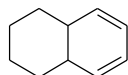
J) If a complex is formed in stepwise manner, then for the stepwise stability constants Pk_1 and Pk_2 , the following stability relation holds

- a) $pK_1 = Pk_2$
- b) $pK_1 > Pk_2$
- c) $pK_1 < Pk_2$
- d) $pK_1 \geq Pk_2$

K) What is the major product expected from the following reaction?

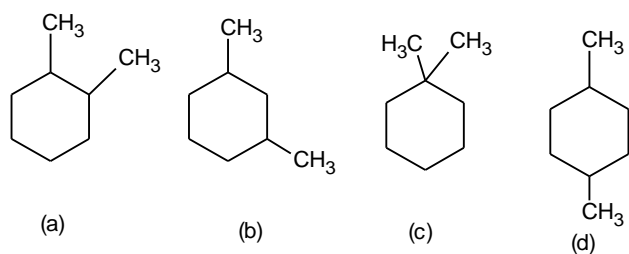


L) What is the λ_{max} for the following compound?

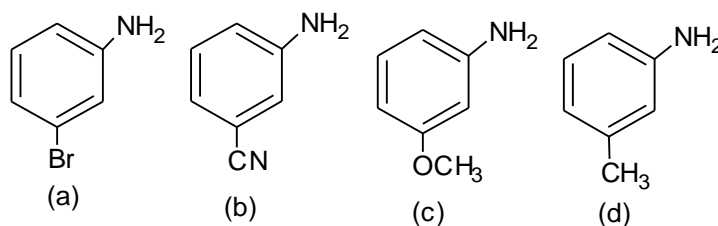


- a) 234nm
- b) 244nm
- c) 273nm
- d) 280nm

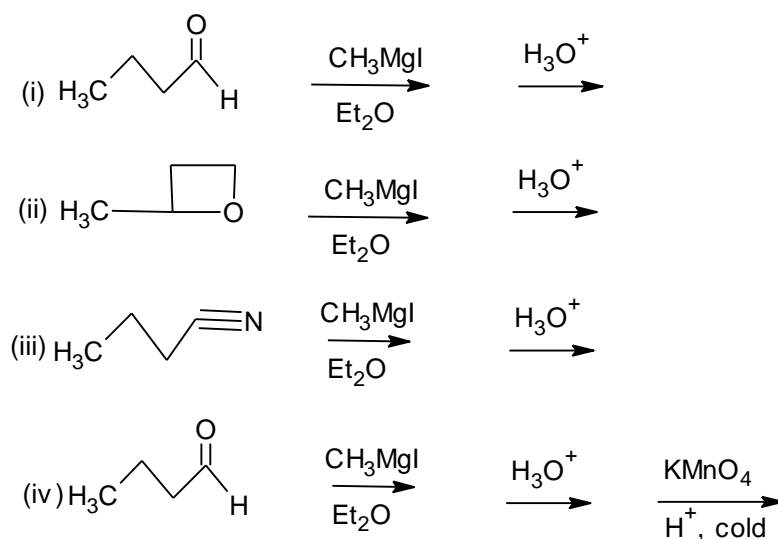
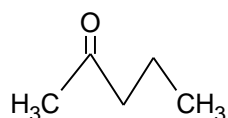
M) The CMR spectrum of an unknown compound shows 4 absorptions and the PMR spectrum shows 4 absorptions. Which of the following compounds is the unknown compound?



N) Which of the following compounds is the best Bronsted base?



O) Which of the following reaction sequences would be the best synthesis of 2-pentanone?



P) For preparation of sample solution in IR spectroscopy, ____ cannot be used as a solvent.

- a) Water b) Methanol c) Hexane d) Chloroform

Q) In analytical instruments the role of transducer is

- a) to convert information in non-electrical domains to information in electrical domains
 b) to identify, record the change in one of the variables in its environment
 c) to disperse light into its characteristic wavelength
 d) to absorb UV radiations.

R) Organic substances X and Y have retention times, 15.30 and 16.45 minutes respectively on a 30 cm long column. An unretained species passes through in 1.10 minutes. The peak widths for A and B are 1.08 and 1.17 minutes respectively. The average number of plates will be

- a) 3211 b) 3163 c) 3101 d) 3187.

S) The nuclei that do not exhibit NMR signal are

- nuclei containing even number of protons and odd number of neutrons.
- nuclei containing odd number of protons and even number of neutrons.
- nuclei containing even number of protons and even number of neutrons.
- nuclei containing odd number of protons and odd number of neutrons.

T) A silver-silver chloride belongs to electrode of

- first kind
- second kind
- third kind
- none of the above.

Q.2 Attempt any three of the following questions:

A) a) Draw a phase diagram for water system. 5

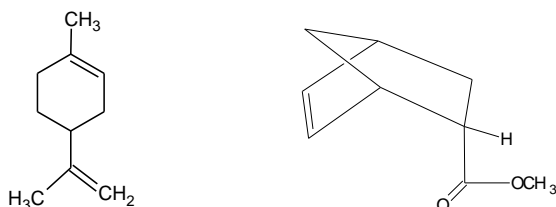
b) Write the Debye-Huckel Onsager equation and explain the terms involved in it. 5

B) a) Although the $\text{Cu}^{2+}/\text{Cu}^{+}$ and $1/2\text{I}_2/\text{I}^{-}$ standard potentials are +0.15V and +0.54V respectively, Cu(II) salts liberate iodine from potassium iodide solution. Explain this observation. 2

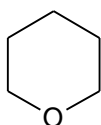
b) Ethylene is a molecule of D_{2h} molecule symmetry. List all the symmetry operations of ethylene. 4

c) Explain briefly the trans-effect. 4

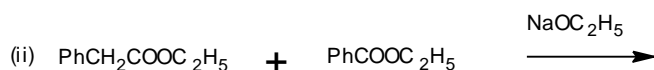
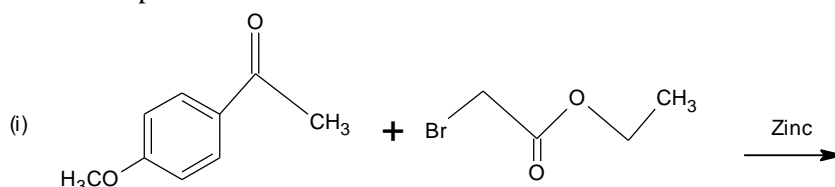
C) a) Give the 'Retro Diels-Alder' fragmentation of the following compounds. 4



b) Devise S_{N}^2 reactions for the synthesis of the following product. 3



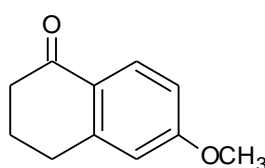
c) Predict the product and name the reaction



- D) a) What are the different methods of calibrating the instrumental methods? Describe anyone of them. 3
 b) What is an arc-source. What are its applications. 3
 c) With the help of labelled diagram, describe the 'Time of Flight' mass analyser 3
 E) a) The activation energy of a reaction is 80.9 KJmol^{-1} . Calculate the fraction of molecules at 400°C which have enough energy to form molecules. 3

- b) Calculate the valence electron count in
 i) $[\text{Ni}(\text{Cp})_2]$ ii) $[\text{U}(\text{C}_8\text{H}_8)_2]$ 2

- c) Calculate the λ_{max} of the following compound 2



- d) 100 cm^3 of an aqueous solution containing 200mg of solute when extracted once with 10 cm^3 of an organic solvent, 120 mg of solute was extracted in organic solvent. Calculate minimum number of extractions required for 99% extraction for each extraction. 3

Q.3 Attempt any two of the following sub questions:

- A) a) What is Joule- Thompson effect? 8

Discuss the experimental techniques used by them to derive its mathematical expression.

- b) Discuss the solution of Schrodinger wave equation for a particle in a three dimensional box with edges of length 'a', assuming that the potential is zero within the box and infinite outside the box. 7

- B) a) Describe in brief, the various methods of preparation of alloys. 7

- b) Discuss 16-electron rule. 4

- c) Comment on the variable oxidation states of transition metals. 4

- C) a) Deduce the structure of a compound based on the following data: 6

Molecular formula: $\text{C}_7\text{H}_{12}\text{O}_3$

I.R. (cm^{-1}): 1740, 1715, 1160, 1030.

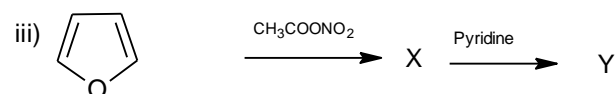
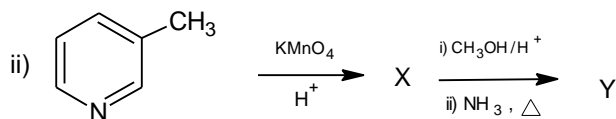
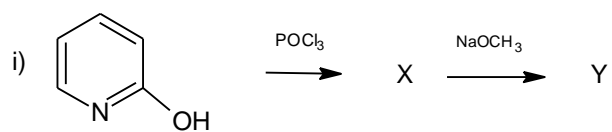
M.S.(m/z): 144(M^+), 129, 99, 74, 55, 43 (base peak).

PMR. (δ): 1.22(3H,t, J= 7Hz), 2.10 (3H,s), 2.6(2H,t, J= 6.5Hz), 2.72(2H, t, J=6.5Hz),

4.1(2H,q, J=7Hz)

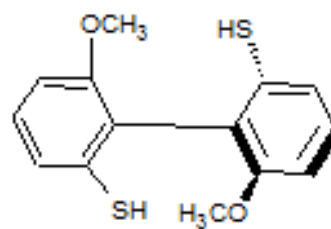
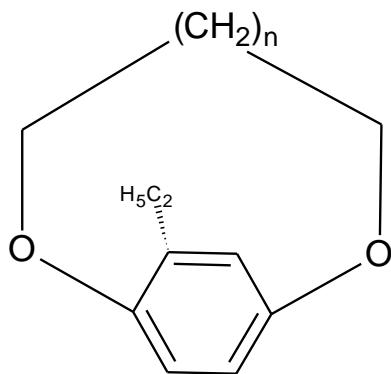
b) Predict the products of the following reactions:

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c) Assign the configurational descriptors to the following compounds:

3



D) a) Describe briefly the principles of the following voltammetric techniques:
 i) d.c.polarography ii) differential pulse polarography iii) cyclic voltammetry
 iv) stripping voltammetry

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b) On the basis of Van Deemter equation, explain longitudinal diffusion. Describe the working of the gas chromatographic detector, selectively used for the determination of pesticide containing phosphorous.

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