Five Year Integrated M.Sc. Examination, 2019

Semester - VI

Course: CH-3-6-2 (Old)

(Chemistry)

Time: Four Hours **Full Marks: 80**

Questions are of value as indicated in the margin.

Group-A

1. Answer ***any ten*** of the following: 10×2=20

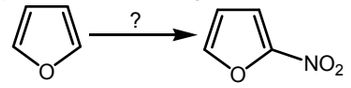
   a) Calculate distance between two successive 111 planes of orthorhombic cell with a = 3 Å, b = 4 Å and c = 5 Å.

   b) Write down general unit cell dimensions of tetragonal and orthorhombic system.

   c) The 222 plane of Tantalum (cubic) give a reflection at $54^o7.2'$, when the X-ray has λ = 1.5418 Å. At what angle would these planes give reflection, when λ = 0.7107 Å? [Sin $54^o7.2' = 0.81$].

   d) Write the aromaticity order of benzene, thiophene and pyrrole.

   e) Write the proper reagent(s) for the following reaction:



   f) Between pyrrole and pyridine, which one is more basic and why?

   g) Pyrrole-2-aldehyde does not undergo Cannizaro reaction whereas furan-2-aldehyde does.

   h) What do you mean by mixed oxides?

   i) How many protons and neutrons are present in a $^{15}N_7$ nucleus? To which of the three groups of nuclei does $^{15}N_7$ belongs?

   j) Why should the proton nuclei in different compounds behave differently in the NMR experiment?

   k) ESR spectra are always recorded in derivative mode. Why?

   l) The 'g' value of $[Fe(CN)_6]^{3-}$ complex is 2. Explain.

Group-B

Answer ***any two*** questions

2. a) What is unit cell and unit cell content? Find the number of unit cell content in FCC crystal lattice. 3

   b) Derive Bragg's law for diffraction of X-ray by a crystalline solid. 3

   c) Why you cannot get C-centre tetragonal lattice? Explain with unit cell diagram. 2

   d) Calculate the packing fraction for a FCC crystal lattice. 2

3. a) How many crystal lattices and how many space/bravice lattices are there? Write their names. 3

   b) Show that for an orthorhombic crystal lattice, the distance between two planes $1/d_{hkl}^2 = (h/a)^2 + (k/b)^2 + (l/c)^2$, where a, b and c are the sides of the crystal. 3

   c) The first order reflection from a crystal plane in a cubic crystal system occurs at $13^o41'$. Find the Miller indices of the plane. Given 'a' = 5.63 Å and λ = 1.54 Å [$Sin^2 13^o41' = 0.056$]. 4

4. a) Compare the structure of NaCl and CsCl. 2

   b) Tungsten has a body centred cubic lattice and each lattice point is occupied by one atom. Calculate the length of the cubic edge. [Given the density and its atomic weight are 19.30 $g.cm^{-3}$ and 183.9, respectively] 4

   c) A crystal plane intercepts the three crystallographic axes at the following multiples of unit distance 2, 3/2 and 1. What will be the Miller indices of the plane? 4

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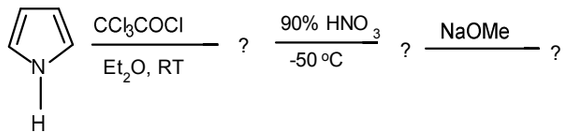
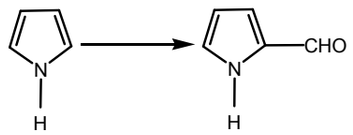
Group-C

Answer ***any two*** questions

5. a) Give the products: 3

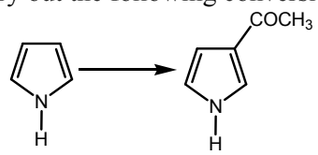


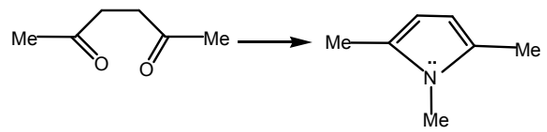
b) How can you carry out the following conversion? Give the mechanism of the reactions involved. 4

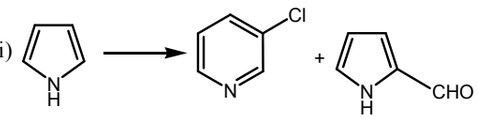


c) Thiophene is more aromatic compared to furan and pyrrole — Explain. 3

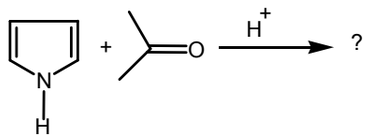
6. Carry out the following conversions: 3+3+4

i) 

ii) 

iii) 

7. a) Pyrrole is acidic like phenol — Explain. 3
   b) Pyrrole becomes protonated on the carbon atom adjacent to the nitrogen atom rather than on nitrogen atom—Account for the fact. 3
   c) Write the product with mechanism of reaction of formation of the product: 4



Group-D

Answer ***any two*** questions

8. a) What is chemical shift (δ) in NMR spectra? Why does it appear in NMR spectra? 2+2
   b) A reference material is used in recording the NMR spectrum of a compound. Why? Write the name of one material which is generally used as the reference material. Discuss the advantages over other materials. 3
   c) The chemical shift of the CH_3 protons in diethyl ether is $\delta = 1.16$ and that of the CH_2 protons is 3.36. What is the difference in local magnetic field between two regions of the molecule when the applied field is 1.9 T? 3

9. a) What is quadrupole moment of a nucleus? Why does it appear in the nucleus? What is quadrupole relaxation? Draw the NMR spectrum of acidified CH_3NH_2 molecule. 1+1+1+2
   b) What is exchange phenomenon? How it can help in simplifying the NMR spectra? Discuss with suitable example. 1+2
   c) The Landé splitting factor (g) is the characteristic property of the nucleus. Explain. 2

10. a) Write the McConnell's equation and explain the terms in it. How can you prove that the electron density over a nucleus should be replaced with the spin density of an electron? 2+2
    b) The ESR spectrum of a molecule having two unpaired electrons (I = 1) shows doublet, instead of singlet. Explain with proper diagram. 3
    c) Draw the ESR spectrum of a free radical containing two equivalent $^{14}N_7$ nucleus (I = 1) and one $^{1}H_1$ proton (I = ½). Mention the relative intensities of the lines. 3
