RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2019

FIRST YEAR (BATCH 2019-22)

Date : 11/12/2019 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 pm **Paper : CC 1** Full Marks : 50

(*Use a separate Answer Book for each group*)

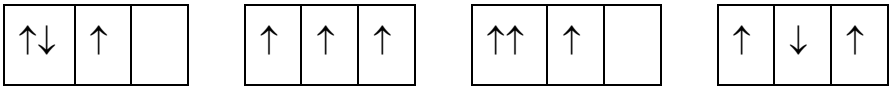
Group A [34 marks]

Unit –I

Answer any one from question nos. 1 & 2 : [1×12]

1. a) Sketch the radial distribution function for the 4p & 3d orbitals and show how many nodal planes are there. [3]

   b) Consider the following possible electron arrangement for p^3 configuration

   Which of these represent the ground state? (ii) Which are impossible states? (iii) In which configuration exchange energy would be maximized? Explanation is expected in each case. [3]

   c) Radius of the first Bohr orbit of H atom is 0.529 Å, Find the radius of the second Bohr orbit of Li^{2+} ions. [2]

   d) Find out the number of waves made by a Bohr electron in one complete revolution in its 3^{rd} orbit. (radius in 3^{rd} Orbit = r) [2]

   e) Write down all the term symbols for an ns^1np^1 configuration. [2]

2. a) Show that stationary orbits are those which contain integer multiple of de Broglie wavelength. [3]

   b) Define radial wave function and angular wave function. Express total wave function in terms of these two. [4]

   c) The wavelength of the first line of Lyman series for hydrogen is identical to that of the second line of Balmer series for hydrogen like ion X. If ionization energy of H is 13.6 eV, calculate the ionization energy of X. [3]

   d) Determine the ground state term symbol of Mn^{2+}. [2]

Unit -II

Answer any one from question nos. 3 & 4 : [1×12]

3. a) What is gas phase proton affinity? Arrange the following bases in order of increasing proton affinity values : HS^-, F^-, I^-, NH^-_2 with appropriate justification. [2+2]

   b) Classify the following species into acids and bases and give the conjugate bases or acids corresponding to each.

   H_3PO_2, $Al(H_2O)_6^{3+}$, NH_4^+, PH_3 [4]

   c) Acidity of anhydrous HF is substantially increased in presence of SbF_5— Explain. [2]

d) Develop a pH scale in liquid ammonia solvent (given $K_{NH_3}\left(-50^oC\right)=10^{-33}$. Mention the neutral pH in this solvent system. [2]

4. a) Why methyl mercury ion is taken as the standard for the SHAB classification? [3]

b) Using hard-soft acid base concept, which direction (left or right) of the following reaction have an equilibrium constant greater than unity? [2]

i) $R_3P.BBr_3 + R_3N.BF_3 \leftrightarrow R_3P.BF_3 + R_3N.BBr_3$

ii) $\left[AgCl_2\right]^-_{aq} + 2CN^-_{aq} \leftrightarrow \left[Ag\left(CN\right)_2\right]^-_{aq}$

c) Enthalpies of reactions of trimethyl borane with NH_3, Me_2NH and Me_3N are $-58, -74, -81$ and $-74\ kJ.mol^{-1}$. Why is trimethyl amine out of line? [2]

d) Using pauling rule identify the structural formula that are nearly consistent with the actual PKa values (i) 2.12 for H_3PO_4 (ii) 2.0 for H_3PO_2. [2]

e) Calculate the pH of a titration of 0.025 M NaOH solution against 50 ml of 0.025 M acetic acid $\left(Ka = 5\times10^{-5}\right)$ at the stages when (i) 49.0 (ii) 50.0 and (iii) 51 ml NaOH solutions were added. [3]

Unit -III

Answer <u>any one</u> from question nos. 5 & 6 : [1×10]

5. a) Write down the Born-Lande equation indicating the terms/symbol in the equation. [2]

b) Using Born-Haber cycle, calculate the electron affinity of iodine from the following data :

Lattice energy of KI(s) = 153.0 Kcal mol^{-1}

Heat of formation of KI(s) = 78.3 Kcal mol^{-1}

Sublimation energy of K(s) = 21.4 Kcal mol^{-1}

Ionisation Potential of K (g) = 100.0 Kcal mol^{-1}

Dissociation energy of I_2(g) = 51.0 Kcal mol^{-1} [3]

c) Standard electrode potential of $AsO_4^{3-} / AsO_3^{3-} = 0.56V$ and $I_2 / 2I^- = 0.54V$, but in $NaHCO_3 + Na_2CO_3$ buffer medium I_2 can oxidised AsO_3^{3-} to AsO_4^{3-}. Explain with reason. [3]

d) Heat of formation of CaF negative yet CaF readily disproportionate to CaF_2. Comment. [2]

6. a) Establish Nerst equation for the couple VO_3^- / VO^{2+}. Standard potential of this couple at 25°C in 1 (M) acid medium is 0.92 V. Find its formal potential at pH = 7. [2+2]

b) Explain Cu^{2+} ion readily liberates iodine from iodide but in presence of Etherleuediamine it does not. [2]

c) $1(N)\,KMnO_4$ may mean either 0.33 (M) or 0.20 (M) ; Comment. [2]

d) Determine the limiting radius ratio for coordination number 3. [2]

Group B [16 marks]

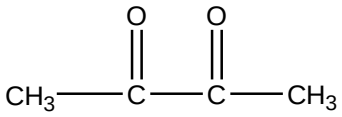
Answer <u>any one</u> from question nos. 7 & 8 : [1×16]

7. a) Give the IUPAC names of the following compounds: [2]

i) $BrCH_2CH_2NH\ CH_2\ CH_2\ CH_3$

ii) CH_2=CH-CH_2-CO-C $\equiv$ CH

b) Which one of the following diketones has higher dipole moment and why? [2]



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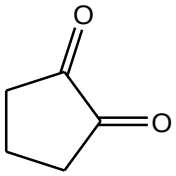
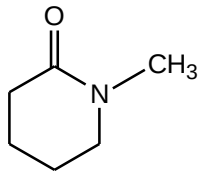


c) Draw the orbital picture of ketene $CH_2 = C = O$ and also indicate the hybridization of each carbon atom. [2]

d) Arrange the following amides in increasing order the basicity; Give reason. [3]



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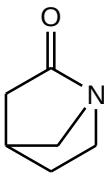

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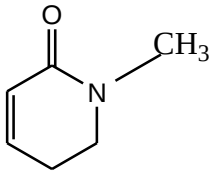
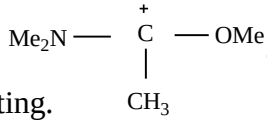


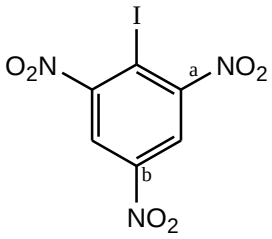
(III)

e) Write the canonical forms of 

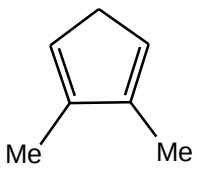
and indicate with reason, which one is the most contributing. [2]

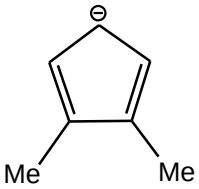
f) Calculate double bond equivalent (DBE) for a compound having molecular formula C_4H_8ONCl. [1]

g) Which C-N bond (a or b) has higher bond length and why? [2]



h) Classify the following molecules or ions as aromatic, non aromatic or antiaromatic; Give reasons. [2]



(I)


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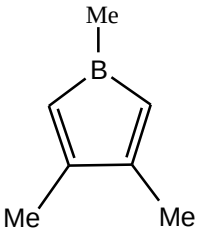
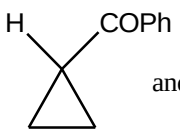


(III)

8. a) Identify A and B, explain those observations. [2]

$$Ph_3CCl \xrightarrow[\text{ether}]{\text{Na-Hg}} A\text{[yellow red in colour]} \xrightarrow{H_2O} B \text{ [Colourless]}$$

b) Compare the acidity for the following pair and justify. [2]



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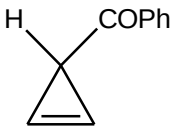
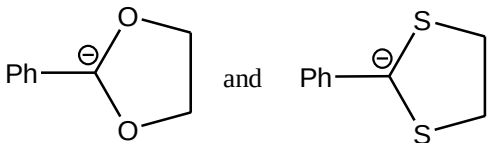
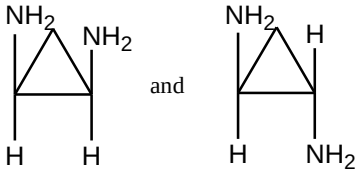


c) Compare the stabilities of the following compounds with reason. [2]



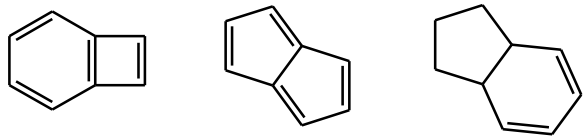
d) Compare the basity for the following molecules. [2]



e) Draw the $\pi - MO$ diagram of 1,3,5 – hexatriene and also indicate HOMO and LUMO for the molecule. [3]

f) Arrange the isomeric pentanes with the increasing order of boiling points and explain. [2]

g) Classify the following molecules as aromatic, non-aromatic or anti aromatic. [3]



(I) (II) (III)

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