RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2017
FIRST YEAR [BATCH 2016-19]

Date : 20/05/2017

Time : 11 am – 1 pm

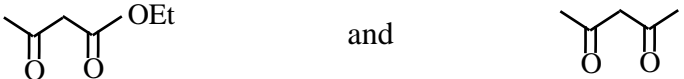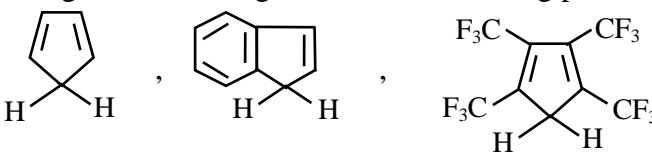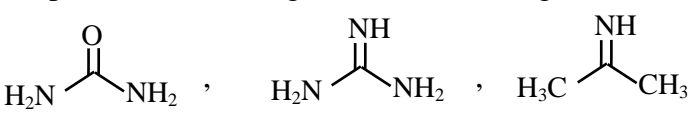**CHEMISTRY (Honours)**
Paper : II [Gr-B]

Full Marks : 35

[Use one Answer Book for Unit I and another Answer Book for Unit II, III & IV]

(*Attempt one question from each Unit*)

Unit I [10 marks]

1. a) Give an example of nucleophilic catalysis. Draw the respective energy profile diagram. [2]

   b) (*E*)-Isomer of $HO_2CCH = CHCOO^{(-)} \overset{(+)}{Na}$ is a stronger base than its corresponding (Z)isomer. Explain. [2]

   c) $Ph_3C - OH \xrightarrow{50\% \ H_2SO_4}$ (Yellow solution) $\xrightarrow{H_2O}$ Colour disappears. Explain the (colourless) observation. [2]

   d) Which carbocation in each of the following pairs is more stable and why? [1+1]

   i) $MeO - CH = CH - \overset{(+)}{CH_2}$ and $H_2C = \overset{(+)}{C} - CH_2$
   $\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $
   $\qquad\qquad\qquad\qquad\qquad\qquad\ OMe$

   ii) $\overset{(+)}{H_2C} - CH_2 - CO_2Et$ and $H_3C - \overset{(+)}{CH} - CO_2Et$

   e) At 100°C, $t_{1/2}$ of $\rangle O \!-\! O \langle$ is 200 hours while that of Ph⤢ is half an hour only. Explain the stability difference between the two peroxides. [2]

2. a) Draw reaction free energy diagram for a reaction stated below that meets the following criteria. Standard free energies are $C < A < B$ and rate limiting step of the reaction is $B \rightleftharpoons C$.
   Reaction : $A \rightleftharpoons B \rightleftharpoons C$. [2]

   b) Explain the higher enol content of one over the other, in liquid state, between

   (8% enol content at equilibrium) and (76% enol content at equilibrium) [2]

   c) Arrange the following in order of increasing pK_a values : [2]

   d) Nitration of benzene does not show any primary kinetic isotope effect. Write down a suitable mechanism for the above reaction clearly stating and explaining the rate determining step. [2]

   e) Compare the base strengths of the following molecules : [2]

(1)

Unit II [8 marks]

3. a) Explain the following :
   i) U-238 cannot be commonly used as a nuclear fuel. [1·5]
   ii) Fission reactions are different from nuclear spallation. [1·5]

   b) An old piece of a wooden sample kept in a museum has a disintegration rate which is 30% of the disintegration shown by an equal weight of a fresh wood sample. Find the age of the wooden sample. (Given : $t_{1/2}$ for $^{14}C = 5740$ yr) [3]

   c) What is the probable energy source of the sun? [2]

4. a) A certain radioactive sample has a half-life period of 40 days. How long will it require for $\frac{3}{4}$ th of it to disintegrate? What fraction will remain unchanged after 3 half lives? [3]

   b) What is magic number? Give the significance of the magic number? [1+2]

   c) The slow neutrons are better projectiles compared to the fast neutrons in the nuclear fission of U-235. Why? [2]

Unit III [9 marks]

5. a) The estimated radius of NH_4^+ ion (148 pm) suggests a CsCl-type structure of NH_4F. But NH_4F adopts the Wurtzite structure – comment. [2]

   b) Using VSEPR mode, predict the shapes of (i) SO_2Cl_2 (ii) XeF_5^- and (iii) CF_3^+ . [1×3]

   c) Among $MgSO_4$ and $BaSO_4$, which is expected to decompose as $MSO_4 \rightarrow MO + SO_3(g)$ at lower temperature? [2]

   d) Why is the melting point of CuCl (422°C) much lower than that of KCl (776ºC)? [2]

6. a) Explain the term lattice energy as applied to an ionic solid. Calculate the lattice energy of CsCl using the following data (KJ. mol^{-1}) noted in parenthesis against each.

   $Cs(s) \rightarrow Cs(g)$ (+79·9), $Cs(g) \rightarrow Cs^+(g)$ (+374·05)
   $Cl_2(g) \rightarrow 2Cl(g)$ (+241·84), $Cl(g) + e^- \rightarrow Cl^-(g)$ (–397·90)

   and $Cs(s) + \frac{1}{2} Cl_2(g) \rightarrow CsCl(s)$ (–623·0) [3]

   b) Account for the shape of XeF_6 molecule in gas phase. [2]

   c) Lattice energy of hypothetical $NaCl_2$ is expected to be higher than that of NaCl, but $NaCl_2$ does not exist. —Explain. [2]

   d) The bond angles in NH_3 (107°) and NF_3 (102°) show reverse order in comparison to PH_3 (94°) and PF_3 (98°) —Explain. [2]

Unit IV [8 marks]

7. a) Discuss the structure of $BeCl_2$ in gas phase (high temperature) and solid phase. [2]

   b) What happens when gold (III) chloride solution is treated with stannous chloride? Give equation. [2]

   c) Justify : i) Lithium can form Li_3N but potassium cannot.
               ii) $MgCO_3$ is thermally less stable than $CaCO_3$. [2+2]

8. a) Explain, in short, the behaviour of Na-metal in liquid NH_3. [3]

   b) Is it possible to obtain Hg_2^{2+} salts free of Hg^{2+}? Give reason of your answer. [2]

   c) Write down the preparation and structure of basic berryllium nitrate. [2+1]

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