RAMAKRISHNA MISSION VIDYAMANDIRA
(Residential Autonomous College affiliated to University of Calcutta)
B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2019
FIRST YEAR [BATCH 2018-21]
Date : 21/05/2019

Time : 11 am – 1 pm

CHEMISTRY (Honours)
Paper : II [Gr-B]
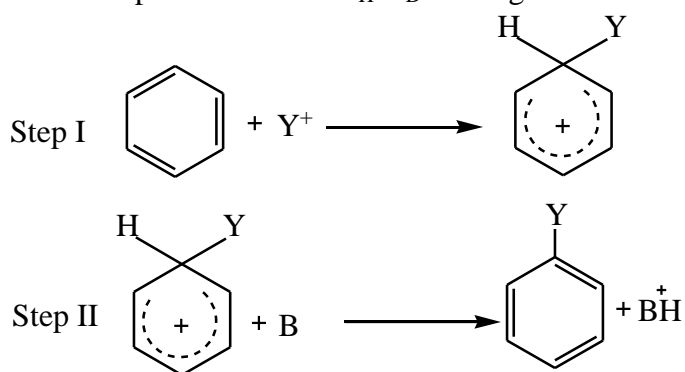
Full Marks : 35

[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) Which one is more basic between diethylamine and triethylamine in aqueous medium?   [2]

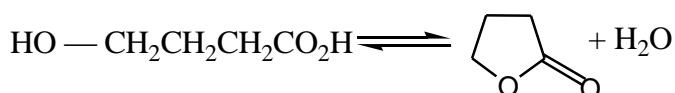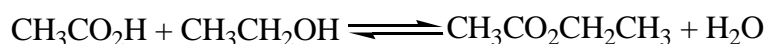   b) A two-step reaction with $K_H/K_D = 7$ is given below.   [3]

   Draw and explain the energy profile diagram for the reaction showing the transition state(s). Also indicate the rate determining step.

   c) Draw the orbital picture of diphenylcarbene and explain its triplet/singlet character.   [2]

   d) Which of the two α-diketones has higher enol content and why?   [2]
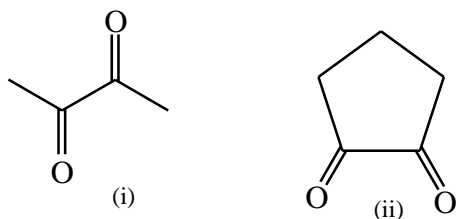
   e) Give the IUPAC name of the compound $Me_2CHCH = CHCO_2Et$.   [1]

2. a) Arrange the following in increasing order of acid strength : 4- nitrophenol; 3,5- dimethyl -4-nitrophenol and 2,6-dimethyl-4-nitrophenol. Give reason.   [2]

   b) Which of the following two reactions conducted at the same temperature is expected to have larger value of equilibrium constant and why?   [3]

   $$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

   $$HO - CH_2CH_2CH_2CO_2H \rightleftharpoons \text{[lactone]} + H_2O$$

   c) Indicate the products obtained in the reaction of E – and Z- butenes with carbene generated from diazomethane in absence and presence of an insert gas. Account for the observation.   [4]

   d) Give IUPAC name for the following molecule.   [1]

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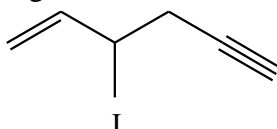
UNIT-II [8 marks]

3. a) What do you understand by "magic numbers"? Why it is so called? Cite an evidence in its favour from the "Binding Energy" curve. [2+1+1]

   b) Calculate the nuclear binding energy per nuclei. [3]

   in $_3^7Li$. Given : me = 0.000549 amu

   $\quad\quad\quad m_p$ = 1.007277 amu

   $\quad\quad\quad m_n$ = 1.008665 amu

   and atomic mass of $_3^7Li = 6.9814$ amu.

   c) What is nuclear isomerism? Give an example. [1]

4. a) Which one of the two nuclides, ^7Li and ^7Be, would be more stable and why? How would the less stable one decay to the more stable one? [1+2]

   b) The skull of a prehistoric man gives 2.8 counts per minute per gram of carbon due to radioactivity of ^{14}C, while a living man gives 15.3 counts. How long ago did the man live? $\left(t_{1/2} \text{ of } ^{14}C = 5730 \text{ years}\right)$ [3]

   c) How does the Meson theory of exchange force explain the nuclear stability? [2]

UNIT-III [9 marks]

5. a) In spite of the fact that the hypothetical $NaCl_2$ is expected to have higher lattice energy as compared to NaCl, it ($NaCl_2$) does not exist — explain. [2]

   b) The F-S-F bond angle in NSF_3 is very small $\left(94^o\right)$ Explain. [2]

   c) Calculate the lattice energy of CaO using the following data: Madelung constant = 1.75, interionic distance = 2.4 Å and Born exponent = 7. [2]

   d) Using VSEPR theory, predict the shapes and indicate the state of hybridisation of the central atom of the following (any three) :- [3]

   i) $IO_2F_2^+$ ii) XeF_5^- iii) ClF_3 iv) BrF_4^- v) XeO_2F_2

6. a) Establish Born Haber Cycle for the formation of MgS(s) starting from Mg(s) and $S_8(g)$ and hence calculate the electron affinity of S(g) for the reaction $S(g)+2e \rightarrow S^{2-}(g)$ using the thermochemical data given below. [3]

   Enthalpy of formation of MgS(s) = 345 KJmol^{-1}

   Enthalpy of sublimation of Mg(s) = 153 KJmol^{-1}

   Sum of 1st and 2nd ionisation potentials of Mg(g) = 2187 KJmol^{-1}

   Enthalpy of atomisation of $S_8(g)$ = 559 KJmol^{-1}

   Lattice energy of MgS(s) = 2948 KJmol^{-1}

   [Here (s) stand for solid and (g) stand for gas]

   b) State Bent's rule. Applying Bent's rule, predict the structure of PCl_3F_2. [2]

   c) Between $\overset{.}{C}H_3$ and $\overset{.}{C}F_3$, one is pyramidal and other is planner. Which one is which and why? [2]

   d) Calculate the limiting radius ratio for tetrahedral lattice structure. [2]

(2)

7. a) First ionisation potentials of coinage metal fall in the order Cu > Ag < Au — Explain. [3]

 b) How is basic beryllium acetate prepared ? Discuss its structure. [2+1]

 c) The reaction $4MO_2(s) + 2CO_2 \rightarrow 2M_2CO_3(s) + 3O_2$

 may be used for the regeneration of oxygen in a spacecraft containing living creatures. Discuss the choice of the alkali metal, M in selection of a superoxide for this purpose. [2]

8. a) The freezing point of a molar solution of potassium iodide is $-3.2^{\circ}C$. When mercury (II) iodide (which is insoluble in pure water) is added in excess, the freezing point is raised to $-2.4^{\circ}C$. Comment on this result. [2]

 b) Give an account of the alkali metal hydrides. What special behaviour of hydrogen is noted in these compound? [2+1]

 c) How is Caesium auride prepared? [1]

 d) Mercury is very peculiar among other group metals. — Discuss. [2]

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