

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [2016-19]

B.A./B.Sc. THIRD SEMESTER (July – December) 2017

Mid-Semester Examination, September 2017

Date : 12/09/2017

Time : 11 am – 1 pm

CHEMISTRY (Honours)

Paper : III

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

Unit – I

[8 marks]

1. Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of 40eV. Also calculate the wavelength of a tennis ball of mass 57g travelling at 80 km h⁻¹. Comment on the nature of electron and tennis ball as either classical or quantum. [3]

OR,

Determine which of the following functions are eigenfunctions of the inversion operator 'i'? ('i' is making the replacement x to -x) [3]

- a) $x^3 - kx$ b) $\cos kx$

Also state the eigenvalue, when relevant.

2. Evaluate the commutators : a) $\left[\frac{1}{x}, p_x \right]$, b) $[H, x]$, where $H = p_x^2 + V$ and V is a constant. [2+3]

OR,

In Compton scattering, the light as well as the recoiling electrons are emitted from the metal body.

- a) Write down the momentum conservation equation and explain the terms. [2]
b) What makes one to conclude that the light behaves as particle? [2]
c) Find the maximum Compton shift. [1]

Unit – II

[8 marks]

[Attempt any one question]

3. Consider a general reaction $n_a A + n_b B \rightarrow n_c C + n_d D$.
a) Define the term 'degree of advancement' (ξ) for the reaction. [2]
b) Express the free energy change of the above reaction $\Delta G \left(= \frac{\delta G}{\delta \xi} \right)$ in terms of chemical potentials of the reactants and products for the above reaction. [2]
c) From the above, arrive at the relation $\Delta G_0 = -RT \ln K_p$. [2]
d) From the above, show that (inserting without derivation the Gibbs' Helmholtz relation) :
$$\left(\frac{\partial \ln K_p}{\partial T} \right)_p = \frac{\Delta H_0}{RT^2}.$$
 [2]
4. a) Consider a reaction that has reached equilibrium. Show that if suddenly the pressure is increased (at a constant temperature) the reaction would advance towards the direction in which volume decreases. [2]
b) Comment whether the value of the equilibrium constant of a reaction depends on the (i) choice of standard state (ii) stoichiometric representation of the reaction. [3]

- c) A solute A dissolves in both the solvents B and C which are immiscible themselves. Consider an equilibrium between A dissolved in B and the same dissolved in C. Show that the ratio of the concentrations of A in the two solvents is constant at a given temperature provided the solute has the same chemical structure and physical form of aggregation in both the solvents. [3]

Group – B

[Attempt one question from each Unit]

Unit – III

[9 marks]

5. a) Give equations to explain why adding ammonium acetate to either zinc amide (s) in liquid ammonia or, zinc acetate (s) in acetic acid causes the solid to dissolve. [3]
- b) Estimate pK_1 values of phosphoric and arsenic acids. Refine your statement by deciding which acid is stronger. [3]
- c) Which would be the effect on acidity of the medium when
- Copper sulfate is added to aqueous ammonium sulfate.
 - Mercuric oxide is added to an aqueous solution of potassium iodide.
- Give necessary equations to explain your answer. [3]
6. a) Explain the enthalpies of adduct formation given in KJ mol^{-1} for the following acid-base pairs : $\text{H}_3\text{N} \cdot \text{B}(\text{CH}_3)_3$ 13.75; $\text{CH}_3\text{NH}_2 \cdot \text{B}(\text{CH}_3)_3$ 17.64; $(\text{CH}_3)_2\text{NH} \cdot \text{B}(\text{CH}_3)_3$ 19.26; $(\text{CH}_3)_3\text{N} \cdot \text{B}(\text{CH}_3)_3$ 17.62. [3]
- b) Discuss the variation of gas phase acidity of hydrides of p-block elements with the help of a Born-Haber type cyclic process. [3]
- c) $(\text{CH}_3)_2\text{N} - \text{PF}_2$ has two donor atoms. One is bound to boron in a complex with diborane; the other to boron in a complex with boron trifluoride. Which is which and why? [3]

Unit – IV

[9 marks]

7. a) Sketch the molecular orbital energy level diagram and account for the differences in dissociation energies and bond lengths tabulated below for NO, NO^+ and NO^- . [2+1+1+1]
- | Species | N–O bond dissociation energy (KJ/mol) | N–O bond distance (pm) |
|---------------|---------------------------------------|------------------------|
| NO | 626.86 | 115.1 |
| NO^+ | 1046.9 | 106.3 |
| NO^- | 487.8 | 125.8 |
- b) Distinguish between extrinsic and intrinsic semiconductors. Give examples. [3+1]
8. a) Construct the inphase and out of phase interactions of two atomic orbitals for a diatomic homonuclear molecule like H_2 , and hence explain the probability of electrons to be found in the resultant orbitals with respect to the atomic orbitals. [3]
- b) HF reacts with F^- to form HF_2^- and two F atoms in the latter are equivalent. Explain in the light of molecular orbital concept. [3]
- c) A and B are atoms of the second and third period of the periodic table, respectively. Assuming x-axis as the bond axis, show that different π mos, A can form with B with pictorial presentations. [3]

Group – C

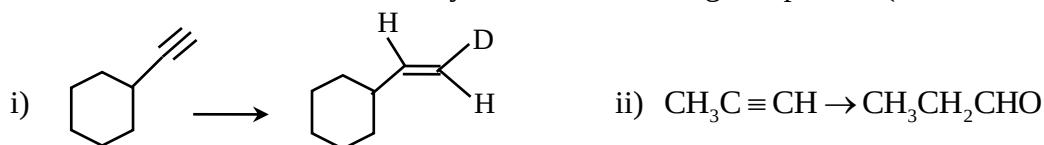
[Attempt one question from each Unit]

Unit – V

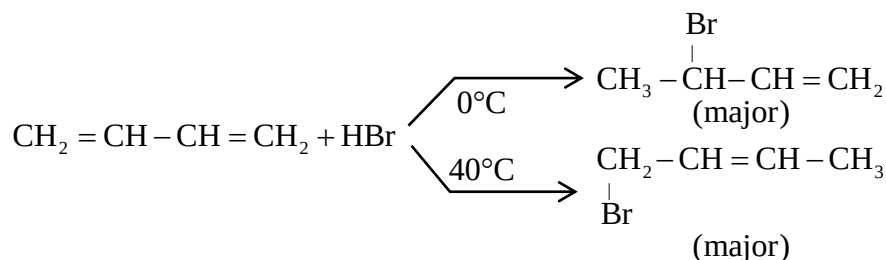
[8 marks]

9. a) Furan can undergo [4+2] cycloaddition reaction but similar [4+2] cycloaddition reaction is not observed for Pyrrole under normal condition — Explain. [2]

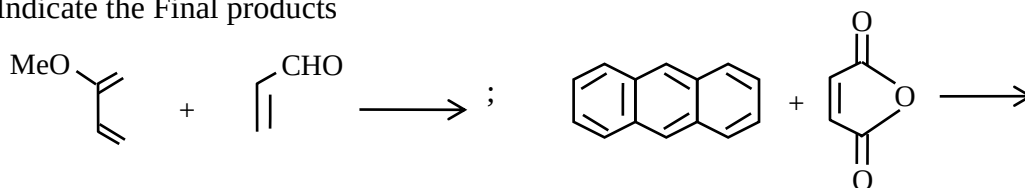
b) Draw the reaction outline for the synthesis of following compounds (no mechanism needed) [2]



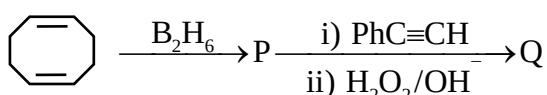
c) Explain the following observation [2]



d) Indicate the Final products [2]



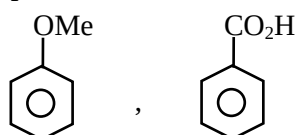
10. a) Indicate the structure of the products P and Q (no mechanism needed) [2]



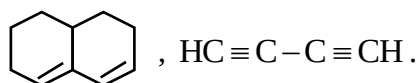
b) Draw the reaction outline for the synthesis of following compounds (no mechanism needed) [2]



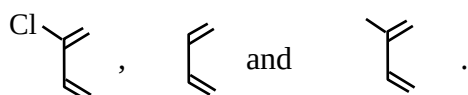
c) Give the final product for Birch reduction with proper explanation. [2]



d) Explain why the following diene can't undergo Diels-Alder Reaction. [1]



e) Arrange the following Dienes in the order of increasing reactivity in Diels-Alder Reaction. [1]



Unit – VI

[8 marks]

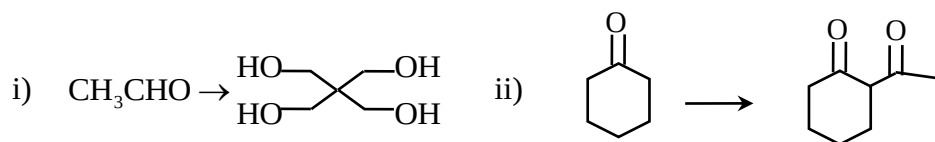
11. a) p-Nitrobenzaldehyde can't undergo self condensation during Benzoin condensation reaction but cross product was observed with benzaldehyde —Explain. [2]

b) Cyclopropanone can undergo hydration in a faster rate than acetone —explain. [1]

c) Thioketals are stable in acid condition but can be hydrolyzed easily by Hg^{2+} salt —Explain. (No mechanism needed) [1]

d) Carry out the following conversion (No mechanism needed)

[2+2]

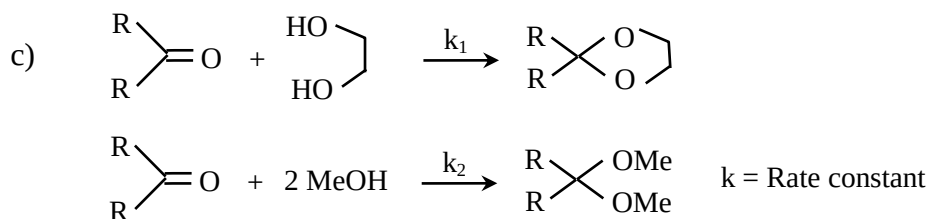


12. a) Benzoin condensation was observed only for aromatic aldehyde but not in aliphatic aldehyde — Explain.

[2]

b) During 2,4-DNP test aldehyde reacts at room temperature where ketone require heating — Explain

[1]

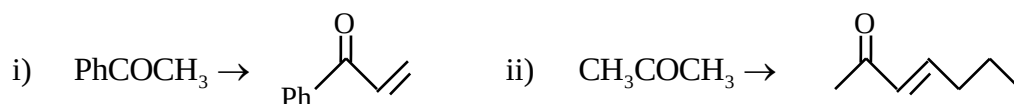


Compare the rate of reaction (No mechanism needed).

[1]

d) Carryout the following conversions

[2+2]



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