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M.Sc. RNLKWC-/CEM-302/22

2022

ADVANCE PHYSICAL CHEMISTRY-I
M.Sc. Third Semester End Examination - 2022
PAPER - CEM-302

Full Marks : 40

Time : 2 hours

*The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in their own
words as far as practicable.
Illustrate the answers wherever necessary.*

Group-A

1. Answer any four of the following questions $2 \times 4 = 8$
- (i) What do you mean by the term Semi-empirical method of electronic structure calculation?
 - (ii) Name two examples of semi-empirical methods.
 - (iii) Write one general advantage and one general disadvantage of semi-empirical methods.

(Turn Over)

(2)

- (iv) Write down two parameterizations considered in Hückel's Method.
- (v) Considering Hückel's method, define resonance energy of a conjugated N-carbon system.
- (vi) What do you mean by the node of a π -Molecular Orbital? Explain with an example.

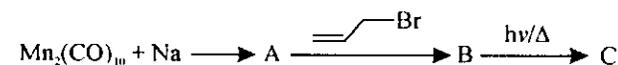
Group - B

B. Answer any four of the following questions. 8×4=32

2. Considering Hückel's treatment, write down linear homogeneous equations for butadiene system (N=4). Also write the corresponding secular determinant. 6+2
3. Draw a neat diagram of Hückel's π -molecular Orbital energy level diagram for cyclobutadiene system showing all nodes and corresponding energies in terms of α & β . Symbols have their usual meaning. 4+4
4. Starting from the secular determinants, find out the energy expressions for Hückel's π -Molecular Orbital of allyl system (N=3). 8

(3)

5. a) Delocalization energy of an arbitrary conjugated hydrocarbon. Explain with example.
- b) What do you mean by the term DEPE? Explain.
- c) Define Aromaticity and anti-aromaticity in terms of DEPE. 3+3+2=8
6. a) Find A, B and C in the given reaction. Also predict the number of ^1H NMR signals with their appropriate ratios for complex C at both low and high temperature.



- b) Explain how acetic acid is prepared by using Monsanto process. Mention the catalyst used in this process. Also point out the rate determining step of the Monsanto acetic acid process. 3+2+3=8

OR

- a) What are the basic assumptions of Hückel's molecular orbital theory. 3

(4)

- b) Consider a particle in a 1D box of length L with the potential given below :

$v(x) = \int v_0 x(L-x)$ when $0 \leq x \leq L$ otherwise the first order correction energy. 5

7. a) Write a short note on Ziegler Natta polymerization of olefin.
- b) Explain Wacker process. What is the role of copper in Wacker process. 4+4=8

OR

- a) State and prove Rayleigh-Ritz variation principle
- b) Pauli spin matrices are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Show that they anticommute.

4+4=8