# RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

**B.A./B.Sc. FIFTH SEMESTER EXAMINATION, MARCH 2022**
**THIRD YEAR [BATCH 2019-22]**
Date : 03/03/2022 **CHEMISTRY (HONOURS)**
Time : 11 am – 1 pm **Paper : DSE1** Full Marks : 50

[Attempt **one question** from **each Unit**]

## Unit –I

[1×18]

1. a) Derive the working formula for numerical differentiation (forward, backward and central difference methods) starting from the first principle. [6]

   b) Explain which of the above methods gives best result. [2]

   c) Derive the working formula for numerical implementation of least square method. [6]

   d) Consider the van-der-Waals equation, you were given the value of P and T, explain how you would calculate the value of V by numerical programming. What would be the guess value that you would start with? [4]

2. a) i) Derive the working formula for numerical integration (Sympson's 1/3 rule and Newton Raphson).

   ii) Explain which of the above mentioned methods gives better result. [6+4]

   b) Derive the formula for solving an ordinary differential equation by Euler's method. [4]

   c) Explain why the error for numerical integration is less than that of numerical differentiation. [4]

## Unit II

[1×18]

3. a) Consider a butadiene molecule. Considering the linear combination of the four $p_z$ orbital as the trial solution for the π electron system, the secular equations that may be derived applying the variation principle is given below (the symbols carry their usual significance):

$(w-H_{AA})c_A+(ws_{AB}-H_{AB})c_B+(ws_{AC}-H_{AC})c_C+(ws_{AD}-H_{AD})c_D=0$

$(ws_{BA}-H_{BA})c_A+(w-H_{BB})c_B+(ws_{BC}-H_{BC})c_C+(ws_{BD}-H_{BD})c_D=0$

$(ws_{CA}-H_{CA})c_A+(ws_{CB}-H_{CB})c_B+(w-H_{CC})c_C+(ws_{CD}-H_{CD})c_D=0$

$(ws_{DA}-H_{DA})c_A+(ws_{DB}-H_{DB})c_B+(ws_{DC}-H_{DC})c_C+(w-H_{DD})c_D=0$

The corresponding secular determinant may be simplified invoking Huckel's approximation.

(i) Clearly mention each of the approximations and

(ii) Write down the simplified form of the secular determinant.

(iii) Next derive the possible energy states in terms of α (the diagonal element of the hamiltonian matrix) and β (the element of hamiltonian matrix for two neighboring atoms). [given that the expansion of the determinant produces the biquadratic equation : $(w-\alpha)^4-3\beta^2(w-\alpha)^2+\beta^4=0$ ]

(iv) How would you now place the four π electrons in these energy levels for the ground state configuration ?

(v) What is the corresponding value of total energy ?

(vi) Show whether it is more stable with respect to isolated diene system. [2+2+2+2+2+2]

b) (i) Write down the trial wave function for a hydrogen molecule both for the valence bond approach and a molecular orbital approach

(ii) Comparing the two forms and explain the major difference. [3+3]

4\. a) (i) Write down the Hamiltonian for a $H_2^+$ molecular ion explaining the significance of each term.

(ii) Explain how this Hamiltonian may be simplified applying Born-Oppenheimer approximation.

(iii) If you are to solve the Schrodinger equation for the $H_2^+$ ion what should be your choice of trial wave function ?

(iv) Explain how would you now advance to solve the equation through variation method (no need to derive, just write down the principle and the mathematical conditions that it leads to). [4+2+2+4]

b) Writing down the secular matrix calculate the energy values. [4]

c) Explain from a valence bond approach why $He_2$ does not exist. [2]

## **Unit III**

[1×14]

5\. a) (i) State 3rd law thermodynamics from Planck's point of view.

(ii) Use the law to give a scheme for calculating the entropy of water at $45^0$C. Also give the significances of the terms involved. [No need to use the numerical value of any physical constants]. [1+3]

b) Einstein's equation for $C_V$ is a function of Einstein's characteristic temperature. But at very high T, it becomes 3R. Explain with necessary equation/s. [3]

c) Arrive the Nernst heat theorem from Gibbs Helmholtz equation, with the help of an appropriate graphical plot of $\Delta G$ vs T. [4]

d) One mole of $O_2$ at 298K and $1.013\text{x}10^5$ $Nm^{-2}$ pressure is available. If the characteristic vibrational temperature of $O_2$ is 2230K, calculate its molar specific heat. [3]

6\. a) (i) Consider a 2D crystal with vibrations in the 2D only. Molar partition function being the product of all individual vibrational partition function due to each mode, calculate the $C_V$ of this crystal.

(ii) Do you think that $C_V$ for this system will be zero towards 0K? Explain.

(iii) How does one correlate the hardness of the diamond in the Einstein's view? [4+2+2]

b) Give a schematic plan with proper graphical plot to attain the absolute zero temperature. Also explain the different processes involved. [3]

c) The standard entropy change for the formation of HCl(g) is 9.916J ($K^{-1}$). Calculate the entropy change for the formation of HCl(g) at 400K from the following data:

$C_P$ (HCl) = $28.16 + 1.8\times(10^{-3})T$

$C_P$ ($H_2$) = $29.08 + 0.84\times(10^{-3})T$

$C_P$ ($Cl_2$) = $31.72 + 10.12\times(10^{-3})T$

The data given are for all molecules in their gaseous state. [3]

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