## MAR IVANIOS COLLEGE (AUTONOMOUS) THIRUVANANTHAPURAM

Reg. No. :
Name :
Fifth Semester B.Sc. Degree Examination, November 2016
First Degree Programme under CBCSS
Core Course: Chemistry - VI
AUCH543: Physical Chemistry - II
Time: $\mathbf{3}$ Hours
Max. Marks: 80

## SECTION - A

Answer ALL questions in one or two sentences.

1. Give the Lewis Randall statement of third law of Thermodynamics.
2. Write down the mathematical expression of Nernst heat theorem.
3. State Hardy - Schulze law.
4. State the Born - Oppenheimer approximation.
5. Calculate the wavelength of radiation that has an energy, $4.95 \times 10^{-19} \mathrm{~J}$
6. What are overtones?
7. State Franck - Condon principle.
8. What is meant by Larmor precession ?
9. What is meant by hyperfine splitting in esr spectrum ?
10. Write the Clausius - Mosotti equation for molar polarization and explain the terms.

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(10 \times 1=10 \text { Marks })
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## SECTION - B

Answer any EIGHT questions, each in a short paragraph not exceeding 50 words.
11. Distinguish between statistical probability and thermodynamic probability.
12. Explain the term gold number.
13. Differentiate between imbibitions and syneresis of gel.
14. Explain zeta potential.
15. What are the conditions of a wave function, $\Psi$ to be acceptable ?
16. In the rotational spectrum of HF , the lines are $41.9 \mathrm{~cm}^{-1}$ apart. Calculate the moment of inertia of the molecule. [At.mass, $\mathrm{H}=1.008, \mathrm{~F}=19.0$ ].
17. What is the rule of mutual exclusion?
18. Sketch the schematic ESR spectrum of methyl radical.
19. How many peaks will be obtained in a NMR spectrum of benzene? Why?
20. What is meant by optical exaltation ?
21. Define parachor. Show that parachor is an additive property.
22. What is meant by specific magnetic susceptibility?
( $8 \times 2=16$ Marks )

## SECTION - C

Short essay type: Answer any SIX questions.
23. What is the difficulty in determining absolute entropy of a substance ? How has the problem being solved by Debye?
24. What are micelles? Explain critical micelle concentration.
25. What are the consequences of electrical double layer in colloids?
26. Explain the postulates of quantum mechanics.
27. What is Raman shift ? Give the classical theory of Raman effect.
28. Given that the fundamental vibrational band for CO is $2140 \mathrm{~cm}^{-1}$, calculate the force constant of Carbon - Oxygen bond. [At. Mass, $\mathrm{C}=12, \mathrm{O}=16$ ].
29. What are the factors influencing chemical shift?
30. Given for a free electron, the electron $\mathrm{g}-$ factor $=2.0023$ and Bohr Magneton $=$ $9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$. Calculate the magnetic field required to its resonance at a frequency of 9.53 GHz .
31. At $25^{\circ} \mathrm{C}$, the molar magnetic susceptibility of water is $-13.0 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$ and its density is $0.9970 \mathrm{~g} \mathrm{~cm}^{-3}$. Calculate
a) the specific magnetic susceptibility and
b) the magnetic permeability of water at this temperature.

## SECTION - D

Long essay type: Answer any TWO questions.
32. a) Derive the thermodynamic expressions for internal energy $U$, molar heat capacity $\mathrm{C}_{\mathrm{v}}$, entropy S and work function A in terms of Partition functions.

10 Marks
b) $\mathrm{C}_{\mathrm{v}}$ for Uranium metal is $3.04 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ at 20 K . Calculate the absolute entropy of the metal in $\mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ at 20 K .

5 Marks
33. a) Briefly discuss the postulates of Langmuir's adsorption theory and derive the Langmuir adsorption isotherm.

7 Marks
b) Derive the wave equation for a particle in a 3-dimensional box applying the separation of variables method.

8 Marks
34. a) What are quantum numbers ? Discuss the significance of each quantum number.

7 Marks
b) Derive the expression for rotational energy of a rigid diatomic molecule. Give the selection rules for their rotational spectrum.
35. a) Explain briefly the basic principles of NMR spectroscopy.
b) Calculate the molar refraction of benzene molecule. [Given: Atomic refraction; $\mathrm{C}=2.42, \mathrm{H}=1.1$, Structural refraction; $\mathrm{C}=\mathrm{C}=1.73$, 6 -membered ring $=-0.15]$

3 Marks
c) Discuss how parachor measurements have been useful in the structure determination of compounds.

5 Marks
( $\mathbf{2} \times \mathbf{1 5}=\mathbf{3 0}$ Marks)

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