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3. a) Describe the similarities and differences in assumptions of Einstein's and Debye's models to explain temperature dependence of specific heat of simple molecular solids at lower temperature range.
- b) Find an expression for pressure of a gaseous system contained in volume, V at temperature, T containing N particles, each with individual mass, m. The canonical partition function associated with the system is given as,

$$Q = \left(\frac{V - Nb}{N} \right)^N \cdot \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3N}{2}} e^{\frac{N^2 a}{V k_B T}}$$

(a, b : two constants; Other symbols have their usual meanings)

- c) State the statistical mechanical definition of thermodynamic temperature of a thermodynamic system. Comment on whether a system may be associated with negative absolute temperature value under some special condition. 3+4+3

Ex/SC/Chem/UG/DSE/TH/03/2023

B. SC. CHEMISTRY EXAMINATION, 2023

(6th Semester)

CHEMISTRY (DSE)

PAPER: DSE/CHEM/TH/03

Time : Two Hours

Full Marks : 40

Use a separate answer script for each unit.

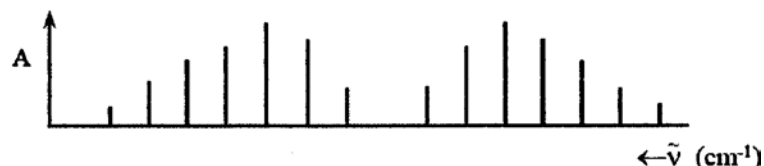
UNIT : 6031-P

1. Answer *all* questions.
- a) Explain various classifications of photochemical reactions according to the nature of potential energy surface. Describe a suitable experimental method to obtain rate constant of a photochemical reaction for the triplet state by addition of a competitive quencher. $1\frac{1}{2} + 2\frac{1}{2}$
- b) What is transition moment integral? Explain briefly its significance for the spectroscopic selection rule. 2
- c) Why microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities? 2
- d) A schematic rotational-vibrational absorption spectrum of a diatomic molecule is shown below. The bond length is assumed to be the same in the two vibrational states. Sketch the qualitatively comparative resulting spectrum in the absence of any other changes, (a) the bond length of both

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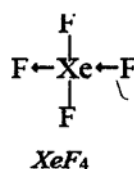
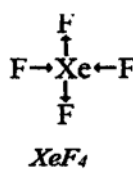
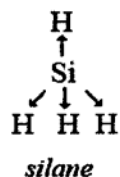
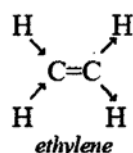
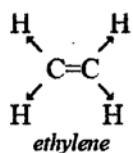
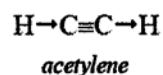
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vibrational states is increased, (b) the bond force constant is increased, and (c) the bond length of just the upper of vibrational state is increased. 3



e) The rotational constant of diatomic AB molecule is 2 cm^{-1} . If the atom A has two isotopes and the atom B has three isotopes then how many absorption lines will be observed in $1\text{-}10 \text{ cm}^{-1}$ region in the pure rotational spectrum of this molecule? 2

f) Which of the following normal modes are infrared active and which are Raman active? The arrows indicate the movement of the exterior atoms. In the asymmetric stretches, the central atoms also move to maintain a fixed center of mass, but that movement is not shown. $2\frac{1}{2}$



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g) The experimental fundamental vibration frequencies in infrared absorption for N_2O are 2224 cm^{-1} , 1285 cm^{-1} , and 588 cm^{-1} . Assuming N_2O linear, determine if the bonding configuration is NNO or NON . 2

h) C-H stretching vibration in organic compounds occur near 2900 cm^{-1} . Approximately what wave number would be the C-D stretching vibration? $2\frac{1}{2}$

UNIT : 6032-P

2. a) Define an ensemble, and name ensembles for a closed system and an open system.

b) Write a brief note on importance and significance of canonical partition function (Q).

c) Obtain expressions for the vibrational partition function and the vibrational contribution to the molar internal energy for a closed system of diatomic molecule at constant temperature and volume.

d) The canonical distribution function for a closed thermodynamic system is given by, $P_j = \frac{e^{-\beta E_j}}{Q}$.

Establish the expression involving P_j for average entropy of the system. [E_j is the energy of the system in its j^{th} state, Q is the canonical ensemble partition function and $\beta = 1/k_B T$.] 2+2+3+3

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