GROUP - C

5. Explain the condition for non-zero *"transition moment integral"* value between two energy states. On the basis of such integral value, derive the spectroscopic selection rule for radiation induced energy transfer in the particle-in-a-box system. 2+3

6. a) Which of the following will show a microwave rotational spectrum ? Justify your choice with proper reasoning. HCl, CH_4, CH_3Cl, SF_6

   b) The first line of rotational spectrum of carbon monoxide appears at $3.8423 cm^{-1}$. Calculate the moment of inertia and C=O bond distance for CO molecule. The given atomic mass of O and C are 15.9994 and 12.0000, respectively.

   c) What are P- and R- branch spectra for a diatomic vibrating rotor ? Explain briefly the effect for *"Breakdown of Born-Oppenheimer Approximation"* on the transition frequencies of P- and R- branch spectral lines 3+4+(2+2)

FINAL B. SC. EXAMINATION, 2018

(2nd Semester, Special Supplementary)

CHEMISTRY (HONOURS)

PAPER - XV

PHYSICAL CHEMISTRY

Time : Two hours   Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. a) Briefly state two limitations of classical thermodynamics.

   b) Based on statistical thermodynamics principles, obtain the equation of state for n moles of an ideal gas (of molecular mass, m) at temperature, T and volume, V. Given, the molucular partition function, $q = V/(\Lambda^3)$ with the de Broglie wave length, $\Lambda = \left(h^2/2\pi mk_BT\right)^{\frac{1}{2}}$. (Other symbols have usual meanings).

   c) State briefly the important assumptions of Einstein for understanding the theory of heat capacity (C_v) of monatomic crystals. Obtain the low and high temperature limiting values from the result,

   $$C_v = 3Nk_B\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{-\Theta_E/T}}{\left(1-e^{-\Theta_E/T}\right)};$$

   Where, θ_E = Einstein Temperature.   1+4+4

[Turn over

2. a) Obtain an expression for the Vibrational contribution to the internal energy of a system of diatoimic gas molecules under harmonic oscillator approxmation.

   b) Determine the nubmer of particles in their two energy levels for a system containing 10^6 distinguishable particles at 298K. Consider that each particle having two non-degenerate energy levels at 0.015eV and 0.025eV.

   c) State the statistical defination of temperature for a system and comment whether it can have negative value.

$$4+3+1$$

GROUP - B

3. a) "MASER" is more probable than LASER"-Justify of criticize the statement from Einstein's treatment of absorption and emission.

   b) Why do the chemical properties in the photoexcited state of a molecular system change relative to the same in its ground state ? Illustrate with an example.

   c) How would you differentiate static and dynamic quenching ?

$$4+(1\tfrac{1}{2}+1\tfrac{1}{2})+2$$

4. a) Which force is responsible for the condensation of nonpolar molecules like hydrogen or argon at low temperatures ? How does it work ?

   b) Outline the Gouy balance method to determine the magnetic susceptibility of a substance.

   c) The refractive index of C_nH_{2n+2} is 1.00139 at STP. If atomic refractions for H and C are 1.1 and 2.42 cm^3 mol^{-1}, respectively, find the molecular formula of the alkane.

OR

At STP, the dipole moment of NH_3 is reported to be 1.44D. Atomic and electronic polarization totals about 6cm^3 mol^{-1}. Calculate the dielectric constant assuming NH_3 to be an ideal gas.

$$2\tfrac{1}{2}+3+2\tfrac{1}{2}$$