GROUP - C

5. a) Show that in the spectrum of a non rigid rotator, the separation between successive lines decreases steadily with increasing j value. 4

   b) The equilibrium vibration frequency of the iodine molecule is 215 cm^{-1} and the anharmonicity constant is 0.003. What is the intensity of the hot band relative to that of the fundamental band, if the temperature is 300 K ? 4

6. Answer ***any two*** questions :

   a) Show that the principal doublet term separation in atomic spectra of sodium is greater than that of diffused doublet. 4

   b) What is the average period of rotation of HCl molecule if it is in the j = 1 state. The internuclear distance of HCl is 0·1274 nm. Given the mass of hydrogen and chlorine atoms are $1{\cdot}673 \times 10^{-27}$ kg and $58{\cdot}06 \times 10^{-27}$ kg respectively. 4

   c) Show that in a diatomic vibrating rotator, the separation between the maxima in the P and R branches is

$$\Delta\bar{\nu} = \sqrt{\frac{8kTB}{hc}} + 2B$$

   where the terms have their usual meaning. 4

FINAL B. SC. EXAMINATION, 2017

(2nd Semester)

CHEMISTRY (HONOURS)

PHYSICAL CHEMISTRY

PAPER - XV

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each group.

GROUP - A

1. a) Describe briefly the significance of Γ – phase space and the representative points in it. State the ***"Principle of equal a-priori probability"*** postulate of Statistical Thermodynamic.

   b) State the statistical definition of Temperature and derive the expression of Pressure, P of a closed gaseous system of N particles of mass m at temperature, T and volume, V. The canonical partition function (Q) associated with the system is given as,

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

   (k_B : Boltzmann Constant ; a, b are constants)

c) Calculate the possible number of ways of arranging 3 particles among 6 energy states if the particles are :

(i) distinguishable, (ii) Bosons. (2+1)+3+2

2. a) Obtain the low and high temperature results from the expression of specific heat of molecular crystals (with N molecules at temperature, T and characteristic Einstein frequency, ν_E) derived by Einstein as,

$$C_v = 3Nk_B\left(\frac{h\nu_E}{k_BT}\right)^2 \frac{e^{-h\nu_E/k_nT}}{\left(1-e^{-h\nu_E/k_BT}\right)^2}.$$

Comment briefly on the limitation of the results.

b) Show that the molecular rotational partition function of a heavy hetero-nuclear diatomic molecule at relatively higher temperature T is (T/θ_{rot}). Comment on the modification of result for a symmetric molecule like Benzene. θ_{rot} : Rotational temperature of the molecule.

c) Find the difference in molar Helmholtz free energies between two ideal gasses A and B kept separately in two containers of volume V and 2V respectively at 25K, where the mass of a particle of gas-A is twice that of gas-B. 3+3+3

GROUP - B

3. a) With proper explanation compare the characteristics of $n\pi^*$ and $\pi\pi^*$ absorption bands of a compound. Comment on the shift of maximum of the $n\pi^*$ absorption band (λ_{max}) of a compound with an increase in the solvent polarity.

b) Justify or criticize the statement, "Static quenching leads to a reduction in the fluorescence intensity, but not in the fluorescence lifetime". How would you differentiate static and dynamic quenching ? (3+2)+(2+2)

4. a) Which force causes nonpolar molecules like hydrogen or argon to condense at low temperature ? Explain how it works.

b) What is meant by the polarizability of a molecule ?

c) Explain why the polar molecules experience a drop in molar polarization when the frequency of the alternating current is increased to $10^{10} - 10^{12}$ Hz.

d) At STP, the dipole moment of NH_3 is reported to be 1.44 D. The sum of the atomic and electronic polarization is about 6 $cm^3\ mol^{-1}$. Calculate the dielectric constant assuming NH_3 to be an ideal gas.

$2\frac{1}{2}+1+2+2\frac{1}{2}$