2+2

7. The fundamental and first overtone transitions of the NO molecule are centered at 1876 and 3724 cm^{-1}, respectively. Evaluate : i) the equilibrium vibrational frequency, ii) the exact zero point energy. 4

OR

i) The term symbol for a particular atomic state is quoted as $^4D_{5/2}$. What are the values of L,S, and J for this state ? What are the minimum number of electrons which could give rise to this state ? ii) What are the term symbols for the following pair of equivalent electrons : s^2 and p^2?

2+2

Ex/CHEM/H/32/XV/A/77/2018

FINAL B. SC. EXAMINATION, 2018

(2nd Semester)

CHEMISTRY (HONOURS)

PAPER - XV

PHYSICAL CHEMISTRY

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each group.

GROUP - A

1. a) "The concepts of equilibrium in Statistica thermodynamics recognize the existence of fluctuations from equilibrium for a thermodynamic system"–justify or criticize.

   b) Using Boltzmann's statistical definition of entropy, derive an expression that relates entropy with the equilibrium probability distributions for a closed thermodynamic system and comment on it.

   c) Evaluate the Helmholtz free enegry at 298K temperature of a mole of localized particles, each of which can exist in levels of energy 0, 25·7meV, 51.4meV and 77·1meV having degeneracy 1, 3, 3 and 1 respectively.

   d) The rotational constant of I_2 molecules being 0·0374 cm^{-1} , evaluate the rotational partition function for I_2 molecules at 100K temperature under rigid rotator approximation. 1+3+3+2

2. a) Describe briefly the assumptions of Einstein and Debye models for analysing the specific heat of monatomic crystals.

   b) In a gaseous system of Chlorine atoms at 1000K, estimate the population ratio between the atoms in their first excited electronic level and the ground electronic level. The difference in these energy levels is 0.11eV.

   c) Provide suitable justification in favour of the statistical definition of temperature of a thermodynamic system and comment briefly on the possibility of its negative value.

   2+3+3

GROUP - C

5. What is *"transition moment integral"* 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.* 1+3

6. Answer ***any two*** of the following :

   a) Define *"space quantization of angular momentum"* for a rotating system and explain its significance for rotational selection rule. For linear diatomic molecule, show that $J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$ for maximum populated rotational level. $1\frac{1}{2} + 2\frac{1}{2}$

   b) Why does the energy-gap between two consecutive energy levels decrease with the increase of the vibrational quantum number when the potential energy curve of a diatomic vibrating system follows Morse function ? "It is impossible to distinguish between *hot band* and *overtone band* experimentally"–Justify or criticize the statement with poper explanation. 2+2

   c) What are P-and R-branch spectra for a diatomic vibrating rotor ? Explain briefly the effect for *"Break down of Born-Oppenheimer Approximation"* on the transition frequency of P-and R-branch spectral lines.

GROUP - B

3. a) Justify or criticize the statement " emission and fluorescence are synonymous".

   b) Using absorption spectroscopy how would you determine the concentration of a given solution of a dye if you are given the dye and the solvent ?

   c) Stern-Volmer equation does not provide the entire information for quenching of fluorescence–justify or criticize.

   d) Describe the basic principle of flash photolysis. What is the use of this technique ? $1\frac{1}{2}+2+2\frac{1}{2}+3$

4. a) Write down the expression of Lennard Jones potential, mentioning all the trrms in it. What is the significance of ε ? $1+1\frac{1}{2}$

   b) What do you underdysnd by the polarizability volume of a molecule ? Derive its unit. 1+1

   c) Calculate the dipole-induced dipole $[u_{d-id}(r)]$ interaction energy acting between two HCl (g) molecules separated . . . . . $\mu_{HCl}=3.44\times10^{-30}$ C m and $\alpha'_{HCL}=2.63\times10^{-30}\,m^3$). Compare this with the thermal energy at 300K and comment on your findings. $2\frac{1}{2}+1$

OR

Molar polarization of a certain vapor obeys the relation $P_m(cm^3\,mol^{-1}) = 60+\frac{20.5}{T}$ (K) assuming ideal behavior. Calculate the molar polarization, dipole moment and the dielectric constant associated with the vapor at STP.

$3\frac{1}{2}$