FINAL B. SC. EXAMINATION, 2019

(2nd Semester)

CHEMISTRY (HONOURS)

PAPER - XV

PHYSICAL CHEMISTRY

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use separate answerscript for each group.

GROUP - A

1. a) Define an Ensemble. Name two ensembles corresponding to open and isolated thermodynamic systems.

   b) Using expression of entropy as, $S = -k_B \sum_j P_j \ln P_j$; P_j being canonical distribution function, evaluate an expression for Helmholtz free energy in terms of canonical partition function. 2+2

2. Estimate the molecular partition function, q associated with an ideal gas. Using the result, derive the equation of state for an ideal gas. Given the density of states,

$$\omega(\varepsilon) = 2\pi\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} .V.\varepsilon^{\frac{1}{2}}$$

(Symbols having usual meanings) (2+2)

3. Considering the ideal monatomic gas model, estimate the fraction of Bromine atoms present in the ground electronic level at 1500K. (Consider only two energy levels are of relevance having energy difference of 0.45eV). 3

4. a) For a gas of diatomic molecules at temperature, T with vibrational temperature, θ, the vibrational molecular partition function is. $q_v = e^{-\frac{\theta}{2T}} / \left(1 - e^{-\frac{\theta}{T}}\right)$. Derive an expression for the vibrational contribution to the specific heat for the gas. Find its high temperature limiting value. Estimate the same for a homo-nuclear diatomic molecular gas at 1200K. Given, for the molecules, $\theta = 3375K$

(3+1+2)

OR

(b) (i) For a mole of O_2 gas with rotational temperature 2.07K, estimate the rotational contribution to A (Helmholtz free energy) at 25^0C (under, Rigid rotor approxmation).

ii) Describe briefly the differences and similarities between Einstein's and Debye's descriptions for analyzing the specific heat of monatomic crystals.

3+3

GROUP - B

5. a) Explain why carbazole is more acidic in the photoexcited state than in its ground state. 2

b) How do you know whether a quencher quenches the fluorescence of a fluorophore by 'static' or 'dynamic' quenching or both operating simultaneously ? 5

8. Calculate first three lines in the absorption spectra arising from transitions from the 3s level of hydeogen atom; what is ionization energy of this level ? (Rydberg constant = $109677.581 cm^{-1}$). What are the different electronic arrangements possible for $^2P_{3/2}$ and $^3S_1$ atomic states ?

(2+2)

9. The separation between P-and R-branch maxima for CO is about $55 cm^{-1}$ temperature 300K. Calculate the value of rotational constant (B) (given : $h = 6.626 \times 10^{-34} m^2 kg\ s^{-1}$; $k = 1.381 \times 10^{-23}\ m^2 kg\ s^{-2} K^{-1}$). Then calculate equilibrium oscillation frequency and anharmonicity constant, if the mid-point frequency of $P_{(1)}$ and $R_{(0)}$ is at $2143.26 cm^{-1}$. 4

c) Describe the basic principle of the method of determination of lifetime of the lowest triplet state of an organic compound that does not emit. 2

6. a) Draw the energy diagram assuming square well potential of intermolecular interaction and comment on its merits over the hard sphere model. 2

OR

Show that the induced charge per unit area (σ_{ind}) is nothing but polarization (P) of a dielectric. 2

b) The polar molecules experience a drop in molar polarization when the frequency of the alternating current is increased to 10^{10}–10^{12}Hz — Explain. 2

c) Explain the origin of London dispersion force and hence calculate its value for two CH_4 molecules seperated by 0.3nm (Given, $\alpha' = 2.6\times10^{-30}\,m^3$ and $I \approx 700 kJ\ mol^{-1}$). (2+2)

OR

How many different types of polarization can be there when a molecule is placed under an electrostatic field ? How are they related ?

For SO_2 gas at STP (273 K & 1 atm), the dielectric constant (or relative permittivity) is 1.00993. The molecule has a permanent dipole moment of 1.63 D.

Assuming ideal behavior, calculate orientation polarization, distortion polarization and distortion polarizability. $(1\frac{1}{2}+2\frac{1}{2})$

GROUP - C

7. Amswer any two of the following : 4×2

a) Write wave-function and transition moment integral expressions for an electron confined by a central positive charge within length "x" ? Is the transition from energy level n=1 to n=3 an allowed transition ? Explain with proper reasoning. $(1\frac{1}{2}+2\frac{1}{2})$

b) What is anharmonicity constant of an anharmonic oscillator ? Explain how it effects on the frequency of fundamental as well as various overtone transitions with respect to equilibrium oscillation frequency ? How many fundamental stretching and bending vibrations are possible for CO_2 molecule ? (1+2+1)

c) What is centrifugal distortion constant of a rotating molecule ? Explain its contribution on the rotational transition frequemcies? Why the intensity is much weaker for hot band than fundamental band frequency at room temperature ? (1+2+1)