This question paper contains 7 printed pages.]

Your Roll No. .....

# 1264

## B.Sc. (Hons.) / III A

## CHEMISTRY – Paper XVIII

## (Physical Chemistry – IV)

**Time : 3 Hours** **Maximum Marks : 38**

*(Write your Roll No. on the top immediately on receipt of this question paper.)*

Attempt **six** questions in **all**.
Question No. **1** is compulsory.
Attempt at least **two** questions from each section '**A**' and '**B**'.
Scientific calculators are allowed.

1. Answer any **four** : **4 × 2**

   (a) What is meant by degeneracy ? Calculate degeneracy for the J = 0, 1 and 2 rotational energy levels.

   (b) What is the difference between internal conversion and intersystem crossing ?

   (c) Why is n = 0 not permitted in the equation

$$En = \frac{n^2 h^2}{8 m_e a^2} ?$$

(d) Why is the molar polarization of a non-polar molecule independent of temperature ?

(e) Which of the following are eigen functions of the $\frac{d^2}{dx^2}$ operator,

$\sin 3x$, $6 \cos 4x$, $5x^2$, $3e^{-5x}$ ?

(f) How can the intensity of antistokes lines in Raman vibrational spectrum be increased ?

## SECTION – A

2. (a) Assign the Miller indices to a plane which intersects the three axes at 1a, 2b and 3c in a cubic system.

(b) State the law of rational indices.

(c) The X-ray powder pattern for Molybdenum has reflections at

$\theta = 20.25°, 29.30°, 36.82°, 43.81°, 50.69°, 58.80°, 66.30°$ and other larger angles when X-rays from Cu are used ($\lambda = 154$ pm).

(i) What is the type of cubic crystal formed by Mo ?

(ii) What is the length of the side of the unit cell ?

(iii) What is the density of Mo ? **(1, 1, 4)**

3. (a) How is the magnetic susceptibility of a substance determined ?

(b) How is molar refraction related to molar polarisation ?

(c) The molar polarization, $P_M$ is given by

$$P_m = \frac{N_\alpha}{3\epsilon_0} + \frac{18.27 \times 10^{-58}}{T} \mu^2$$

where '$\mu$' is the dipole moment in cm.

The molar polarization of $CHCl_3$ measured over a range of temperatures is as follows :

| T(K) | 193 | 203 | 213 | 233 | 253 | 273 | 293 |
|---|---|---|---|---|---|---|---|
| $P_M$ | 29.447 | 29.63 | 47.96 | 47.42 | 46.96 | 46.26 | 44.9 |

The melting point of $CHCl_3$ is 209 K. Calculate the dipole moment and polarisability of the molecule at 300 K and comment on the nature of the graph. $1\frac{1}{2}, 1\frac{1}{2}, 3$

4. (a) What are the essential characteristics of a well behaved wave function ?

(b) Calculate $\langle x \rangle$ and $\langle p \rangle$ for a particle in a one dimensional box. What is the physical significance of the two results ?

(c) A cubic box of edge 1.2 nm contains 10 electrons. Applying simple particle in a box theory, calculate the value of $\Delta E$ for the first excited state of this system. $1\frac{1}{2}, 2, 2\frac{1}{2}$

5. (a) State and explain the variation theorem.

(b) Assuming that the hydrogen molecule has a pure covalent bond,

(i) Write down the valence bond wave function.

(ii) Normalise this wave function.

(iii) What is the molecular orbital wave function that describes a polar molecule HX in which the electron spends 64% of its time in an orbital $\psi_H$ on atom H and 36% in $\psi_X$ on atom X, assuming that the overlap integral is zero ?

(c) Write down the Hamiltonian for the $He^{2+}$ molecule ion. $1\frac{1}{2}, 3, 1\frac{1}{2}$

## SECTION – B

6. Derive the following :

(a) $V_{max} = \frac{1}{2x_e} - 1$

where $x_e$ is the anharmonicity constant of a molecule. Also derive the expression for the spectroscopic dissociation energy.

(b) $\frac{\Delta\bar{\epsilon}}{(cm^{-1})} = \sqrt{\frac{8\,BKT}{Ch}}$

where $\Delta\bar{\epsilon}$ is the energy separation between the maxima in P and R branches of a vibrational-rotational spectrum of a polar diatomic molecule. All symbols have their usual meaning.

(c) Calculate the population of $J_{10}$ relative to the ground state of a molecule if B, the rotational constant is 0.2 $cm^{-1}$ at 300 K. **2, 2, 2**

7. (a) What is Larmor-precession ? Derive the expression for the Larmor precessional frequency of a spinning nucleus.

(b) The vibrational spectrum of NaF molecule shows O → 1 and O → 2 transitions at 528.44 $cm^{-1}$ and 1049.22 $cm^{-1}$ respectively. Calculate $\bar{\nu}_e$ and $x_e$ for the molecule.

(c) Sketch the PMR spectrum of

(i) $C_2H_5OH$ and

(ii) $CH_3CHO$

both under low and high resolution. **2, $1\frac{1}{2}$, $2\frac{1}{2}$**

8. (a) State and explain the rule of mutual exclusion.

(b) A molecule $XY_2$ has the following IR and vibrational Raman spectral data :

| $\bar{r}$ ($cm^{-1}$) | IR | Raman |
|---|---|---|
| 1243 | Inactive | Active |
| 2920 | Active (PR) | Inactive |
| 786 | Active (PQR) | Inactive |

Giving proper explanation, arrive at the geometry of the molecule. Assign the wave numbers to specific vibrations.

(c) In the absence of air, benzene solution in dioxane reacts with Li to give benzene anion

$$C_6H_6 + Li \longrightarrow (C_6H_6)^- + Li^+$$

Sketch and explain the EPR spectrum of the benzene anion, showing the hyperfine lines with relative intensities. in the absence of any exchange reaction between benzene and benzene anion. **1, 3, 2**

9. Write short notes on :

(a) Fluorescence

(b) Predissociation

(c) Factors controlling widths of spectral transitions. **2, 2, 2**

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