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*Your Roll No.* .....

**920**

**B.Sc.(Hons.)/III** **C**

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 as well as log tables is allowed.

**Physical Constants**

$N_0 = 6.023 \times 10^{23}$ mol$^{-1}$

$h = 6.626 \times 10^{-34}$ Js

$k = 1.38 \times 10^{-23}$ JK$^{-1}$

$c = 3 \times 10^{8}$ ms$^{-1}$

$\epsilon_0 = 8.854 \times 10^{-12}$ C$^2$N$^{-1}$m$^{-2}$

1 cm$^{-1}$ = 11.958 J/mol

$m_e = 9.11 \times 10^{-31}$ kg

$\pi = 3.14$

$\beta = 9.273 \times 10^{-24}$ JT$^{-1}$.

P.T.O.

1. Attempt any *four* of the following : 4×2

(*a*) Arrange the following in order of increasing magnitude : 10 $cm^{-1}$, $1 \times 10^{23}$ J, 10,000 MHz, 0.01 m.

(*b*) What is accidental degeneracy ? Explain with an example.

(*c*) What is the effect of isotopic substitution on the rotational spectra of the molecule ?

(*d*) Homo-nuclear diatomic molecules are IR inactive and Raman active. Why ?

(*e*) Sketch all possible modes of vibration in $CO_2$. Which of these vibration are active/inactive in vibrational and Raman vibrational spectrum. Is the rule of mutual exclusion applicable in this case ?

(*f*) Which of the following are eigen functions of the $d^2/dx^2$ operators, $\sin 3x$, $6\cos 4x$, $5x^2$, $3e^{-5x}$ ?

## Section A

2. (*a*) The Weiss indices of a planes are ½, ½, ½. What are the Miller indices ?

(*b*) A certain solid X (atomic mass 27) crystallises in a fcc structure. If the density of X is 2.7 g $cm^{-3}$, what is the unit cell length $\alpha$ ?

(*c*) Explain the following elements of symmetry :

(*i*) Centre of symmetry

(*ii*) Rotation-reflection axis of symmetry. 2,2,2

3. (*a*) An experimental study of polarization as a function of temperature for the hydrogen halides revealed that at low temperatures the order is HCl > HBr > HI while at higher temperatures the ordering is reversed. Explain.

(*b*) Explain briefly the Gouy's method for the determination of molar magnetic susceptibility.

(*c*) Derive Clausius-Mossotti equation. 2,2,2

P.T.O.

4. (*a*) Calculate the ground state translational energy of :

(*i*) a hydrogen molecule in a one-dimensional box of length 0.001 m. The mass of a hydrogen molecule is $3.348 \times 10^{-27}$ kg.

(*ii*) an electron in a one-dimensional box of length 0.1 nm. Comment on your answers.

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

(*i*) Write down its valence bond wave function;

(*ii*) Normalize this wave function.

(*c*) What is the MO 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. 2,2,2

5. Taking the case of the hydrogen molecule ion, $H_2^+$, within the framework of LCAO-MO theory carry out the following using the trial wave function :

$$\Psi = C_1 \Psi_A + C_2 \Psi_B$$

where $\Psi_A$ and $\Psi_B$ respectively correspond to the 1s wave functions of the hydrogen atoms A and B in $H_2^+$.

(*a*) Write the expression for energy indicating the terms called Coulomb integral, the resonance integral and the overlap integral.

(*b*) Optimize the energy with respect to $C_1$ and $C_2$ separately and express the result in the form of a secular determinant.

(*c*) Expand the secular determinant and get the two roots of energy keeping in view that the atomic orbitals that have been mixed are identical in nature. 2,2,2

## Section B

6. (*a*) Show diagrammatically the high resolution NMR spectrum of :

(*i*) acidified ethanol;

(*ii*) ethanol in presence of deuterium.

(*b*) What are $\delta$ and $\tau$ scales ? How they are related to each other ?

(*c*) Which of the following molecules can show a vibrational Raman spectrum ?

$CH_4$, $CO_2$, $SF_6$, $C_2H_6$. 2,2,2

7. (*a*) The HCl molecule in the gaseous state shows pure rotational lines at the following frequencies (in $cm^{-1}$) 20.7, 41.5, 62.0, 83.0 and 103.8. Assign these lines to the rotational transitions, $J \rightarrow J + 1$. From the observed spectrum calculate the bond distance of HCl.

(*b*) A molecule $AB_2$ has the following infrared and Raman spectra :

| $cm^{-1}$ | **Infrared** | **Raman** |
|---|---|---|
| 3756 | V. Strong; perpendicular | — |
| 3652 | Strong; Parallel | Strong (polarized) |
| 1595 | V. Strong; Parallel | — |

The rotational fine structure of infra-red bands is complex and does not show simple PR or PQR characteristics. Predict the geometry of the molecule on the basis of the given spectra. Assign the observed frequencies to the various modes of vibrations. Give reason in each case.

(*c*) Derive an energy expression for the rotational energy corresponding to the most populated rotational energy level $J_{max}$. 2,2,2

8. (*a*) Explain the difference between Fluorescence and Phosphorescence with the help of potential energy diagram.

(*b*) Why do nuclei such as $^{12}C$, $^{16}O$, which do not possess nuclear spin do not show NMR spectra ?

(*c*) Draw hyperfine splitting ESR spectra of ethyl radical. 2,2,2

9. State and explain the following :

(*a*) Franck-Condon principle

(*b*) Rule of mutual exclusion principle with an example

(*c*) Dissociation and predissociation. 2,2,2