Serial No. 11146

A–GSE–P–DIB

CHEMISTRY

Paper—II

Time Allowed : Three Hours | *Maximum Marks : 200*

INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions :

There are ***THIRTEEN*** *questions divided under* ***THREE*** *sections.*

Candidate has to attempt ***TEN*** *questions in all.*

The ***ONLY*** *question in Section A is compulsory.*

In Section B, ***SIX*** *out of* ***EIGHT*** *questions are to be attempted.*

In Section C, ***THREE*** *out of* ***FOUR*** *questions are to be attempted.*

The number of marks carried by a question / part is indicated against it.

All parts and sub-parts of a question are to be attempted together in the answer book.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Answers must be written in ***ENGLISH*** *only.*

Neat sketches are to be drawn to illustrate answers, wherever required.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Any page or portion of the page left blank in the answer book must be clearly struck off

Some Useful Constants

Rydberg constant = 2.178×10^{-18} J

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$c = 2.998 \times 10^{8}$ ms^{-1}

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

$m_e = 9.109 \times 10^{-31}$ kg

$k_B = 1.381 \times 10^{-23}$ JK^{-1}

$R = 8.314$ JK^{-1} mol^{-1}

$\pi = 3.142$

SECTION—A

(Question No. 1 is compulsory)

1. Answer **all** of the following : 16×5=80

(a) What is virial equation of state for real gases ? Express van der Waals equation in the form of virial equation. Discuss the physical significance of virial coefficients. 5

(b) A capillary tube of radius 0.001 cm is inclined at an angle of 45° to the surface of the liquid. The liquid wets the wall of the tube. Calculate the distance along the capillary to the miniscus of the liquid if the density of the liquid is 0.85 g cm^{-3} and the surface tension is 36 dynes cm^{-1}. 5

(c) Justify the following statements :

(i) The net entropy of the Universe increases.

(ii) X rays are used for diffraction by crystals.

5

(d) Applying the law of equipartition of energy, estimate the energy of H_2 molecule assuming that all the degrees of freedom are excited and contribute towards the energy of the molecule. Give the statement of the law. 5

(e) Calculate the fall in temperature of He gas initially at temperature 15°C when it is suddenly expanded to eight (8) times its volume. (Given $\gamma = 5/3$) 5

(f) Deduce the equation to show the variation of K_p with temperature and show that K_p is independent of Pressure. 5

(g) Calculate the pH of 0.01 M NH_4Cl in water at 25°C. pK_b for NH_4OH is 4.74. Ion product of water is 10^{14}. 5

(h) Explain the term reverse-osmosis. 5

(i) The following data were obtained for the reaction $A + B \rightarrow$ products. Derive the rate law.

[A] mole dm^{-3}	**[B]** mole dm^{-3}	**Rate** mole dm^{-3} s^{-1}
6.0×10^{-3}	1.0×10^{-3}	0.012
6.0×10^{-3}	2.0×10^{-3}	0.024
2.0×10^{-3}	1.5×10^{-3}	0.002
4.0×10^{-3}	1.5×10^{-3}	0.008

5

(j) 130 ml of N_2 (corrected to 0°C and 1 bar pressure) was required to form a monolayer on a solid. Calculate the surface area of the solid. Cross sectional area of N_2 is 16.2 Å^2. 5

(k) A current of 800 mA was passed through a dilute solution of $CuSO_4$ for 20 minutes. What are the products liberated at anode and cathode ? Find the amount. 5

(l) If sufficient energy is absorbed by an atom, an electron can be lost by the atom and a positive ion formed. The amount of energy required is called the ionization energy. In the hydrogen atom, the ionization energy is that required to change the electron from $n = 1$ to $n = \infty$. Calculate the ionization energy (in kJ mol^{-1}) for He^+ ions. Is the ionization energy of the He^+ ion more or less than that of hydrogen ? 5

(m) Using a radiation source of 250 W at 250 nm, a compound was irradiated for 90 mins. 40% of the light was reflected off and the rest was absorbed by the compound. After irradiation, 0.02 moles of the compound was found to have decomposed. Calculate the quantum yield for the decomposition. 5

(n) Show that the function $A \sin \frac{n\pi x}{L}$ for a particle in a one-dimensional box of length L is not an eigenfunction of the momentum operator, $\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$, but it is so of $\hat{p}^2$. Discuss the significance of the result. 5

(o) Discuss the molecular orbitals and the various electronic transitions possible in formaldehyde, CH_2O. Draw an appropriate energy level diagram displaying these transitions. 5

(p) By predicting the appearance of its proton NMR spectrum, show how each member of the following pair of isomers may be distinguished :

1, 1-dimethoxyethane, and

1, 2-dimethoxyethane. 5

SECTION—B

(Attempt any SIX questions)

2. A space capsule is filled with neon gas at 1.0 atm and 290 K. The gas effuses through a pinhole into outer space at such a rate that the pressure drops by 0.30 torr/s.

   (i) If the capsule were filled with NH_3 at the same temperature and pressure, what would be the pressure drop ? 5

   (ii) When the capsule was filled with 30.0 mol % helium, 20 mol % oxygen and 50 mol % nitrogen at the total pressure of 1.0 atm and at the temperature of 290 K, what would be the rate of pressure drop ? 5

3. Define chemical potential. Deduce the Gibbs-Duhem equation and show that the variation of chemical potential affects the value of other component. 10

4. What do you mean by an orthorhombic crystal ? Show that for an orthorhombic lattice, the distance (d_{hkl}) between two crystal planes defined by (hkl) is given by

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

a, b and c are the length of the edges. 10

5. For two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$ find equations for the concentration of A, B and C as a function of time. Represent graphically. 10

6. For the dissociative chemisorption of gaseous A_2 at pressure P $A_{2(g)} \rightleftharpoons 2\,A_{(ads.)}$, derive equation for the fractional surface coverage (θ) using Langmuir theory. 10

7. A series of photophysical measurements are carried out on an aqueous solution of compound X. The fluorescence quantum yield is found to be 0.6, the fluorescence lifetime is 20 ns and the intersystem crossing (S_1 to T_1) quantum yield is 0.4. The phosphorescence quantum yield is 0.1 and the phosphorescence lifetime is 1s. No photochemical

decomposition occurs. Draw a Jablonskii energy level diagram showing the ground (S_0) and first excited (S_1) singlet electronic states and the lowest triplet (T_1) electronic state for molecule X. Using the photophysical information provided above, indicate in your diagram all the radiative and non-radiative processes operating between these states following absorption of light. 10

8. The harmonic oscillator model provides a means of interpreting the vibrations of small molecules. When applied to a homonuclear diatomic molecule made up of atoms with mass m, the model yields vibrational energy levels given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

where n = 0, 1, 2, ... is the vibrational quantum number, $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, k is the force constant of the chemical bond, and $\mu = \frac{1}{2}m$ is the reduced mass.

(i) Sketch an energy level diagram for the harmonic oscillator, showing the first four energy levels in units of $h\nu$.

(ii) The ground state wavefunction for the harmonic oscillator is given by

$$\psi_0 \propto \exp(-\beta x^2)$$

where x is the deviation from the equilibrium bond separation and $\beta = \sqrt{\mu k}/\hbar$. Sketch the wavefunction and then determine the most probable value of x and the average value of x.

(iii) The vibrational wavenumber of diatomic chlorine, $^{35}Cl_2$, is 559.71 cm^{-1}. Calculate the force constant for the Cl-Cl bond. Assume that the atomic weight of Cl is exactly 35. 3,3,4

9. (a) Explain concisely what is meant by nuclear spin-spin coupling using the ^1H NMR spectrum of $CHBr_2$ CHO as an example. Explain how spin-spin coupling arises in this example. 8

(b) What is meant by the term coupling constant (J) ? 2

SECTION—C

(Attempt any **THREE** questions)

10. (a) Calculate the energy in Joule to disperse one spherical drop of radius 3.0 mm into spherical drops of radius 3.0×10^{-3} mm if the surface tension of the drop is 72.8 dynes cm^{-1}. 10

(b) Deduce the expression for the work done W, change of internal energy ΔU and change of enthalpy ΔH for the reversible expansion from volume V_1 to volume V_2 for a van der Waals gas. 10

11. Define zeta potential. Explain its significance. Discuss one method of determining zeta potential. 20

12. (a) (i) HI molecules absorb radiation of wavelength $2309.5\ cm^{-1}$. Calculate the accompanying change in internal energy of an HI molecule in Joule.

(ii) Determine the number of normal vibrational modes of each of the following molecules : hydrogen chloride; hydrogen cyanide, ethene, benzene.

(iii) Deduce which of the following molecules will show a microwave (rotational) spectrum and explain your answer :

Br_2; NO; O_2. . 3,4,3

(b) (i) What are Rayleigh, Stokes and Anti-Stokes lines ? Is the intensity of Stokes lines different from that of the anti-Stokes lines ? Explain.

(ii) Sketch the normal modes of vibration of CO_2 and explain which of these are Raman and which are IR active. 5,5

13. (a) In the rotational spectrum of a diatomic molecule, the first three transitions are observed at 17.68 cm^{-1}, 35.36 cm^{-1} and 53.04 cm^{-1}.

(i) Calculate the rotational constant, $\tilde{B}$, of the molecule.

(ii) Predict the wavenumber of the transition from $J = 4$ to $J = 5$.

(iii) What other information would you need to be able to calculate the bond length of the molecule ? Explain your answer. 2,2,2

(b) Calculate the wavelength of light that an electron in a 1×10^{-9} m box must absorb to change its quantum number from 1 to 2. In what region of the spectrum would this be found ? 7

(c) A sample of a diene in methanol in a 1.00 cm cell shows an absorbance of 0.65 at 242.5 nm. What is the concentration of the diene ? The molar absorptivity at this wavelength is 13,100. 7