Bachelor of Science (B.Sc.) Semester–IV Examination

CHEMISTRY (Physical Chemistry) CH-402

Paper—II

Time : Three Hours] [Maximum Marks : 50

Note :— (1) All **FIVE** questions are compulsory and carry equal marks.

(2) Draw diagrams and give chemical equations wherever necessary.

1. (A) Derive Gibb's-Helmholtz equation. The free energy change (ΔG) accompanying a given process is – 88.77 kJ at 298 K and –83.68 kJ at 308 K. Calculate the change in enthalpy (ΔH) for a process at 303 K. 5

(B) Derive relation between standard free energy change (ΔG°) and equilibrium constant (Ka) of the reaction. 5

OR

(C) Calculate the amount of heat supplied to Carnot engine working between 368 K and 288 K if the maximum work obtained is 895 Joules. 2½

(D) Calculate the total entropy change when 5 moles of ice is converted into water at 0°C. The latent heat of fusion of ice is 80 cal gm^{-1}. 2½

(E) Explain physical significance of Gibb's free energy. 2½

(F) State and explain partial molar quantities. 2½

2. (A) Derive expression for ΔH in terms of EMF of a cell and the temperature coefficient of EMF. Calculate the enthalpy change at 298 K for the reaction occurring in the cell :

$Zn \mid 1.0\ M\ ZnCl_2, AgCl(s) \mid Ag.$

The EMF of the cell at 298 K is 0.805 V and $\left(\frac{\partial E}{\partial T}\right)_P$ is -3.98×10^{-4} V/K.

Faraday = 96,500 coulombs. 5

(B) Derive an expression for EMF of a concentration cell with transference.

Calculate the EMF of the following cell at 298 K.

$Pt \mid H_2\ (1\ atm) \mid HCl \mid HCl \mid H_2(1\ atm) \mid Pt$
$(a = 0.001) \qquad (a = 0.1)$

Given, Transference Number of H^+ ion = 0.84. 5

OR

(C) What is galvanic cell ? Explain with reference to the Daniell cell. 2½

(D) Derive Nernst equation for EMF of a cell at 298 K. 2½

(E) What is liquid junction potential ? How can it be eliminated ? 2½

(F) How is pH of a solution calculated by using glass electrode ? 2½

3. (A) Discuss the liquid drop model of nucleus. What are the evidences in its favour ? Give its limitations. 5

(B) Explain orientation of dipoles in an electric field. Discuss the graphical method for determination of dipole moment of a substance. 5

OR

(C) Discuss the nuclear stability on the basis of average binding energy per nucleon and mass number. 2½

(D) Discuss applications of radioisotopes in any two fields. 2½

(E) The internuclear distance in HCl molecule is 1.26 Å if the bond is 17.7% ionic. Calculate its dipole moment. (Given $q = 1.602 \times 10^{-19}$ C). 2½

(F) How is dipole moment measurement used in predicting geometry of triatomic molecules ? 2½

4. (A) Derive an expression for the wave number of rotational lines in a rotational spectrum of rigid rotator.

What is the moment of inertia of a diatomic molecule whose internuclear distance is 150 pm and the reduced mass is 1.5×10^{-27} kg. 5

(B) What are the harmonic and anharmonic oscillators ? Draw their potential energy level diagrams. What is fundamental band and overtones ? 5

OR

(C) Which of the following molecules show pure rotational spectra and why ?

$H_2(g)$, HCl(g), CO(g), $NH_4Cl(s)$. 2½

(D) How do the intensities of rotational spectral lines vary ? 2½

(E) Define force constant. Calculate the force constant of N_2, given that the fundamental frequency is 2.358×10^5 m^{-1}. The reduced mass of N_2 is 1.163×10^{-26} kg. ($C = 3.0 \times 10^8$ ms^{-1}). 2½

(F) Briefly explain the different types of degrees of freedom possessed by linear and non-linear molecules. 2½

5. Attempt any **TEN** questions out of the following :—

(i) What do you mean by efficiency of a system ?

(ii) Define standard free energy change.

(iii) Write integrated form of Van't Hoff equation.

(iv) What is EMF of the cell ?

(v) What do you mean by standard electrode potential ?

(vi) State two advantages of potentiometric titrations.

(vii) Define 'Nuclear Fusion'.

(viii) What is bond moment ?

(ix) When the dipole moment of a molecule is zero, what will be its shape ?

(x) What is zero point energy ? What does it indicate ?

(xi) Write Morse equation.

(xii) Give two examples of infrared-active molecules. 1×10=10