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

CH 402 : CHEMISTRY (Physical Chemistry)

Paper—II

Time—Three Hours] [Maximum Marks—50

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

(2) Give diagrams and chemical equations wherever necessary.

1. (A) What is Carnot cycle ? Derive an expression for efficiency of a reversible Carnot engine working between temperatures T_1 and T_2. 5

(B) Derive van't Hoff's equation upto its integrated form. 5

OR

(C) Derive Gibbs-Helmholtz's equation. 2½

(D) Show that $\Delta G \leq 0$ is criterion for spontaneity and equilibrium. 2½

(E) Calculate the entropy change when one mole of an ideal gas is heated from 300 K to 600 K at constant pressure. The molar heat capacity at constant volume $C_v = \frac{3}{2} R$.

($R = 8.314\ J\ K^{-1}\ mol^{-1}$.) 2½

(F) In the hypothetical reaction $A \rightleftharpoons B$ at 300 K, equilibrium is established when the pressure of the product B is one tenth of that of the reactant A. Calculate ΔG° when A at 1 atm. is converted to B at 1 atm. 2½

2. (A) What do you understand by the EMF of a cell ? How can it be measured experimentally ? The EMF of the cell :

$Cd \mid CdCl_2\ 2.5\ H_2O$ (Sat.) $\| AgCl$ (s) $\mid Ag$ is found to be 0.6753 V at 25° C and 0.6915 V at 0° C. Calculate ΔH of the cell reaction at 25° C. (1F = 96500 coulombs) 5

(B) Explain electrolyte concentration cell with transference with suitable example. At 298 K the EMF of the following cell is 0.027 V. Calculate transport number of H^+ and Cl^- ions.

Pt, H_2 (1 atm.) | HCl (0.008 m) | HCl (0.029 m) | H_2 (1 atm.), Pt. 5

OR

(C) What do you mean by reversible and irreversible cells ? 2½

(D) Derive Nernst equation for EMF of a cell at 25° C. 2½

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

(F) Explain how pH of a solution can be determined using a hydrogen electrode. 2½

3. (A) Define :

(i) Mass defect and

(ii) Binding energy.

Calculate the binding energy per nucleon in helium atom ^4_2He has a mass of 4.0026 amu. Calculated atomic mass is 4.03298 amu. (1 amu = 931.5 MeV) 5

(B) Explain the application of dipole moment in :

(i) Predicting the geometry of molecules and

(ii) Differentiating o, m and p isomers. 5

OR

(C) Compare shell model with Liquid drop model. 2½

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

(E) Explain polarization of molecules in an electric field. 2½

(F) Describe graphical method for determination of dipole moment of a substance. 2½

4. (A) Derive an expression for the wave number of rotational lines in a rotational spectrum. Calculate rotational constant B of HCl molecule if its bond length is 136×10^{-12} m and the atomic masses of H and Cl are 1.673×10^{-27} kg and 58.06×10^{-27} kg respectively.

($h = 6.626 \times 10^{-34}$ JS, $C = 3 \times 10^{8}$ ms^{-1}) 5

(B) What are harmonic and anharmonic oscillators ? Draw their energy level diagrams. Write energy expression for them. 5

OR

(C) Derive an expression for the rotational energy of a diatomic molecule taking it as a rigid rotator. 2½

(D) Explain why do molecules behave as a non-rigid rotor. 2½

(E) Define force constant. Calculate the force constant of N_2, given that the fundamental vibrational frequency is $2.358 \times 10^5\ m^{-1}$. The reduced mass of N_2 is 1.163×10^{-26} kg ($C = 3 \times 10^8\ m\ s^{-1}$) 2½

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

5. Attempt any **TEN** of the following :

(i) Give two statements of second law of thermodynamics.

(ii) Define standard free energy change.

(iii) Define 'Chemical potential'.

(iv) Write the relation between EMF of a cell and equilibrium constant of cell reaction.

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

(vi) State two advantages of potentiometric titrations.

(vii) Define 'Nuclear Fusion'.

(viii) Draw a graph between average binding energy per nucleon and atomic mass number.

(ix) Define 'Bond Moment'.

(x) What types of molecules exhibit rotational spectra ?

(xi) Write Morse equation.

(xii) How the intensity of the rotational spectral lines varies ?`

$10 \times 1 = 10$