

Bachelor of Science (B.Sc.) Semester-IV (C.B.S.) Examination

CHEMISTRY

(Physical Chemistry) CH-402

Paper-II

Time : Three Hours]

[Maximum Marks : 50

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

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

1. (A) Define entropy change. Derive an expression for the calculation of the entropy changes of an ideal gas when the temperature changes from T_1 to T_2 and the pressure changes from P_1 to P_2 . 5
- (B) Define standard free energy change. Derive relation between standard free energy change and equilibrium constant of the reaction. 5

OR

- (C) The free energy changes accompanying a reaction are found to be -75.8 kJ at 298 K and -72.6 kJ at 308 K. Calculate the enthalpy change of the reaction at 303 K. 2½
- (D) Show that $\Delta G \leq 0$ is criteria for spontaneity and equilibrium. 2½
- (E) 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
- (F) State and explain partial molar quantities. 2½
2. (A) What do you understand by the EMF of a cell ? Derive expressions for ΔG , ΔH and ΔS in terms of EMF of a cell and the temperature coefficient of EMF. 5
- (B) What is reference electrode ? Explain how the pH of a solution is determined by using quinhydrone electrode.
Determine the pH of the solution at 25° C from the following data :
Pt, H_2 (1 atm.) | H^+ ($a = x$) || normal calomel electrode.
 $E_{\text{cell}} = 0.6346$ V and $E_{\text{calomel}} = 0.2800$ V. 5

OR

- (C) Describe briefly reversible and irreversible cells. 2½
- (D) Derive Nernst equation for EMF of a cell at 25° C. 2½
- (E) 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. 2½
- (F) Explain how redox titrations are carried out potentiometrically ? 2½
3. (A) What is nuclear fission ? How it is explained by liquid drop model ? Compare nuclear shell model with liquid drop model. 5
- (B) Explain the application of dipole moment in :
(i) Predicting the geometry of molecules and
(ii) Differentiating ortho, meta and para isomers. 5

OR

(C) Calculate the binding energy per nucleon in helium atom ${}^4_2\text{He}$, which has a mass defect 0.03038 amu. 2½

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

(E) The bond distance in H-I is 1.61 Å and its dipole moment is 0.4 D. Calculate the percentage ionic character of H-I bond. (Given $q = 1.602 \times 10^{-19}$ C, $1\text{D} = 3.336 \times 10^{-30}$ cm.) 2½

(F) Explain polarisation of molecules in the electric field. 2½

4. (A) Derive an expression for the rotational energy of a diatomic molecule taking it as a rigid rotator. Calculate the energy in Joules and eV of CO molecule in the first excited rotational level. (Given, Moment of Inertia, $I = 1.46 \times 10^{-46}$ Kg m², $h = 6.626 \times 10^{-34}$ JS, $1\text{eV} = 1.602 \times 10^{-19}$ J) 5

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

OR

(C) What types of molecules exhibit rotational spectra? Out of CO_2 , H_2O , C_6H_6 , NO which will exhibit pure rotational spectra? 2½

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

(E) Calculate the force constant for the bond in HCl from the fact that the fundamental vibrational frequency is $8.667 \times 10^{13} \text{ S}^{-1}$. The atomic masses are $\text{H} = 1.673 \times 10^{-27}$ Kg and $\text{Cl} = 58.06 \times 10^{-27}$ Kg. 2½

(F) What do you understand by normal modes of vibration of a polyatomic molecule? Show diagrammatically the different normal modes of vibration of H_2O molecule. 2½

5. Attempt any **TEN (10)** questions out of the following :

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

(ii) What is the basis of thermodynamic scale of temperature?

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

(iv) What is Galvanic cell?

(v) How is an oxidation-reduction electrode set up?

(vi) What is liquid junction potential?

(vii) Define nuclear fusion.

(viii) What is bond moment and group moment?

(ix) Write any two applications of radioisotopes in structure determination.

(x) What is spectroscopy?

(xi) Why the energy levels of a harmonic oscillator are equally spaced?

(xii) What do you understand by degree of freedom of molecule? 1×10=10