



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.

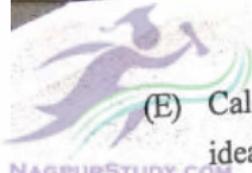
1. (A) What is Carnot cycle ? Derive an expression for efficiency of a reversible Carnot engine working between temperatures T_1 and T_2 . 5

(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 $C_v = \frac{3}{2} R$.

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

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 :

$\text{Cd} | \text{CdCl}_2 \text{ 2.5 H}_2\text{O (Sat.)} || \text{AgCl (s)} | \text{Ag}$ 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 $25^\circ C$. 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. $^4_2 He$ 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 $2.358 \times 10^5 \text{ m}^{-1}$. The reduced mass of N_2 is $1.163 \times 10^{-26} \text{ kg}$ ($C = 3 \times 10^8 \text{ m s}^{-1}$) 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 :

- Give two statements of second law of thermodynamics.
- Define standard free energy change.
- Define 'Chemical potential'.
- Write the relation between EMF of a cell and equilibrium constant of cell reaction.
- What do you mean by standard electrode potential ?
- 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?

$10 \times 1 = 10$