

Bachelor of Science (B.Sc.) Semester—IV (C.B.S.) 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 wherever necessary.

1. (A) Describe carnot cycle. Derive an expression for efficiency of reversible heat engine working between temperatures T_1 and T_2 . 5
- (B) Derive Gibb's—Helmholtz equation. The Gibb's free energy change of a reaction at 300 k and 310 k are – 121 kJ and – 123.5 kJ respectively. Calculate the change in enthalpy for reaction in this temperature range. 5

OR

- (C) Derive an expression for free energy change for n moles of an ideal gas at constant temperature. 2½
- (D) Calculate the change in entropy when 5 moles of an ideal gas expand isothermally at 330 k until its volume has increased to six times the original volume. 2½
- (E) Derive integrated form of Van't Hoff equation showing temperature dependence of equilibrium constant of a reaction. 2½
- (F) Define partial molar free energy and partial molar volume. 2½
2. (A) Derive the relationship between EMF of the cell and heat of cell reaction. The emf of the cell,
 $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{HCl}, || \text{KCl}, \text{Hg}_2\text{Cl}_2 | \text{Hg}$ is 0.2676 V at 298 k and its temperature coefficient is – 0.000319 V k^{-1} . Calculate ΔH for the cell reaction. 5
- (B) What are concentration cells ? Derive an expression for emf of the concentration cells with transference. 5

OR

- (C) What is an electrochemical cell ? Explain with reference to the Daniel cell. 2½
- (D) Derive Nernst equation for the reaction :

$$\text{Zn(s)} + \text{Cu}^{2+} (\text{aq.}) \rightleftharpoons \text{Zn}^{2+} (\text{aq.}) + \text{Cu(s)}. \quad \text{2½}$$
- (E) How pH of the solution can be determined by using glass electrode ? 2½
- (F) Define liquid junction potential. How can it be eliminated ? 2½
3. (A) Explain with suitable examples :
 (i) Nuclear fission and
 (ii) Nuclear fusion.
 Compare shell model with liquid drop model. 5
- (B) Discuss the application of dipole moment in :—
 (i) Determination of geometry of molecules and
 (ii) Differentiating O, M and P-isomers. 5

OR

- (C) Discuss the nuclear stability on the basis of average binding energy per nucleon and mass number. 2½
- (D) Write a note on carbon dating. 2½
- (E) Explain polarization of molecules in an electric field. 2½
- (F) Calculate the percentage ionic character of Li – H bond, if its observed dipole moment is 1.963×10^{-29} C on and the bond length is 1.595 Å.
(Given, $q = 1.6 \times 10^{-19}$ C). 2½
4. (A) Derive an expression of rotational energy of a diatomic molecule. Draw rotational energy levels for $J = 0, 1, 2$ and 3. 5
- (B) Discuss IR spectrum of diatomic molecule considering it as a simple harmonic oscillator. Calculate the force constant of N_2 , given that the fundamental vibrational frequency is 2.358×10^5 m⁻¹. The reduced mass of N_2 is 1.163×10^{-26} kg. 5
- OR**
- (C) What do you understand by non-rigid rotor ? Explain how its spectra differs from rigid rotor. 2½
- (D) The pure rotational spectrum of a gaseous molecule consist of series of equally spaced lines separated by 3.7978 cm⁻¹. Calculate moment of inertia of a molecule. 2½
- (E) Discuss normal modes of vibration in H₂O molecule. 2½
- (F) What are anharmonic oscillators ? Explain energy level diagram. 2½
5. Solve any **TEN** of the following :—
- (i) Give limitations of First law of thermodynamics.
 - (ii) What is criteria of spontaneity and equilibrium in terms of entropy change ?
 - (iii) What is the relationship between free energy change and equilibrium constant ?
 - (iv) What are irreversible cells ?
 - (v) What is standard electrode potential ?
 - (vi) Mention any two advantages of potentiometric titrations.
 - (vii) What is mass defect ? How is it related to binding energy of the nucleus ?
 - (viii) Write Clausis—Mosotti equation.
 - (ix) Calculate the dipole moment of HCl molecule if the equilibrium bond-length is 1.2746 Å
($q = 1.602 \times 10^{-19}$ C).
 - (x) What are electromagnetic radiations ?
 - (xi) What type of molecules will give potational spectra ?
 - (xii) Calculate the wave number of a spectral line of wave length 930 nm. 1×10=10