

**Fourth Semester Bachelor of Science (B. Sc.)  
Examination**



**PHYSICAL CHEMISTRY**

**Paper – II (CH – 402)**

Time : Three Hours ]

[ Max. Marks : 50

- N. B. :** (1) All Five questions are compulsory and carry equal marks.  
(2) Draw diagrams wherever necessary.

1. (A) Derive an expression of work-done in Carnot Cycle. 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. Determine the change in enthalpy for the reaction in this temperature range. 5

**OR**

(C) Give any five statements of 2<sup>nd</sup> Law of thermodynamics. 2  $\frac{1}{2}$

(D) Starting from the equation  $\Delta G^0 = -RT/nk_p$  derive the integrated form of Van't Hoff's equation. 2  $\frac{1}{2}$

(E) Calculate the entropy change when 2 moles of an ideal gas is allowed to expand at 300 K, from pressure of 10 atm to 2 atm. 2  $\frac{1}{2}$

(F) (i) Define partial molar free energy.

(ii) Write the relationship between  $\Delta G$  and  $\Delta A$ . 2  $\frac{1}{2}$

- (A) Derive Nernst equation for emf of a cell at  $25^{\circ}\text{C}$ .  
How can the equilibrium constant of a cell reaction be calculated from emf ? 5
- (B) Derive the relations :  
(i) Between emf and change in free energy of a cell reaction.  
(ii) Between emf and heat of reaction. 5

OR

- (C) Discuss briefly reversible and irreversible cells.  $2\frac{1}{2}$
- (D) Derive an expression for the emf of a concentration cell without transference.  $2\frac{1}{2}$
- (E) The emf of the cell using quinhydrone electrode was found to be 0.264 V at  $25^{\circ}\text{C}$ . Calculate the  $\text{pH}$  of solution.  
(Given :  $E^{\circ}_{\text{SCE}}$  (reduction) = 0.2415 V and  $E^{\circ}_{\text{Q}}$  (oxidation) = - 0.6994 V).  $2\frac{1}{2}$
- (F) What is salt bridge ? What are its functions ?  $2\frac{1}{2}$

3. (A) Define :

- (i) Mass defect.  
(ii) Binding Energy and  
(iii) Binding Energy per nucleon.

Calculate the binding energy per nucleon of  $^{16}_8\text{O}$ , whose mass defect is 0.1370148 amu. 5

(B) What is dipole moment ? How is it used to

calculate the percentage ionic character of a covalent bond ?

Calculate the percentage ionic

character of Li - H bond. If its observed dipole moment is  $1.963 \times 10^{-29}$  Cm. and the bond length is  $1.595 \text{ \AA}$ .

(Given :  $q = 1.6 \times 10^{-19} \text{ C}$ ) 5

OR

- (C) Give the applications of radioisotopes in medical science and agriculture.  $2\frac{1}{2}$
- (D) How ortho, meta and para substituted isomers of Benzene can be distinguished from dipole moment measurements ?  $2\frac{1}{2}$
- (E) Compare nuclear shell model with liquid drop model.  $2\frac{1}{2}$
- (F) Explain polarisation of molecules in the electric field.  $2\frac{1}{2}$

4. (A) What is the relationship between dipole moment and Rotational Spectra ?  
Derive an expression of rotational energy of diatomic molecule by considering it as rigid rotor. 5

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

OR

- (C) The rotational constant of NO molecule is  $166 \text{ m}^{-1}$ . Calculate bond length if its reduced mass is  $1.24 \times 10^{-26} \text{ kg}$ .  $2\frac{1}{2}$
- (D) Calculate number of modes of Vibrations in  $\text{CO}_2$  molecule. How can they be represented

$2\frac{1}{2}$

(E) Amongst  $\text{H}_2(\text{g})$ ,  $\text{CO}(\text{g})$ ,  $\text{HCl}(\text{g})$ ,  $\text{NH}_4\text{Cl}(\text{s})$  and  $\text{H}_2\text{O}(\text{g})$ , which molecules will give pure rotational Spectra.  $2\frac{1}{2}$

(F) (i) What do you know about non-rigid rotor ?

(ii) What is force constant ?

$2\frac{1}{2}$

5. Solve any ten of the following :—

(i) What are the limitations of 1<sup>st</sup> Law of thermodynamics ?

(ii) Give the criteria of thermodynamic equilibrium in terms of free energy.

(iii) Give an expression of Van't Hoffs reaction isotherm.

(iv) What is emf of the cell ?

(v) Give the reduction half cell reaction of calomel electrode.

(vi) What is liquid junction potential ?

(vii) What is bond moment and group moment ?

(viii) Explain nuclear fission with one example.

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

(x) Draw rotational energy level diagram.

(xi) Write Morse equation and explain the terms involved in it.

(xii) What is the selection rule for the transition between rotational energy levels ?  $1 \times 12 = 12$