2022 B.A./B.Sc. **Fifth Semester** CORE - 12**CHEMISTRY** Course Code: CHC 5.21 (Physical Chemistry-V)

Total Mark: 70 Time: 3 hours

Pass Mark: 28

Answer five questions, taking one from each unit.

UNIT-I

| 1. | (a) | How does the liquid junction potential relate to the transport number of ions t^+ and t^- . Explain with relevant mathematical expressions. | 5 |
|----|-----|--|---|
| | (b) | Explain why Walden rule is valid more accurately in larger ions than | , |
| | | that of smaller ions. | 3 |
| | (c) | What does it mean by relaxation effect? | 3 |
| | (d) | Write a short essay on concentration cells without transference with a | a |
| | | relevant example. | 3 |
| 2. | (a) | Discuss the principle underlying conductometric titrations. How would you carry out conductometric titrations of a strong acid versus strong base. $2+4=6$ | |
| | (b) | Calculate the mean activity coefficient Υ_2 of NaCl at the molality of | |
| | | 0.01 m. | 4 |
| | (c) | How does the solubility product help us to predict the precipitation | |
| | | reaction. | 2 |
| | (d) | Explain the term ionic product of water. | 2 |
| | | UNIT H | |

UNIT-II

| 3. | (a) | What are redox electrodes? Explain with suitable examples. | 4 |
|----|-----|---|---|
| | (b) | Explain the cell reactions taking place in a calomel electrode in the | |
| | | electric field. | 4 |

(c) The EMF of the cell Cd, $CdCl_2 2.5H_2O$ saturated II AgCl(s), Ag in which the cell reaction in

 $Cd(s)+2AgCl(s)+aq \Rightarrow CdCl_2.5/2H_2O+(satu)+2Ag(s)$

in 0.6753 V at 25°C at 0.6915 V at 0°C. Calculate the free energy change and enthalpy of the cell reaction at 25°C. 4

- (d) Give an example each of the following: 1+1=2
 - (i) Metal-amalgam electrode
 - (ii) Metal-metal insoluble salt electrode
- 4. (a) What is Helmholtz Perrin model? Why is it also known as parallel plate condenser model? 3+2=5
 - (b) Write a short essay on electro catalysis and its applications. 3

 $3 \times 2 = 6$

- (c) Write a short note on the following:
 - (i) Quinone-hydroquinone electrodes
 - (ii) Glass electrode
 - (iii) Hydrogen electrode

UNIT-III

| 5. | (a) | Write short notes on the following: | 3×3=9 |
|----|-----|---|--------|
| | | (i) Symmetric and anti-symmetric nature of BMO and a BM | 0 |
| | | (ii) Need of approximation techniques | |
| | | (iii) Paramagnetic nature of oxygen molecule | |
| | (b) | Outline the solution of the Schrödinger equation for H_2^+ ion. S | ketch |
| | | the BMO and ABMO with respect to electron density on the | bond |
| | | axis. | 5 |
| 6. | (a) | Construct a MO wave function for the bond between H and C | Cl in |
| | | HCl assuming that the bond is formed from the 1s electron of | Hatom |
| | | and 3p electron of Cl atom. | 4 |
| | (b) | Explain the paramagnetic nature of oxygen along with its appli- | cation |
| | | in medical and war field. | 4 |
| | (c) | Write a short essay on the need of approximation techniques in | n |
| | | quantum mechanics. | 4 |
| | (d) | Give a comparison of MO and VB theory. | 2 |

UNIT-IV

| 7. | (a) | Give a statement of Frank quantum principle. Explain the principle | |
|--------|-----|---|----|
| | | for the electronic transition of a diatomic molecule. 1+4 | =5 |
| | (b) | Write short notes on the following: $3+3=$ | =6 |
| | | (i) Free electron model of polyenes | |
| | | (ii) Larmor precision | |
| | (c) | Using the free electron modal theory, estimate wave number of the | |
| | | lowest energy transition in the 1,3,5-hexatriene molecule. | 3 |
| 8. | (a) | Explain the singlet and triplets states in electronic transition. | 4 |
| | (b) | Discuss the spin-spin interaction in NMR. | 4 |
| | (c) | Explain the hyperfine structure of methyl radical using ESR spectra | |
| | | | 4 |
| | (d) | Calculate the ESR frequency of an unpaired electron in a magnetic | |
| | | field of 0.33 T given that for the free electron $g_{a}=2$ and | |
| | | $\mu B = 9.273 \times 10^{-24} \text{ J/T.}$ | 2 |
| UNIT-V | | | |

| 9. | (a) | Write short notes on the following with supporting formulae: 3×3 | =9 |
|-----|-----|---|---------|
| | | (i) Molar extension coefficient | |
| | | (ii) Photochemical rate law | |
| | | (iii) Integrated absorption coefficient | |
| | (b) | Explain why the quenching of florescence occurs. | 3 |
| | (c) | Explain the term electromagnetic radiation. | 2 |
| 10. | (a) | Explain the reasons for low and high quantum yield in photochemic reaction. | al 4 |
| | (b) | Derive the photochemical rate law in terms of Lambert-Beer law. | 5 |
| | · / | What does it mean by bioluminescent reaction? Explain with suitab | ole |
| | | example. | 3 |
| | (d) | What is meant by photosensitization reaction? | 2 |