**PAPER VI**

**Spectroscopy**

1. Why is molecular spectra considered more complicated than atomic spectra?

2. Why does molecular spectra appear as a band?

3. What are the different types of molecular spectra?

4. What kind of effects on molecules can be expected when molecules absorb radiation in (i) visible region 9ii) infra ared region?

5. Name the region of the spectrum associated with the change in (i) electronic state (ii) vibration state (iii) rotational state.

6. What is an important requirement for a molecule to be microwave-active? Name a molecule which is (i) microwave active and (ii) microwave inactive.

7. Write the expression for vibrational energy of a diatomic molecule at v=0

8. What is meant by selection rule?

9. Name the types of molecular spectra? In which range of wavelength EM spectra is found?

10. Define zero point energy.

11. State Hooks law.

12. In which region of electromagnetic spectrum is vibrational spectra observed and why?

13. What is meant by force constant? What is its significance?

14. Write an expression for the vibrational energy and the vibrational frequency in wave numbers.

15. What is the selection rule for (i) rotational (ii) vibrational transitions?

16. What is zero point energy? What does it signify?

17. Write the expression for zero point energy and force constant of a diatomic molecule. Explain their significance.

18. What is an important requirement for a molecule to be IR active?

19. How are the vibrational energy levels spaced if a molecule is assumed to be perfectly harmonic?

20. What is meant by anharmonicity?

21. Define the terms (a) fundamentals (b) overtones

22. How is IR spectra useful for closely spaced lines in IR spectra even though the vibrational transitions of a diatomic molecule is supposed to give a single line?

23. How do you account for a diatomic molecule is supposed to give a single line?

24. Write the general expression for energy change involved in vibration spectra in which 

25. Name the region in EM spectra in which vibration spectra and rotational spectra occur?

26. Name any two modes of vibration in a polyatomic molecule other than stretching.

27. What are the total number of modes of vibration in a (i) linear (ii) non-linear polyatomic molecule?

28. Calculate the total number of modes of vibration for (i) methane (ii) benzene (iii) carbon tetrachloride molecules.

29. Calculate the total number of modes of vibration for (i) CO2 and ii) H2O molecules.

30. CO2 and H2O molecules are both triatomic but the number of modes of vibration are different, explain.

31. Sketch the normal modes of vibration in water molecule and indicate the IR active ones.

32. Sketch the normal modes of vibration in carbon dioxide molecule. Which of these are IR active? How many fundamental vibrational frequencies does this molecule have? Why?

33. How is Raman spectroscopy different from IR spectroscopy?

34. What is Raman shift?

35. What is meant by (i) elastic collision (ii) inelastic collision?

36. How are stokes lines and anti-stokes lines formed? How are their frequencies related to frequency of incident radiation?

37. Explain Raman spectra in detail.

38. How do you account for a weaker intensity of anti-Stokes lines as compared to Stokes lines?

39. What are the conditions for a molecule to be 9a) IR active (b) Raman active?

40. Define the rule of mutual exclusion.

41. IR and Raman spectral data together provide valuable information about the structure of the molecule-justify.

42. Write a brief note on applications of Raman spectra.

43. Chlorine is IR inactive whereas HCl is IR active. Why?

44. In what region of electromagnetic spectrum are the vibration-rotation spectral lines observed?

45. What other transitions accompany an electronic transition?

46. State Franck-Condon principle.

47. How do you explain the presence of an intense vibrational spectral line in electronic spectra though all vibrational transitions are equally probable.

48. Draw a neat sketch and explain Franck-Condon principle.

49. Give the relation between force constant and vibration frequency.

50. Explain the terms (i) allowed transition (ii) forbidden transition.

51. Define the term a) diffusion current b) half wave potential

52. Give any two applications of polarography.

53. Write 2 advantages of dropping mercury Electrode (DME)

54. Using suitable diagram indicate Raman transition.

**Essay type questions**

1. What are the different types of molecular spectra? In which region of electromagnetic spectrum are they found? What information regarding molecular structure is obtained in each case?
2. Using energy level diagram account for the formation of (i) rotation spectra (ii) vibration-rotation spectra (iii) electronic spectra.
3. Explain the requirements for a molecule to be (i) microwave active (ii) IR active (iii) Raman active.
4. Write the differences between Raman and IR spectra?
5. What are the selection rule for Raman spectra?
6. Show that in a rotational spectrum, the spectral lines are equally spaced.
7. Derive an expression for the vibrational energy levels in terms of vibrational quantum number.
8. Sketch the energy levels for a perfect harmonic oscillator and for a typical diatomic molecule. Explain the anharmonic behavior of a diatomic molecule.
9. What are (i) fundamentals (ii) overtones and (iii) hot bands? Explain.
10. Write a note on the applications of the IR spectra.
11. What are PQR bands? Explain with a neat diagram.
12. Discuss the origin of Raman spectra. Explain the terms

(i) Rayleigh scattering

(ii) Stokes lines

(iii) anti-Stokes lines.

1. Give the general characteristics of Raman lines.
2. Explain the mutual exclusion rule taking examples CO2 and H2O.
3. Give the differences between IR and Raman spectra.
4. What are the advantages of Raman spectra over conventional IR spectra.

**Problems**

1. The pure rotational spectra of HCl has equidistant lines at 2110 m-1. What is the moment of inertia of the molecule? H=6.626X10-34 Js, c=3X108 ms-1.
2. The internuclear distance in CO is 1.23X10-12 m. Calculate the energy in joules of this molecule in the first excited rotational level. The reduced mass of CO is 1.14X10-26 kg and h=6.626X10-34 Js.
3. Calculate the wave number of fundamental vibration due to C=O group. The force constant is 1840 Nm-1.[atomic mass of C= 2x10-26kg,O=2.7x10-26kg]
4. The redused mass of diatomic molecule is 2.5 x10-26kg and its vibrational frequency is 29x104m-1.Calculate its force constant.
5. The vibrational-rotational spectrum of HBr shows an absorption and band centered at 2.652X105m-1. Calculate the force constant given that C=3x108ms-1 and reduced mass of HBr is 1.64X10-27kg.
6. The force constant of HBr is 410Nm-1. The moment of inertia is 2.5X10-27 kg m2. The internuclear distance is 0.128nm. Calculate the frequency of vibration of HBr given c=3X108 ms-1.

 **V SEMESTER-PHYSICAL CHEMISTRY (PAPER VI)**

 **TWO MARKS QUESTIONS:**

1. Define molar conductance. Give its SI units.
2. Give the relation between e.m.f and free energy change.Explain the terms involved in it.
3. What is an electrochemical cell? Give an example.
4. What is transport number of an anion and cation.
5. Write any two advantages of glass electrode.
6. Give any two limitations of glass electrode.
7. Explain the effect of dilution on molar conductance of a weak electrolyte.
8. Write any two advantages of conductometric titrations.
9. Write Debye-Huckel-Onsager equation and explain the terms.
10. Define specific conductance. Give the SI units.
11. Write any two limitations of Arrhenius theory of electrolytic dissociation.
12. What is abnormal transport number?
13. Define equivalent conductance. Give its SI units.
14. Explain the effect of dilution on specific conductance and equivalent conductance of weak electrolyte.
15. Give an example for a primary reference electrode. Represent it symbolically.
16. State Kohlrausch law of independent migration of ions.
17. Give any two advantages of potentiometric titrations.
18. Explain asymmetric effect.
19. Explain electrophoretic effect.
20. Define specific conductance. How does it vary with dilution?
21. What are concentration cells?
22. Mention two limitations of S.H.E.
23. Write the Nernst’s equation for single electrode potential and explain the terms in it.
24. What is meant by cell constant of a conductivity cell?
25. Why is Weston Cadmium cell used as a standard cell?
26. Define standard electrode potential.
27. Write a short note on potentiometric titrations.
28. What is meant by liquid junction potential? How can it be minimised?
29. Give two disadvantages of Quinhydrone electrode.
30. What are concentration cells?
31. Explain the principle behind the potentiometric titrations.
32. Give an example each for: i) gas ion electrode ii) metal-insoluble salt/anion electrode.
33. Why is the transport number of cadmium ion in cadmium iodide abnormal at high concentrations?
34. What is a salt bridge? Mention its function.
35. Write an expression for the e.m.f of a concentration cell?
36. Name a primary and a secondary reference electrode.
37. What is the value of S.H.E at 300k?
38. What is the use of salt bridge in an electrochemical cell?
39. How is free energy change of a reaction related to the cell potential of the galvanic cell?
40. Write the cell reaction for the cell, cd/cd2+(0.1M) // Ag+(0.1M)/Ag
41. Why direct current is not used in conductance measurement/
42. Give reason: CdI2 is chosen as an indicator electrolyte in the determination of transport number of H+ ion in HCl.
43. Why Zn displaces cu from CuSO4 solution?
44. Give reason: Zn is better reducing agent than Cu.
45. Why quinhydrone electrode can not be used to determine PH of solutions > 10?
46. Give any two advantages of potentiometric titrations.
47. Why transport number of Cl¯ ion is not the same in the electrolytic solution of KCl and HCl?
48. What is a redox electrode? Give an example.
49. What is a gas – ion electrode? Give an example.
50. Give reason: Lithium is lighter than sodium but has a lower transport number.

 **FOUR MARKS QUESTIONS:**

1. Describe the conductometric titration of strong acid v/s strong base.
2. Explain Debye-Huckel theory of strong electrolytes.
3. How the solubility of a sparingly soluble salt is determined by conductivity method?
4. How is PH of a solution determined by using quinhydrone electrode?
5. Describe the construction and working of Weston cadmium cell.
6. Explain conductometric titration of strong acid with weak base.
7. Describe the moving boundary method of determining the transport number of H+ ion in HCl solution.
8. How is the molar conductance of 0.01N sodium chloride solution determined by conductivity method?
9. Describe the construction of calomel electrode. Write the electrode reaction
10. State Kohlrausch’s law of ionic conductance. Mention its applications.
11. How is the potential (E0) of a zinc electrode determined. Explain.
12. Explain the determination of potential of copper electrode by coupling with S.H.E. write electrode reactions.
13. Derive Nernst equation for the electrode potential of an electrode system thermodynamically.
14. Describe the experimental determination of specific conductance of 0.1 M sodium

 nitrate solution.

1. Draw a neat labeled diagram of a Weston cadmium standard cell and write its cell reaction.
2. Explain conductometric titration of weak acid with strong base.
3. State and explain Kohlrausch law of ionic mobility, explain its application in determining degree of dissociation of a weak electrolyte.
4. Describe the experimental determination of e.m.f of a cell by compensation method.
5. Describe the determination PH of a solution using hydrogen electrode and calomel electrode.
6. What are concentration cells? How concentration cells are used to determine the solubility of AgCl in water?
7. How is the of potential of Zinc electrode calculated by coupling with hydrogen electrode. Write electrode reactions.
8. Represent Daniel cell symbolically and write electrode reactions and e.m.f expression.
9. Represent the cell symbolically formed by coupling copper and hydrogen electrodes. Write electrode reactions and sign of the copper electrode.
10. Explain the construction and working of S.H.E . How is the PH of an unknown solution determined using S.H.E?
11. Explain conductometric titration of weak acid with weak base

 **PROBLEMS:**

1. In a conductivity cell, the cell constant is 217 m-1. Concentration of electrolyte is 137 mol m-3 was found to have a conductance of 6.5x 10-3. Calculate molar conductivity (2m)
2. The specific conductivity of saturated solution of BaCl2 is 3.06x10-4sm-1. If molar conductance at infinity dilution is 14.3x10-3sm2mol-1. What is the solubility of BaCl2 (2M)
3. Calculate the molar conductance at infinite dilution of monochloroacetic acid from given data: λ∞ NaCl= 12.6x10-3sm-2mol-1, λ∞ ClCH2COONa=9x10-3sm2mol-1 and λ∞HCl= 42.6x10-3sm2mol-1
4. Calculate the resistance of 0.1 M NaCl solution whose specific conductance is

1.12 sm-1 and cell constant is 1.01m-1(2M)

1. The specific conductance of a saturated solution of BaSO4 after substracting that of water is 1.133x10-3sm-1. Calculate the solubility of BaSO4. Given molar conductance of BaSO4 at infinite dilution is 1.44x10-2sm2mol-1(2M)
2. A solution of specific conductance is 1.35sm-1 is placed in a conductivity cell. The resistance of solution is found to be 160.8Ω Calculate the cell constant(2M)
3. Molar conductance of HCl, NaCl and CH3COONa at infinite dilution are 4.2616x10-2, 1.2645x10-2 and 9.1x10-3 sm2mol-1 respectively. Calculate the degree of dissociation of 0.01 M acetic acid solution. The molar conductance of acetic acid at 0.01 M is 1.58X10-3 sm2mol-1
4. Cell constant of a conductivity cell is 103m-1. If the resistance of 0.2 moldm-3 solution of a salt placed in its cell is 50Ω at 298k, calculate specific conductance and molar conductance of the electrolyte.
5. Molar ionic conductances at infinite dilution of Na+ and Cl¯ ions are

50.11x10-4sm2mol-1 and 76.34x10-4sm2mol-1 respectively.

1. Calculate the equivalent conductance at 200 C of NH4OH at infinite dilution.

Given: λ∞ (NH4Cl) =130X10-4 sm2eq-1

 λ∞ (OH-1) =174X10-4 sm2eq-1

 λ∞ (Cl¯ ) = 66X10-4 sm2eq-1

1. Calculate emf of the cell Zn/Zn2+(0.05 MǁZn2+(0.25M)/Zn at 298k.
2. The standard reduction potentials of Ag/Ag+ and Cu+2/Cu electrodes are 0.8V and +0.34V respectively. Write the cell reaction and calculate e.m.f of the cell
3. Molar conductance of HCl, NaCl and CH3COONa at infinite dilution are

425x10-4sm2mol-1,125x10-4sm2mol-1 and 91x10-4 sm2mol-1 respectively. Calculate the degree of dissociation of 0.01M acetic acid solution. Molar conductance of 0.01M acetic acid is 16.3X10-4Sm2mol-1.

1. Calculate the electrode potential of the half cell Zn/Zn2+ at 298k.

Given[Zn2+ ]=1x10-3 M, E0Zn= - 0.76V.

1. In a moving boundary method 0.1 N HCl placed in a cell having cross section of area 1.15x10-4 m2 on passing 0.0012 faraday current, the boundary moved a distance of 0.075m, calculate the transport number of cation.
2. The standard reduction potentials of Zn and Cu electrodes are - 0.76V and + 0.34V respectively. Find the free energy change for the spontaneous cell reaction.
3. Find the solubility of AgCl in 0.01M KCl solution. The solubility product of AgCl is 1.44x10-10 at a given temperature.
4. Calculate the dissociation constant at a concentration of a 1:1 weak organic acid whose molar conductance at a concentration of 4 mol m-3 is 0.035m2 mol-1. Its molar conductance at infinite dilution is 4x10-2sm2mol-1.
5. Calculate the electrode potential of zinc electrode dipped in 1.5M ZnSO4 solution at 298k. E0Zn2+ / Zn= - 0.76V
6. λ∞Values of NaCl, NH4Cl, and NaOH are respectively.12.6x10-3,15x10-3 and

 24.81x10-3Sm2 mol-1. Calculate λ∞ for NH4OH.

1. A solution of specific conductance 1.4sm-1 was placed in a conductivity cell. The

 resistance of the solution was found to be 160Ω. Calculate the cell constant.

1. For the cell Cd ׀Cd2+ (1M) ǁ Cu2+ (1M) ׀ Cu , calculate the EMF and the free energy change for the above cell reaction. GivenE0cd=-0.403V and E0Cu = 0.340V
2. The hydrogen electrode dipped in a solution of unknown PH is coupled with a saturated calomel electrode. The emf of the cell was found to be 0.46V. Calculate PH of the solution, if E0 calomel = 0.242V.
3. Molar ionic conductance at infinite dilution of Na+ and Cl- ions are

50.11x10-4 sm2mol-1 and 76.34x10-4 sm2 mol-1 respectively. Calculate the transport number of Na+ ion.

1. A solution having a resistance of 50 ohm was placed in a conductivity cell having a cell constant of 221m-1, calculate its specific conductance.
2. Calculate the resistance of 0.1M KCl solution whose specific conductance is

 1.33x10-3 sm-1(cell constant is 1.6m-1)

1. The specific conductance of a saturated solution of SrSO4 after substracting that of water is 1.33x10-3 sm-1.calculate the solubility of SrSO4 (molar conductance of SrSO4 at infinite dilution is 1.392x10-2 sm2mol-1)
2. Calculate the emf of the following cell at 298k Pb/Pb2+ (0.01M) // Cu2+ (0.05M) / Cu

(E0 of pb2+ is = -0.13V and E0 of cu2+ is = +0.34V)

1. A solution of an electrolyte has a specific conductance of 1.8sm-1, when placed in a conductivity cell at 298k. The resistance of the solution was found to be 160 ohms. Calculate the cell constant.
2. Calculate the free energy change for a Daniel cell having the emf of 1.1V at 298k, the cell reaction is Zn(s) + Cu 2+(aq) Cu(s) + Zn2+ (aq) (1F=96500C)
3. The equivalent conductance of a decimolar CH3COOH solution was found to be 1.58x10-3 sm2 eq-1 at a given temperature. Calculate the degree of dissociation of acetic acid.
4. In a moving boundary experiment with 1M KCl using CdCl2 as indicator, a current of 0.0115A was passed for 30 minutes and the boundary moved through a volume 1.06x10-7 m3. Calculate the transport number of K+ion.

**Ionic Equilibrium**

**Two mark questions**

1. Account for the following:
i) Aqueous solution of sodium chloride is neutral to litmus.
ii) Aqueous solution of sodium acetate is basic to litmus.
2. What is the effect of dilution and temperature on the degree of hydrolysis the salt formed from weak acid and weak base? or on the hydrolysis of ammonium acetate
3. State and explain common ion effect with an example.
4. Define solubility product and ionic product or Give the differences between solu- bility product and ionic product
5. Based on the magnitudes of Ksp and Ionic product values of a salt solution, how the prediction of saturated, supersaturated and undersaturated solution can be made?
6. Why is ammonium chloride added in excess prior to ammonium hydroxide during the detection of third group basic radicals in the inorganic qualitative analysis?

**Four mark questions**

1. Define
i) Hydrolysis ii) Degree of hydrolysis of salts iii) Ionic product of water
2. Derive a relation between hydrolysis constant(Kh), ionic product of water Kw and dissociation constants of acid and bases in the hydrolysis of the salt formed from weak acid vs. weak base(Ka and Kb), and an expression for the degree of hydrolysis.
3. Derive the relation: pH = 7 + 1/2 pKa + 1/2 pKb in the case of salt hydrolysis of weak acid and weak base.
4. Account for the following
i) Silver and lead are precipited by hydrogen sulphide gas in acid medium where as Zinc and manganese is precipitated in basic medium with the same hydrogen sulphide gas.
ii) Ammonium chloride and ammonium hydroxide are added before passing hydrogen sulphide to the salt solutions of IV group basic radicals.
5. What are buffer solutions? Give an example each for an acidic, basic and a neutral buffers.
6. What is meant by Buffer action? Explain the buffer action of an acidic buffer.
7. Explain the buffer action of a basic buffer- NH4OH + NH4Cl
8. Derive Henderson’s equation for an acidic buffer
9. Derive Henderson’s equation for an basic buffer
10. Write a note on Analytical and biological applications of buffers
11. What are Indicators. Explain acid base theory of indicators with phenolphthalein as example.

**Physical Properties and Molecular Structure**

**Two mark questions**

1. Define polarization.
2. What are polar and non-polar molecules? Give two examples for each.
3. Define dipole moment.
4. The dipole moment of HF,HCl, HBr and HI are 2,1.3, 0.8 and 0.4 Debye. Arrange them in the increasing order of polar character.
5. p-dichlorobenzene has a zero dipole moment where p-dihydroxy benzene has a net dipole moment of 1.64D. Give reason.
6. Chloroform has a permanent dipole moment while carbon tetrachloride does not have. Explain
7. Explain why CO2 has a zero dipole moment and SO2 has a positive dipole-moment(2)
8. Write the structure of dichloroethene which has zero dipole moment.
9. Maleic acid possesses a permanent dipole moment but not fumaric acid. Explain.
10. Write a note on applications of dipole moment.
11. What is meant by induced dipolemoment?
12. Write Clausius-Mosotti equation and indicate the terms involved
13. Explain the term Magnetic susceptibility.
14. What is paramagnetism? What are the factors contributing to paramagnetism in a substance?
15. What are paramagnetic and diamagnetic substances? Give two example each.
16. What are ferro magnetic substances? Mention their characteristics.
17. What is the effect of temperature on the paramagnetic property of a substance?
18. Explain the significance of curie temperature.
19. What is peltier effect?

**Four mark questions**

1. Explain Seebeck effect and Thomson effect with examples?
2. What are semi conductors? Give examples
3. Explain the following with examples: i) Piezo electricity, ii) Inverse Piezo electricity
4. Write a note on: i) Ferroelectricity and ii) Pyroelectricity
5. Give the characteristics of paramagnetic and diamagnetic substances.
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