Date:

Register number:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
B.Sc. CHEMISTRY - V SEMESTER
SEMESTER EXAMINATION: OCTOBER 2019
CH 5215: PHYSICAL CHEMISTRY

Time - 2 ½ Hours **Max Marks - 70**

This paper contains **THREE** printed pages, **THREE** parts and **21** questions.

PART A

Answer any **SIX** of the following questions. **6 X 2 = 12 marks**

1. Define molar conductance. Write its SI unit.
2. The molar ionic conductances of Na^+ and Cl^- at infinite dilution are 50.11×10^{-4} and 76.34×10^{-4} Sm^2/mol respectively. Calculate the transport number of Na^+ ion.
3. Write the relation between EMF of a cell and free energy change. Explain the terms.
4. What is electrolyte-concentration cell? Write its cell notation.
5. What is zero-point energy? Write an equation for it in terms of frequency.
6. Name the spectroscopy associated with the following regions of the electromagnetic spectrum.
   a) Infrared waves
   b) Microwaves
7. What is a photosensitizer? Explain with an example.
8. Mention any two differences between IR and Raman spectroscopy.

PART B

Answer any **EIGHT** of the following questions. **8 X 6 = 48 marks**

9. a) What is asymmetric effect?

   b) State Kohlrausch's law of independent migration of ions. Using this law, calculate the molar conductance of NH_4OH at infinite dilution, given molar conductances at infinite dilution of NH_4Cl, NaCl and NaOH are 14.49×10^{-3} Sm^2/mol, 12.65×10^{-3} Sm^2/mol and 24.76×10^{-3} Sm^2/mol respectively. (2+4)
10. A conductance cell has two parallel electrodes of area of cross section 1.2×10^{-4} m^2 and 0.11 m apart. When filled with the 0.1 M solution of an electrolyte, the resistance

of the solution was found to be 1800 ohm. Calculate (i) cell constant (ii) specific conductance (iii) molar conductance.

11. a) Mention any two advantages of conductometric titrations.

    b) Draw and explain the conductometric titration curve for the following with suitable examples, taking the acid in the conductivity cell and base in the burette.

    (i) strong acid vs strong base

    (ii) weak acid vs strong base (2+4)

12. a) What is single electrode potential?

    b) Explain the construction and working of standard hydrogen electrode. (2+4)

13. a) Write an expression for Born-Oppenheimer approximation.

    b) Sketch the modes of vibration for CO_2 molecule. Identify the IR active modes of vibration of this molecule. (2+4)

14. a) What is quinhydrone electrode? Write any one of its limitations.

    b) Derive the relationship between the electrode potential of quinhydrone electrode and pH of the solution. (2+4)

15. a) State Hooke's law.

    b) Far infrared spectrum of HI consists of series of equally spaced lines with spacing equal to 12.8 cm^{-1}. Calculate a) moment of inertia b) inter-nuclear distance. The atomic masses of H and I are 1.6735 x 10^{-27} kg and 210.72 x 10^{-27} kg respectively. (2+4)

16. Explain Rayleigh's lines, Stoke's lines and anti-Stoke's lines using energy level diagram.

17. Explain with the help of a reaction mechanism, why the quantum efficiency of photochemical reaction between H_2 and Cl_2 is very high but that of reaction between H_2 and Br_2 is low.

18. a) Write an expression for Raman shift in cm^{-1}. (2+4)

    b) Draw a neat Jablonski diagram and label the various photochemical processes.

PART C

Answer any **TWO** of the following questions. **2 X 5 = 10 marks**

19. The hydrogen halides have following fundamental vibrational frequencies and reduced mass.

Hydrogen halides	Vibrational frequencies (cm^{-1})	Reduced mass (kg)
HF	4141.3	1.5897 x 10^{-27}
$H^{35}Cl$	2988.9	1.6271 x 10^{-27}
$H^{81}Br$	2649.7	1.6534 x 10^{-27}

Find the force constant for HF, $H^{35}Cl$ and $H^{81}Br$. Arrange the hydrogen halides in the increasing order of their bond strength.

20. Given below is the electrochemical series of few electrodes. Based on this table answer the questions that follow.

Electrode	Standard reduction potential (V)
Mg^{2+}, Mg	-2.52
Zn^{2+}, Zn	-0.76
Fe^{2+}, Fe	-0.44
H^{+}, H_2	0.00
Cu^{2+}, Cu	+0.34
Ag^{+}, Ag	+0.79

a) Will Zn displace Mg from aqueous solutions of their sulphates?

b) Which among these metals would be the best reducing agent?

c) Can $CuSO_4$ be stored in a zinc vessel?

d) Which are the two metals that can be combined as anode and cathode to form a cell with maximum EMF under standard conditions? (1+1+1+2)

21. a) The energy of Einstein associated with a radiation is 18.40×10^{-4} J. Calculate the wavelength of this radiation.

c) Calculate the equilibrium constant for the reaction

$$Fe + Cu^{2+} \Leftrightarrow Fe^{2+} + Cu \quad \text{at 298 K.}$$

($E^{o}_{Fe^{2+}/Fe}$ = - 0.44 V, $E^{o}_{Cu^{2+}/Cu}$= 0.34 V) (2+3)

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