

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086
(For candidates admitted from the academic year 2019-20 & thereafter)

SUBJECT CODE: 19CH/MC/PC64

B.Sc. DEGREE EXAMINATION, APRIL 2022
BRANCH IV - CHEMISTRY
SIXTH SEMESTER

COURSE : MAJOR-CORE
PAPER : PHYSICAL CHEMISTRY III
TIME : 3 HOURS

MAX. MARKS :100

SECTION – A

ANSWER ALL THE QUESTIONS: (30x1=30)

I. Choose the correct answer:

- Unit of second order rate constant is
(i) $\text{mol L}^{-1} \text{s}$ (ii) $\text{mol}^{-1} \text{L s}^{-1}$ (iii) $\text{mol}^{-1} \text{L}^{-1} \text{s}$ (iv) $\text{mol L}^{-1} \text{s}^{-1}$
- Cell potential is equal to E° when
(i) K_{eq} is 1 (ii) K_{eq} is 10 (iii) K_{eq} is 100 (iv) K_{eq} is less than 1
- Unit of cell constant is
(i) m^{-1} (ii) m (iii) m^3 (iv) m^{-3}
- The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reactant is doubled. The order of the reaction is
(i) 0 (ii) 1.5 (iii) 2 (iv) 1
- It is only the absorbed light radiations that are effective in producing a chemical reaction". This is the statement of _____.
(i) Lambert Law (ii) Lambert – Beer Law
(iii) Grothus – Draper Law (iv) Stark – Einstein Law
- The role of catalyst is to change _____.
(i) Gibbs energy of reaction (ii) enthalpy of reaction
(iii) activation energy of reaction (iv) equilibrium constant
- The half-life of radioactive sodium is 15.0 hours. It would take _____ hours for a 64 g sample to decay to one-eighth of its original concentration.
(i) 45 (ii) 60 (iii) 30 (iv) 15
- Law of independent migration of ions was given by
i) Arrhenius ii) Nernst
iii) Kohlrausch iv) Ostwald

9. Temperature coefficient of EMF is

- (i) $\left(\frac{\Delta E}{\Delta T}\right)_P$ (ii) $\left(\frac{\Delta E}{\Delta P}\right)_T$ (iii) $\left(\frac{\Delta E}{\Delta T}\right)_V$ (iv) $\left(\frac{\Delta E}{\Delta T}\right)_S$

10. In an Adsorption process, choose the correct thermodynamic parameters from the following –

- (i) $\Delta H = -ve, \Delta G = -ve$ and $\Delta S = -ve$
 (ii) $\Delta H = -ve, \Delta G = -ve$ and $\Delta S = +ve$
 (iii) $\Delta H = +ve, \Delta G = -ve$ and $\Delta S = +ve$
 (iv) $\Delta H = +ve, \Delta G = +ve$ and $\Delta S = +ve$

11. The ionic strength of 0.01M sodium chloride is _____M.

- (i) 0.02 (ii) 0.01 (iii) 0.005 (iv) 0.0025

12. Which one of the following electrolyte does not give a straight line in its plot of λ_c verses \sqrt{C} -

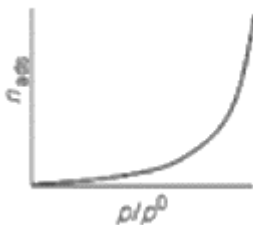
- a) NH_4Cl b) HCN c) KCl d) NaNO_3

II. Fill in the blanks:

13. The activity of 0.01M HCl (Mean activity coefficient = 0.791) is _____.

14. The difference between electrode potentials of two electrodes when no current is drawn through the cell is called _____.

15. The following isotherm is Type _____ isotherm.



16. Electrode potential of SHE is _____.

17. Ionic strength is given by $\mu =$ _____.

18. Freundlich adsorption isotherm is _____.

19. As concentration increases rate of the reaction _____.

20. Quantum yield $\phi =$ _____

III. Match the following

21.	Collision theory	a. Transport number
22.	Ostwald dilution law	b. Zero order reaction
23.	Photosynthesis	c. Surface area
24.	Hittorf rule	d. Bimolecular gaseous reaction
25.	BET Isotherm	e. Weak electrolyte
		f. Strong electrolyte

IV. Answer in a line or two:

26. Give the significance of salt bridge
 27. Represent a cell for the following cell reaction:

$$Pb(s) + Sn^{+4}(aq) \rightarrow Pb^{+2}(aq) + Sn^{+2}(aq)$$

 28. Name any one enzyme used as a catalyst.
 29. What is homogenous catalysis?
 30. What is half life time?

SECTION – B**V. ANSWER ANY FIVE QUESTIONS:****(5x6=30)**

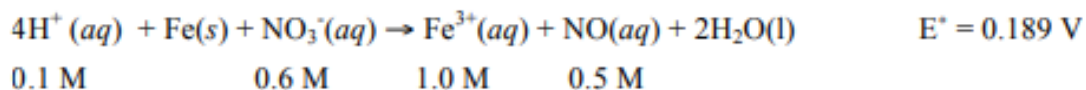
31. a. Derive the expression for rate constant of a second order reaction in which the initial concentrations of the reactants are same. Also deduce an expression for half-life of the reaction. (4)
 b. What is E° for the following balanced reaction? (2)
 $Al(s) + Fe^{3+}(aq) \rightarrow Al^{3+}(aq) + Fe(s)$
 Given: Standard Reduction Potential
 $Fe^{3+}(aq) + 2e^- \rightarrow Fe(s) \text{ -----} +0.771 \text{ V}$
 $Al^{3+}(aq) + 3e^- \rightarrow Al(s) \text{ -----} -1.660 \text{ V}$
32. Distinguish between the following – (3+3)
 i. Physisorption and Chemisorption ii. Electrochemical cell and Electrolytic cell
33. Describe the method of determination of transport number of an ion by moving boundary method.
34. a. Explain the determination of order of reaction by Van't Hoff's differential method. (4)
 b. At 298 K, a cell reaction exhibits a standard emf of 0.0266 V. The equilibrium constant for the cell reaction is 22.4. What is the value of n for the cell reaction? (2)
35. What are concentration cells? Derive an expression for the EMF of a concentration cell (**reversible with respect to a cation**) with transference.
36. a. Calculate the electrode potential (reduction) of the following at 298K – (4)
 i. $Zn|Zn^{2+}(a = 0.2) \quad E_{Zn/Zn^{2+}}^\circ = -0.76 \text{ V}$
 ii. $Ag(s)|AgBr(s)|Br^-(a = 0.5) \quad E_{Ag/AgBr/Br^-}^\circ = 0.071 \text{ V}$
 b. Molar Conductance increases with decrease in concentration of solution – Justify (2)
37. a. Derive a relation for determining the pH of the solution using quinhydrone electrode. (4)
 b. Write the cell representation of the following cells- (2)
 i. $Cd + 2H^+ \rightarrow Cd^{2+} + H_2$
 ii. $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

SECTION – C

VI. ANSWER ANY TWO QUESTIONS:

(2x20=40)

38. (a) Explain kinetics of acid catalysed reaction with an example. (5)
 (b) Explain Debye-Huckel theory of strong electrolytes. (5)
 (c) Discuss the kinetics of the photochemical reaction between hydrogen and bromine. (5)
 (d) Calculate degree of dissociation of 0.01M CH_2ClCOOH , given that the λ_M° values for HCl, KCl and CH_2ClCOOK are 4.261, 1.4986 and 1.132 $\text{Sm}^2\text{mol}^{-1}$ respectively. The molar conductance at 0.01M is 2.134 $\text{Sm}^2\text{mol}^{-1}$. (5)
39. (a) Discuss in detail the different types conductometric titrations. (6)
 (b) Give a detailed account of Langmuir adsorption isotherm. (7)
 (c) Calculate the energy of activation for the decomposition of N_2O_4 , if the specific reaction rate for the reaction is 3.48×10^{-5} at 298K and 4.848×10^{-5} at 318K.
 (Given $R = .314 \text{J/mol/K}$) (4)
 (d) List any three points on how order of a reaction is different from molecularity of a reaction? (3)
40. (a) Discuss in detail the collision theory of gaseous bimolecular reactions. (7)
 (b) Derive the Nernst's equation for the emf of a galvanic cell. Hence arrive at equations relating E_{cell} and thermodynamic parameters ΔG , ΔH & ΔS of system. (5)
 (c) The value of E° for the following reaction is 0.189 V.



Evaluate E_{cell} and ΔG of the above cell? (4)

- (d) a. Write the cell reactions for the following cells – (4)