

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086
(For candidates admitted from the academic year 2023-24)

B.Sc. DEGREE EXAMINATION, APRIL 2026
BRANCH IV - CHEMISTRY
SIXTH SEMESTER

COURSE : **MAJOR-CORE**
PAPER : **PHYSICAL CHEMISTRY III**
SUBJECT CODE : **23CH/MC/PC64**
TIME : **3 HOURS** **MAX. MARKS :100**

Q. No	SECTION A Choose the correct answer (15 x 1 =15 marks)	CO	KL
1.	The unit of cell constant is a) m^{-1} b) m c) m^3 d) m^{-3}	1	1
2.	The role of catalyst is to change _____. a) Gibbs energy of reaction c) activation energy of reaction b) enthalpy of reaction d) equilibrium constant	1	1
3.	The half-life of radioactive sodium is 10.0 hours. It would take _____ hours for a 64 g sample to decay to one-eighth of its original concentration. a) 45 b) 60 c) 30 d) 15	1	1
4.	Cell potential is equal to E^0 when a) K_{eq} is 1 b) K_{eq} is 10 c) K_{eq} is 100 d) K_{eq} is less than 1	1	1
5.	The law of independent migration of ions was given by a) Arrhenius b) Nernst c) Kohlrausch d) Ostwald	1	1
6.	Temperature coefficient of EMF is a) $\left(\frac{\Delta E}{\Delta T}\right)_P$ b) $\left(\frac{\Delta E}{\Delta P}\right)_T$ c) $\left(\frac{\Delta E}{\Delta T}\right)_V$ d) $\left(\frac{\Delta E}{\Delta T}\right)_S$	1	1
7.	In an adsorption process, select the correct thermodynamic parameters from the following – a) $\Delta H = -ve, \Delta G = -ve$ and $\Delta S = -ve$ b) $\Delta H = -ve, \Delta G = -ve$ and $\Delta S = +ve$ c) $\Delta H = +ve, \Delta G = -ve$ and $\Delta S = +ve$ d) $\Delta H = +ve, \Delta G = +ve$ and $\Delta S = +ve$	1	1
8	The ionic strength of 0.02M sodium chloride is _____ M. a) 0.02 b) 0.01 c) 0.005 d) 0.0025	1	1
9.	Which of the following electrolytes does not yield a straight line in its plot of λ_c versus \sqrt{C} - a) NH_4Cl b) HCN c) KCl d) $NaNO_3$	1	1
10.	In the Freundlich adsorption isotherm, the slope of the straight-line graph between $\log(x/m)$ and $\log P$ for adsorption of a gas on a solid is a) $1/n$ b) $\log k$ c) n d) k	1	1

29.	What is half life time?	2	2
30.	Write the rate law for a reaction, $A + 2B \rightarrow 2C$, which is first order with respect to A and B.	2	2
Q. No .	SECTION C Answer any six of the following (6x5 = 30 marks)		KL
31.	Derive the expression for the rate constant of a second-order reaction in which the initial concentrations of the reactants are the same. Also deduce an expression for half-life of the reaction.	3	3
32.	Discuss the Debye-Hückel theory of strong electrolytes	3	3
33.	Describe in detail the Standard Hydrogen Electrode.	3	3
34.	Enlighten on the application of Kohlrausch law in the determination of the dissociation constant of a weak acid. Given λ° of NH_4Cl , OH^- and Cl^- are 129.8, 174 and 65.6 $\text{S.cm}^2.\text{eq}^-$ respectively. Calculate the λ° of NH_4OH . (3+2)	3	3
35.	Explain kinetics of acid catalysed reaction with an example.	3	3
36.	i) Distinguish between Physisorption and Chemisorption. (4) ii) What is E° for the following cell? (2) $\text{Al(s)} \text{Al}^{3+}(\text{aq}) \text{Fe}^{3+}(\text{aq}) \text{Fe(s)}$ Given: Standard Reduction Potential $\text{Fe}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)} \text{ -----} +0.771 \text{ V}$ $\text{Al}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Al(s)} \text{ -----} -1.660\text{V}$		
37.	Derive a relation for determining the pH of the solution using a quinhydrone electrode.	3	3
Q. No .	SECTION D Answer any four of the following (4 x 5 =20 marks)	CO	KL
38.	Describe the moving boundary method for the determination of the transport number of an ion.	4	4
39.	Discuss the kinetics of the photochemical reaction between hydrogen and chlorine.	4	4
40.	Derive a relation for the activity of Na_2SO_4 . Evaluate the activity of 0.1M Na_2SO_4 . Given: mean activity coefficient of sodium sulphate = 0.805. (5)	4	4

41.	What are concentration cells? Derive an expression for the EMF of a concentration cell (reversible with respect to an cation) with transference.	4	4																				
42.	The reaction $2\text{NO}_{(g)} + 2\text{H}_2_{(g)} \rightarrow \text{N}_2_{(g)} + 2\text{H}_2\text{O}_{(g)}$ was studied at 904 °C and the data in the table were collected.	4	4																				
	<table border="1"> <thead> <tr> <th>Experiment</th> <th>Initial [NO] mol/L</th> <th>Initial [H₂] mol/L</th> <th>Initial rate [N₂] mol/L/s</th> </tr> </thead> <tbody> <tr> <td>1.</td> <td>0.420</td> <td>0.122</td> <td>0.136</td> </tr> <tr> <td>2.</td> <td>0.210</td> <td>0.122</td> <td>0.0339</td> </tr> <tr> <td>3.</td> <td>0.210</td> <td>0.244</td> <td>0.0678</td> </tr> <tr> <td>4.</td> <td>0.105</td> <td>0.488</td> <td>0.0339</td> </tr> </tbody> </table>	Experiment	Initial [NO] mol/L	Initial [H ₂] mol/L	Initial rate [N ₂] mol/L/s	1.	0.420	0.122	0.136	2.	0.210	0.122	0.0339	3.	0.210	0.244	0.0678	4.	0.105	0.488	0.0339		
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43	i) Derive the Nernst's equation for the emf of a galvanic cell. Hence, arrive at equations relating E_{cell}^o and thermodynamic parameters ΔG° , ΔH° & ΔS° of the system. (4) ii) Describe the VantHoff differential method and Half-time method to determine the order of reaction. (3+3)	5	5																				
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	i) Give a detailed account of the Langmuir adsorption isotherm. (7) ii) The rate constant of a second-order reaction is $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C and $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 40°C. Calculate the activation energy of the reaction. (3)	5	5																				
44.	i) Discuss in detail the collision theory of gaseous bimolecular reactions. (7) ii) Explain the Freundlich adsorption isotherm. (3)	5	5																				
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	Explain the following i) Types of conductometric titration (Acid - Base) ii) Types of adsorption isotherms. (5+5)	5	5																				