

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086
(For candidates admitted from the academic year 2011-12 & thereafter)

SUBJECT CODE: 11CH/MC/PC64

B.Sc. DEGREE EXAMINATION, APRIL 2015

BRANCH IV - CHEMISTRY

SIXTH SEMESTER

Reg. No

COURSE : MAJOR-CORE
PAPER : PHYSICAL CHEMISTRY - III
TIME : 30 MINUTES

MAX. MARKS : 30

SECTION – A

TO BE ANSWERED ON THE QUESTION PAPER ITSELF.

ANSWER ALL THE QUESTIONS.

(30x1=30)

I. Choose the correct answer:

- For a reaction $2A \rightarrow \text{Products}$. The rate constant has the unit
a) sec^{-1} b) $\text{sec}^{-1}\text{mol}^{-1}\text{L}$ c) $\text{sec}^{-1}\text{mol}^{-1}\text{L}^{-1}$ d) molL^{-1}
- A reaction where free radicals are involved
a) Complex b) Explosion c) Chain d) Parallel
- Adsorption of bromine vapour on silica gel gives adsorption isotherm of
a) Type I b) Type II c) Type III d) Type IV
- The unit of specific conductance
a) Sm^{-1} b) Sm c) S^{-1}m d) S
- The ionic strength 0.01M Na_2SO_4 is given as
a) 0.01m b) 0.02m c) 0.03m d) 0.04m
- The salt that do not undergo hydrolysis
a) NH_4Cl b) CH_3COONa c) KCl d) $\text{CH}_3\text{COONH}_4$
- pH can be determined using
a) H – electrode b) Calomel electrode c) Glass electrode d) All the above
- In concentration cells EMF arises due to
a) Transfer of electron b) Transfer of matter
c) Oxidation at anode d) Reduction at cathode
- When zinc is added to copper sulphate solution
a) zinc is reduced b) zinc is oxidized
c) zinc is precipitated d) no reaction occurs
- According to Debye-Huckel theory, The effect of solvent on the movement of ions in an electrolyte under passage of electricity is known as
a) Viscous effect b) Asymmetry effect
c) Electrophoretic effect d) Electrostatic effect

II. Fill in the blanks:

11. As concentration increases rate of the reaction _____.
12. The effect of ionic strength on rate constant is termed as _____.
13. Transition state theory is also known as _____.
14. The heat of chemisorptions is _____ than physical adsorption
15. As dilution increases specific conductance of an electrolyte _____.
16. The fraction of total current carried by an ion is known as _____.
17. In a galvanic cell _____ energy is converted into _____ energy
18. Standard hydrogen electrode is represented as _____.
19. Precipitation of lead as lead chloride in acidic medium indicates its solubility product is _____ than the ionic product
20. Nernst equation gives the effect of concentration on _____.

III. Match the following:

- | | |
|------------------------|--------------------------|
| 21. Pseudo first order | catalyst |
| 22. Activation energy | weak electrolyte |
| 23. Adsorption | acid hydrolysis of ester |
| 24. Ostwalds' law | High voltage |
| 25. Wien effect | activated charcoal |

IV. Answer in a line or two:

26. Define half life period of a reaction

27. What are potential electrolytes?

28. What is meant by ionic product of water?

29. Give reason for choosing KCl as salt bridge.

30. What is a reference electrode? Give an example.

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COURSE : MAJOR – CORE

PAPER : PHYSICAL CHEMISTRY - III

TIME : 2 ½ HOURS

MAX. MARKS: 70

SECTION – B

ANSWER ANY FIVE QUESTIONS:

(5x6=30)

1. Ethyl acetate was subjected to hydrolysis in normal HCl at 298K. 5 mL of the mixture were withdrawn and titrated against standard NaOH solution at different intervals. Show that the reaction follows first order kinetics

t (min)	0	20	75	120	175	∞
Vol of NaOH(mL)	20.25	21.70	25.20	27.65	30.20	43.95

2. Deduce Langmuir equation of adsorption and discuss the limiting conditions at low pressure.
3. How is transport number of an ion determined by moving boundary method?
4. What is mean ionic activity coefficient of an electrolyte? How will you write it for a uni-univalent and bi-bivalent electrolyte?
5. Write notes on metal- insoluble salt electrodes.
6. How is valency of an ion determined from EMF measurements?
7. Construct a cell for the reaction $\text{Fe} + \text{Ni}^{2+} \rightarrow \text{Fe}^{2+} + \text{Ni}$. Calculate the EMF of the cell at 298K from the standard electrode potential data: $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$. Is the cell reaction spontaneous?

SECTION – C

ANSWER ANY TWO QUESTIONS:

(2x20=40)

8. a) Discuss any two methods to study the kinetics of a reaction. (10)
b) What are the limitations of collision theory? Discuss Lindmann theory of unimolecular reactions (10)
9. a) 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)
b) Discuss the titration curves obtained in the conductivity titration of a strong acid with a weak base. (5)
c) How is conductance of strong electrolytes explained on the basis of Debye – Huckel theory? (10)

10. a) Explain the phenomenon of hydrolysis of salts with CH_3COONa . (5)
b) Derive Henderson - Hasselbalch equation and explain the buffer action of acidic buffer. (10)
c) Calculate the solubility product of a salt MH_2 in water. The solubility of the salt in water is 1×10^{-4} . (5)
11. a) Derive an expression for the EMF of an electrolyte concentration cell with transference. (8)
b) Explain the determination of pH using Quinhydrone electrode (6)
c) Derive the relationship between EMF of a cell and equilibrium constant. (6)
What is the significance of this equation. (6)
