STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600086
(For candidates admitted from the academic year 2015-16 \& thereafter)
SUBJECT CODE: 15CH/MC/PC64

## B.Sc. DEGREE EXAMINATION, APRIL 2021

BRANCH IV - CHEMISTRY
SIXTH SEMESTER
COURSE: MAJOR CORE
PAPER: PHYSICAL CHEMISTRY III TIME: 90 MINUTES

MAX. MARKS: 50

## SECTION - A

## Answer all the Questions

( $15 \times 1=15$ marks)

## I. Choose the correct answer:

1. The rate law for the reaction

$$
\begin{aligned}
& \mathrm{Cl}_{2}(g)+\mathrm{CHCl}_{3}(g) \rightarrow \mathrm{HCl}(\mathrm{~g})+\mathrm{CCl}_{4}(g) \\
& \text { Rate }=k\left[\mathrm{Cl}^{1 / 2}\left[\mathrm{CHCl}_{3}\right]\right.
\end{aligned}
$$

The units for k , assuming time in seconds and concentration in mol/L is
a. $\mathrm{L}^{1 / 2} / \mathrm{mol}^{1 / 2} \cdot \mathrm{~S}$
b. $\mathrm{L} / \mathrm{mol} \cdot \mathrm{s}$.
c. $\mathrm{L}^{-1 / 2} / \mathrm{mol}^{-1 / 2} \cdot \mathrm{~s}$.
d. $\mathrm{L}^{1 / 2} / \mathrm{mol}^{1 / 2} \cdot \mathrm{~s}$
2. The ionic strength $0.01 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$ is given as
a. 0.01 m
b. 0.02 m
c. 0.03 m
d. 0.04 m
3. The specific conductance of an electrolyte of concentration 0.01 M is $1.4 \times 10^{-5} \mathrm{~S} \mathrm{~m}^{-1}$ Its equivalent conductance is
a. 0.14
b. 1.4
c. 14
d. 140
4. When 4 molecules undergo chemical change by the absorption of one quantum of light. The quantum yield is
a. 1
b. 2
c. 3
d. 4
5. The standard reduction potential of a metal is negative. This means the metal can
a. undergo oxidation readily
b. undergo reduction readily
c. undergo displacement readily
d. None of the above
6. The salt that does not undergo hydrolysis is
a. $\mathrm{NH}_{4} \mathrm{Cl}$
b. $\mathrm{CH}_{3} \mathrm{COONa}$
c. NaCl
d. $\mathrm{CH}_{3} \mathrm{COONH}_{4}$
7. A voltaic cell is constructed based on the oxidation of zinc metal and the reduction of silver cations. Solutions of silver nitrate and zinc nitrate also were used. Locate the zinc nitrate on the diagram, and identify the anode.

a. Zinc nitrate $=$ a; anode $=d$
b. Zinc nitrate $=\mathrm{a}$; anode $=$ Zinc
c. Zinc nitrate $=c$; anode $=d$
d. Zinc nitrate $=c$; anode $=$ Zinc

## II. Fill in the blanks:

8. pH of 0.1 N solution of ammonium cyanide $\left(K_{a}=4.9 \times 10^{-10}, K_{b}=1.8 \times 10^{-5}\right)$ is $\qquad$
9. When $\mathrm{NH}_{4} \mathrm{Cl}$ is added to a solution of $\mathrm{NH}_{4} \mathrm{OH}$, the dissociation of $\qquad$ is suppressed.
10. Ostwald dilution law is applicable to $\qquad$ electrolytes.
11. As concentration increases rate of the reaction $\qquad$ .
12. An example of maxima suppressors used in polarography is $\qquad$ .

## III. Answer in a line or two:

13. Represent a cell for the following cell reaction:

$$
P b(s)+S n^{+4}(a q) \rightarrow P b^{+2}(a q)+S n^{+2}(a q)
$$

14.Molecularity
15. Salt bridge

## SECTION B

Answer any three of the following:
$(5 \times 3=15 \mathrm{marks})$
16. Discuss Lindemann's theory of unimolecular reactions.
17.Describe the determination of transport number of an ion using moving boundary method.
18.a. Calculate degree of dissociation of $0.01 \mathrm{M} \mathrm{CH}_{2} \mathrm{ClCOOH}$, given that the $\lambda_{\mathrm{M}}{ }^{\circ}$ values for $\mathrm{HCl}, \mathrm{KCl}$ and $\mathrm{CH}_{2} \mathrm{ClCOOK}$ are 4.261, 1.4986 and $1.132 \mathrm{Sm}^{2} \mathrm{~mol}^{-1}$ respectively. The molar conductance at 0.01 M is $2.134 \mathrm{Sm}^{2} \mathrm{~mol}^{-1}$. (3)
b. What is $\mathrm{E}^{\mathrm{O}}$ for the following balanced reaction? (2)
$\mathrm{Al}(\mathrm{s})+\mathrm{Fe}^{3+}(\mathrm{aq}) \rightarrow \mathrm{Al}^{3+}(\mathrm{aq})+\mathrm{Fe}(\mathrm{s})$
Given: Standard Reduction Potential
$\mathrm{Fe}^{3+}(\mathrm{aq})+2 \mathrm{e}-\rightarrow \mathrm{Fe}(\mathrm{s})----------------+0.771$
$\mathrm{Al}^{3+}(\mathrm{aq})+2 \mathrm{e}-\rightarrow \mathrm{Al}(\mathrm{s})-------------------1.660$
19. Derive an expression for pH of a salt solution of sodium acetate.
20. Give an account on DME.

## SECTION C

## Answer any two of the following:

( $2 \times 10=20 \mathrm{marks}$ )
21.a. Explain concentration cells without transference.
b. Explain the kinetics of formation hydrogen chloride.
22.a. Discuss in detail the transition state theory. (6)
b. The value of $\mathrm{E}^{\circ}$ for the following reaction is 0.189

$$
\begin{aligned}
& 4 \mathrm{H}^{+}(a q)+\mathrm{Fe}(s)+\mathrm{NO}_{3}^{-}(a q) \rightarrow \mathrm{Fe}^{3+}(a q)+\mathrm{NO}(a q)+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
& 0.1 \mathrm{M}
\end{aligned} 0.6 \mathrm{M} \quad 1.0 \mathrm{M} \quad 0.5 \mathrm{M}-\mathrm{E}^{*}=0.189 \mathrm{~V}
$$

Evaluate Ecell and $\Delta \mathrm{G}$ of the above cell? (4)
23.a. Explain the theory involved in use of quinhydrone electrode in the determination of strength of a given acid.
b. Derive an expression for rate constant of first order reaction.
c. The rate constant of a second order reaction is $5.70 \times 10^{-5} \mathrm{dm}^{3} \mathrm{~mol}^{-} \mathrm{s}^{-}$at $25^{\circ} \mathrm{C}$ and $1.64 \times 10^{-4} \mathrm{dm}^{3} \mathrm{~mol}^{-} \mathrm{s}^{-}$at $40^{\circ} \mathrm{C}$. Calculate the activation energy and preexponential factor.

