

**STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86**  
**(For candidates admitted from the academic year 2008–09)**

**SUBJECT CODE: CH/PC/CE24**

**M. Sc. DEGREE EXAMINATION, APRIL 2009**  
**BRANCH IV- CHEMISTRY**  
**SECOND SEMESTER**  
**REG.NO .....**

**COURSE : MAJOR CORE**  
**PAPER : CHEMICAL KINETICS AND ELECTROCHEMISTRY**  
**TIME : 30 MINUTES** **MAX. MARKS: 20**

**SECTION – A**

**TO BE ANSWERED ON THE QUESTION PAPER ITSELF.**

**Answer all the questions.**

**(20 x 1= 20)**

**I Choose the best alternative:**

**(1x5=5)**

- The number of product molecules produced per catalytic site per second is termed as  
 a) Quantum number    b) Quantum yield  
 c) Turn over number    d) Avagadro number
- The transport number of  $H^+$  ion in a solution of concentration  $C_1M$  in  $HCl$  and  $C_2M$  in  $BaCl_2$  can be written as  
 a)  $\frac{\lambda_{(H^+)}}{\lambda_{(H^+)} + \lambda_{(Ba^{2+})} + 2\lambda_{(Cl^-)}}$     b)  $\frac{C_1\lambda_{(H^+)}}{C_1\lambda_{(H^+)} + 2C_2\lambda_{(Ba^{2+})} + (C_1 + 2C_2)\lambda_{(Cl^-)}}$   
 c)  $\frac{C_1\lambda_{(H^+)}}{C_1\lambda_{(H^+)} + C_2\lambda_{(Ba^{2+})} + (C_1 + 2C_2)\lambda_{(Cl^-)}}$     d)  $\frac{C_1\lambda}{C_1\lambda_{(H^+)} + 2C_2\lambda_{Ba^{2+}} + 2C_2\lambda_{(Cl^-)}}$   
 .
- A positive value for the emf of the cell indicates that the process in the given direction is  
 a) irreversible      b) spontaneous      c) reversible      d) none of the above
- According to Debye-Huckel Theory of strong electrolytes an ion moving in an atmosphere of oppositely charged ions experiences a drag. This effect is known as the  
 a) Asymmetric effect    b) Electrophoretic effect  
 c) inter ionic effect    d) concentration effect
- The unit of ionic mobility is  
 a)  $Cm^2V^{-1}S^{-1}$       b)  $CmV^{-1}S^{-1}$       c)  $VCm^{-1}S^{-1}$       d)  $Cm^{-1}V^2S^{-1}$

**II Fill in the blanks :****(1X10=10)**

6. The effective radius of the ionic atmosphere is referred to as \_\_\_\_\_
7. Quantum efficiency is defined as the number of moles of reactants consumed per \_\_\_\_\_ (of photons) absorbed.
8. In solution kinetics the word "collision" is replaced by the term \_\_\_\_\_.
9. Adsorption is invariably accompanied by \_\_\_\_\_ of heat.
10. Rice Herzfeld mechanism is applied to photo chemical reactions involving \_\_\_\_\_ species.
11. The concentration dependence of EMF of a cell is given by \_\_\_\_\_ equation.
12. If the EMF of the cell  $Cd / CdCl_2.25H_2O / AgCl_{(s)} / Ag$  is 0.67531V at 15°C and the temperature coefficient of the EMF is  $-0.00065$ , the change in entropy would be \_\_\_\_\_  $J \text{ deg}^{-1}$ .
13. Salt bridge is employed in EMF measurement to \_\_\_\_\_.
14. The equation describing the diffusion current produced in a polarographic cell is known as \_\_\_\_\_ and is expressed as \_\_\_\_\_.

**III Substantiate the following statements in one or two sentences:****(1x5=5)**

15. Enzyme catalysis cannot be accomplished above 55°C.
16. Neither  $Cu^+$  nor  $Co^{3+}$  is stable in aqueous solution  
[Given  $E^0Co^{3+}/Co^{2+} = 1.82$ ;  $E^0Cu^+/Cu = 0.52$  ].
17. In the electrolysis of concentrated aqueous solution of  $NaCl$ ,  $H_2$  is liberated at cathode and  $Cl_2$  in the anode.
18. Langmuir adsorption isotherm is limited in its application.
19. Zeta potential measurement enables one to predict the stability of colloids.



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TIME : 2 HOURS & 30 MINUTES MAX. MARKS: 80

SECTION – B

ANSWER ANY FIVE OF THE FOLLOWING

5X8=40

1. Define ARRT and explain with examples.
2. a) The adsorption of butane over 2g of metal catalyst has been studied at 273 K. The intercept obtained when  $\frac{p}{v(p^0 - p)}$  is plotted against  $\frac{p}{p^0}$  was found to be  $1.35 \times 10^{-3}$ . The value of the constant  $C$  (from BET equation) was calculated to be  $22.05 \text{ cm}^{-3}$ . Calculate the BET surface area, if the area of cross section of butane molecule is given to be  $44.5 \text{ \AA}^2$ . (4)  
b) (i) Distinguish between order and molecularity. (2)  
(ii) Compare Physisorption and Chemisorption. (2)
3. a) Calculate the ionic strength of the following solution containing 50ml of 0.2 M  $\text{KNO}_3$ , 20 ml of 0.1 M  $\text{K}_2\text{SO}_4$  and 30ml of 0.05 M  $\text{Cu}(\text{NO}_3)_2$ . (5)  
b) Distinguish between Polarizable and Non Polarizable electrodes. (3)
4. Increase in Temperature or use of catalyst enhances the rate of reaction. Using a suitable theory from kinetics explain the above fact in details.
5. a) Calculate how long a hydrogen atom will remain on the surface of solid at 295 K if its desorption activation energy is 25KJ/mol. Assume that  $T_0 = 10^{-12}$  seconds. (4)  
b) Describe any one method of passivation and prevention of corrosion. (4)
6. Illustrate the influence of ionic strength on the rate of ionic reactions and obtain the quantitative expression for the same.
7. Describe with a neat sketch the principle and function of Hydrogen-Oxygen fuel cell. Mention its applications.

## SECTION – C

ANSWER ANY TWO OF THE FOLLOWING

2x20=40

8. a) Obtain the rate law expression for the photo chemical decomposition of acetaldehyde. (10)  
b) State Debye-Huckel-Onsagar equation and discuss in detail the various effects contributing to the conductivity of strong electrolytes. (10)
9. a) Define Hydrogen Over voltage. Also explain the factors influencing Hydrogen over voltage. (10)  
b) Discuss in detail the electro kinetic phenomena. (10)
10. a) State Butler-Volmer equation and deduce its modification at low and high over potential limits. (10)  
b) Give a comparative account of all the three models concerning electrified interfaces. (10)

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