

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted from the academic year 2006 –07)

SUBJECT CODE: CH/PC/CE24

M. Sc. DEGREE EXAMINATION, APRIL 2007
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 Fill in the blanks : (1X10=10)

1. If $\log k$ is plotted against $\frac{1}{T}$, the gradient of the line is _____ and the intercept is _____.
2. For a reaction $A \rightarrow B$ the rate of the reaction doubles as the concentration of A is doubled, the order of the reaction with respect to A is _____.
3. The ILKOVIC equation describing the diffusion current produced in a polarographic cell is given by _____.
4. The departure of the electrode potential from the reversible value as a result of the change of concentration in the vicinity of the electrode is known as _____ polarisation.
5. If the rate law is expressed as $r = K[A]^2[B]^{1/2}$, the units of the rate constant is _____.
6. At 55°C the catalytic function of the enzyme protein is destroyed owing to _____.
7. The study of change is equilibrium by causing a sudden change of temperature and the concentrations as a function of time is referred to as _____ method.
8. The equation that relates the rate co-efficient for an ionic reaction in solution and ionic strength is known as _____ effect.
9. The number of product molecules produced per catalytic site per second is termed as _____ number.
10. The standard free energy change in kilo Joules for the reaction $Cu^+ + I^- \rightarrow CuI$ is _____.

II Multiple Choice**(1x5=5)**

11. The effective radius of the ionic atmosphere is referred to as
(i) Wave length (ii) diameter (iii) Debye length (iv) none of the above
12. Salt bridge is employed in EMF measurement to eliminate
(i) Over potential (ii) Liquid Junction Potential
(iii) Phase over potential (iv) electrochemical over potential
13. In solution kinetics the word "collision" is replaced by the term
(i) solvation (ii) reaction (iii) hydration (iv) encounter
14. The number of quanta of radiation absorbed by gaseous HI absorbing 307 Joules, when irradiated by a light of wave length 253.7 nm is
(i) 3.92×10^{20} (ii) 0.392×10^{19} (iii) 3.92×10^{11} (iv) 0.392×10^{11}
15. The cell potential of the electrochemical cell at 25°C represented as
 $Cu, Cu^{2+}(0.1M) / H^+(0.01M), H_2(1atm); Pt.$ is
(i) 0.192V (ii) 0.384V (iii) 0.428V (iv) 0.236V

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

16. Preexponential factor and the rate constant assume the same unit in Arrhenius equation.
17. Catalyst does not affect the equilibrium constant.
18. In the electrolysis of concentrated aqueous solution of NaCl, H_2 is liberated at cathode and Cl_2 in the anode.
19. The polarographic method is seldom employed for qualitative analysis of substances.
20. Adsorption is invariably accompanied by evolution of heat.

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

SECTION – B

ANSWER ANY FIVE OF THE FOLLOWING

5X8=40

- Distinguish between the following
 - order and molecularity (2)
 - Physisorption and Chemisorption (2)
 - In the adsorption of N_2 at 70.1K on a gram of carbon, it was shown from the BET plot that the intercept was 0.00018 cm^{-3} , calculate the specific surface area of the solid in square meters. given the area of cross section of Nitrogen molecule is equal to 0.162 nm^2 . (4)
- Illustrate the influence of ionic strength on the rate of ionic reactions. (4)
 - Calculate the mean activity coefficient of the following
 - 0.05 molel NaCl
 - 0.1 molal Na_2SO_4 solution (4)
- Mention the assumptions of Laugmuir's theory of adsorption and derive the expression for Langmuir's adsorption isotherm. (8)
- Distinguish between Polarizable and non-polarizable electrodes. (4)
 - Discuss briefly the factors affecting hydrogen over voltage using Tafel equation. (4)
- State Debye-Houkel-Onsagar equation, and discuss briefly on Electrophoretic, Asymmetric and Viscous affects on electrical conductivity. (8)
- Describe the two methods of passivation and prevention of corrosion. (8)
- Discuss the electrokinetic phenomena with special reference to Electroosmosis and steaming potential. (8)

SECTION – C

ANSWER ANY TWO OF THE FOLLOWING

2x20=40

8.
 - a) How would you explain the effect of Temperature and Catalyst on the rate of reaction using collision theory.
 - b) Distinguish between equilibrium approximation and steady state approximation.
 - c) Obtain the integrated Arrhenius equation for calculating activation energy of a reaction.

9.
 - a) Using Rice-Herzfeld mechanism, derive the rate law-expression for the decomposition of acetaldehyde.
 - b) Discuss in detail the significant feature of Stern model for electrified interfaces in comparison with other two models.

10.
 - a) State Butler-Volmer equation and deduce its modification at low and high over potential limits.
 - b) Describe with a neat sketch the principle and function of Hydrogen-Oxygen fuel cell. Mention its applications.

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