

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086  
(For candidates admitted from the academic year 2004-05 & thereafter)

SUBJECT CODE: CH/MC/PC64  
B.Sc. DEGREE EXAMINATION, APRIL 2008  
BRANCH IV - CHEMISTRY  
SIXTH SEMESTER

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

Reg. No .....

MAX. MARKS : 30

SECTION - A  
TO BE ANSWERED ON THE QUESTION PAPER ITSELF.

ANSWER ALL THE QUESTIONS.

(30x1=30)

I. Choose the correct answer:

- A salt bridge containing  $KCl$  should not be used for the cell  $Ag / Ag^+ // Fe^{3+} / Fe^{2+}, Pt$  because  
(i)  $Cl_2$  formed is adsorbed on  $Pt$   
(ii)  $Ag$  and  $K$  would form a solid solution  
(iii)  $AgCl$  would be precipitated.  
a) (i) and (ii)      b) (i), (ii) and (iii)      c) (iii) only      d) (i) only
- The unit of first order rate constant is  
a)  $\text{min}^{-1}$       b)  $\text{mol dm}^{-3} \text{min}^{-1}$   
c)  $\text{mol}^2 \text{dm}^{-6} \text{min}^{-1}$       d)  $\text{mol}^{-1} \text{dm}^3 \text{mol}^{-1}$
- For a reversible reaction  
a)  $\Delta H = \Delta E$       b)  $\Delta H = (E_a)_f - (E_a)_r$   
c)  $\Delta H = (E_a)_r - (E_a)_f$       d)  $\Delta H = \Delta E + (E_a)_f - (E_a)_r$
- According to collision theory, all collisions are fruitful if  
a)  $E_a = 1$       b)  $E_a = k$       c)  $\Delta H = E_a$       d)  $E_a = 0$
- Molar conductance of a substance at a particular concentration is equal to its equivalent conductance at that concentration when  $Eq\ wt = x\ mol\ wt$  then  $x$  is  
1) 1      b) 2      c) 0      d) 3

6. According to Kohlrausch's law,  $\wedge^o_{MgCl_2}$  is equal to
- a)  $\wedge^o_{Mg^{2+}} + \wedge^o_{Cl_2^{2-}}$       b)  $\wedge^o_{Mg^{2+}} + \wedge^o_{Cl_2}$
- b)  $\wedge^o_{Mg^{2+}} + \wedge^o_{Cl}$       b)  $\wedge^o_{Mg^{2+}} + 2\wedge^o_{Cl^-}$
7. Which among the following would not give a straight line in a plot of  $\wedge_c$  vs  $\sqrt{c}$  ?
- a) *NaCl*      b) *KCl*      c) *HCN*      d) *CH<sub>3</sub>COONa*
8. For a cell at equilibrium,
- a)  $E^o_{cell} = 0\text{ V}$       b)  $E^o_{cell} = 1\text{ V}$       c)  $E_{cell} = 1\text{ V}$       d)  $E_{cell} = 0\text{ V}$
9. Which one among the following is true during adsorption?
- a)  $\Delta G = +ve$       b)  $\Delta S = -ve$       c)  $\Delta S = +ve$       d)  $\Delta H = +ve$
10. The standard cell potential of an electrolyte concentration cell is
- a) 1 V      b) 0.76 V      c) 0 V      d) 1.48 V

## II. Fill in the blanks:

11. A pressure cooker reduces cooking time because \_\_\_\_\_.
12. The unit of rate of a reaction is \_\_\_\_\_.
13. In simple collision theory, the steric factor, P, accounts for \_\_\_\_\_.
14. If  $K$  is expressed in  $sm^{-1}$ , then  $\wedge$  can be calculated (in  $sm^2\text{ mol}^{-1}$ ) using the formula \_\_\_\_\_.
15. The pH of an aqueous solution of sodium acetate is \_\_\_\_\_.
16. When aq HCl is added, the solubility of AgCl \_\_\_\_\_.
17. The cell potential of Daniel cell after attaining equilibrium is \_\_\_\_\_.
18. A salt can be used in salt bridge if \_\_\_\_\_.
19. Quinhydrone is an equimolar mixture of \_\_\_\_\_ and \_\_\_\_\_.
20. For the adsorption of a gas on a solid to be spontaneous, the enthalpy of the system should \_\_\_\_\_ to a large extent.

**III. Answer the following in one or two sentences:**

21. What is steric factor?
22. Define activation energy.
23. What is phosphorescence?
24. Write the Freundlich equation.
25. What are transport numbers?
26. Define molar conductance.
27. Calculate the ionic strength of 0.1m KI.
28. Write the Nernst equation for the half-cell reaction  $\text{Zn}^{2+}/\text{Zn}$ .
29. Define liquid junction potential.
30. What is discharge potential?



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SECTION – B

ANSWER ANY FIVE QUESTIONS: (5x6=30)

1. Deduce the expression for 1<sup>st</sup> order rate constant and half life period.
2. The half life of a first order reaction is 10 min. Calculate the time required for 99.9% completion and 87.5% completion of the reaction.
3. Explain the different types of electrodes.
4.  $E_{Fe^{3+}/Fe}^0 = xV$  and  $E_{Fe^{2+}/Fe}^0 = yV$ . Calculate  $E_{Fe^{3+}/Fe^{2+}}^0 = xV$ .
5. Explain (i) Wien effect (ii) Debye & Falkenhagen effect
6. The solubility of  $AgCl$  at a particular temperature is  $1.3 \times 10^{-5} M$ . Also calculate its solubility in  $0.1M HCl$  at that temperature.
7. Distinguish between physisorption and chemisorption.

SECTION – C

ANSWER ANY TWO QUESTIONS: (2x20=40)

8. a) Deduce an expression for rate constant of a bimolecular reaction using collision theory.  
b) Discuss the significance of  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$ .  
c) Illustrate photosensitisation with an example.

9. a) How are transport numbers determined using Hittorf's and moving boundary methods.
- b) Write short notes on
- (i) Ostwald dilution law
  - (ii) Henderson-Hasselbach equation
10. Explain the following
- (i) Lead storage battery
  - (ii)  $H_2 - O_2$  fuel cell
  - (iii) Weston cadmium cell
  - (iv) applications of electrochemical series
11. a) Explain the determination of surface area using BET isotherm.
- b) Derive the Langmuir equation.
- c) Illustrate chemiluminescence with an example.
- d) Explain the determination of  $pH$  by glass electrode.

