SUBJECT CODE :   CH/PC/PC24

M.Sc. DEGREE EXAMINATION APRIL 2011
BRANCH IV – CHEMISTRY
SECOND SEMESTER

REG.NO ………………….

COURSE :   CORE
PAPER   :   ADVANCED PHYSICAL CHEMISTRY
TIME   :   30 MINS   MAX. MARKS :20
SECTION – A

TO BE ANSWERED ON THE QUESTION PAPER ITSELF.
Answer all the questions.   (20 x 1= 20)

CHOOSE THE CORRECT ANSWER:

1. The Gibb's Helmholtz equation is applicable to
   a) all process, chemical or physical
   b) all process, chemical or physical but in a closed system
   c) all chemical processes in a closed system
   d) all physical processes in a closed system

2. Which if the following is true about the criteria of spontaneity?
   a) a spontaneous change is unidirectional
   b) a spontaneous change to occur, time is no factor
   c) once a system is in equilibrium, a spontaneous change is inevitable.
   d) all of the above

3. Einstein's theory fails at
   a) Moderate temperature   b) High temperature
   c) very low temperature   d) moderate and high temperature

4. The percentage of para-hydrogen in hydrogen gas at 0 K, is
   a) 100   b) 96.95   c) 38.5   d) 9.8

5. The transitional partition function equations is
   a) $\frac{(2\pi mkT)^{3/2}}{h^3}.V$ b) $\frac{(2\pi mkT)^2}{h^3}.V^{1/2}$ c) $\frac{(h^3)^{3/2}}{2mkT}.V$ d) $\frac{(2\pi mkT^3)^{1/2}}{h^3}.V$

6. The Lagrangian multiples (β) is equal to
   a) $\frac{K}{T}$ b) KT c) $(KT)^{-2}$ d) $\frac{1}{KT}$

7. There are four molecules each of a A and B in the box, the number of possible collision is.
   a) 4   b) 8   c) 16   d) 32

8. The equation for the rate constant of a diffusion controlled reaction between two different molecules is
   a) $K_D = \left(\frac{4RT}{3\eta}\right)$ b) $K_D = \left(\frac{8RT}{3\eta}\right)$ c) $K_D = \left(\frac{3RT}{8\eta}\right)$ d) $K_D = \left(\frac{4RT}{9\eta}\right)$

9. Electrolytic cells are electrochemical cells in which _____ reactions are forced to occur by the input of electrical energy.
   a) Spontaneous   b) non-spontaneous   c) exothermic   d) endothermic

10. The hydrogen over voltage of Platonised platinum electrode is
   a) 0.09V   b) 0.25V   c) 0.23V   d) 0.00V

FILL IN THE BLANKS:

11. Partial molar free energy $(\bar{G})$ was called as _____ by Gibbs.

12. Fermions obey _____ statistics.

13. The Debye third power law is , $C_V =$ _____.

14. Variation of the rate of the reaction between ions in the presence of an added electrolyte acting as catalyst is called as _____ effect.

15. Over voltage is observed in case of cells working under _____ conditions.

ANSWER IN ONE OR TWO SENTENCES:

16. Write Gibbs phase rule. Name its components.

17. What are ensembles?

18. What is partition function?

19. What do you understand by chain length?

20. Write the Butler-Volmer equation.

⋏⋏⋏⋏⋏⋏⋏⋏⋏⋏

SUBJECT CODE :   CH/PC/PC24

M.Sc. DEGREE EXAMINATION APRIL 2011
BRANCH IV – CHEMISTRY
SECOND SEMESTER

COURSE :   CORE
PAPER   :   ADVANCED PHYSICAL CHEMISTRY
TIME   :   2 HOURS & 30 MINS   MAX. MARKS :80

SECTION – B

Answer any five questions.   **(5x8=40)**

1. Draw and describe the phase diagram of acetic acid-chloroform-water.
2. a) Derive Maxwell's relations.
    b) Explain residual entropy with examples.   (6+2)
3. a) Derive Einsteins theory of specific heat of solids.
    b) Debye's characteristic temperature of copper is 321.3K.
        Calculate C_v at 20.2 K.   (5+3)
4. Discuss Onsager's reciprocal relations.
5. Describe the Rice-Herzfield mechanism in decomposition of acetaldehyde.
6. Write a brief account on Transition state theory.
7. Write notes on (a) Tafel equation   (b) polarization   (4+4)

SECTION – C

Answer any two questions.   **(2x20=40)**

8. a) Derive all forms of Gibbs-Helmoltz equation. Explain its applications.
    b) The e.m.f of the coil $Pb/PbCl_2$ // $AgCl/Ag$ at 298K is 0.49 V.
        If $\left(\frac{\partial E}{\partial T}\right) = -1.86 \times 10^{-4}$ vol deg^{-1}. Calculate $\Delta H, \Delta G, \Delta S$.
    c) Derive all forms of Gibbs-Duhem equation.   (8+6+6)

9. a) Explain Bose-Einstein statistics.
    b) Explain the heat capacity of hydrogen, with its limitations.
    c) Calculate the translational partition function for 1 mole of oxygen at 1atm.
        pressure at 25℃. from the following data. (Assume ideal behavior)
        Volume per mole of the gas $= 0.0469\ m^3 mol^{-1}$
        mass of 1 molecule of oxygen $= 5.314 \times 10^{-26}\ kg$
                                  k $= 1.381 \times 10^{-23}\ J\ K^{-1}$
                                  $h = 6.626 \times 10^{-34}\ J\ s$ (8+6+6)

10. a) Discuss the influence of solvent on reaction rate.
    b) Describe the physical interpretation of standard rate constant.
    c) Draw and explain the structure of the electric double layer.
    d) Evaluate the diffusion controlled rate constant for the reaction between two
        similar molecules in water at 298 K, given that η for water is
        $1 \times 10^{-3}\ kg\ m^{-1}s^{-1}$. [R = $8.314\ K^{-1}\ mole^{-1}$].   (5+5+5+5)

♠♠♠♠♠♠♠♠♠