

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2011–2012)

SUBJECT CODE: 11CH/PC/PC34

M.Sc. DEGREE EXAMINATION, NOVEMBER 2012
BRANCH IV- CHEMISTRY
THIRD SEMESTER

REG.NO

COURSE : CORE

PAPER : ADVANCED PHYSICAL CHEMISTRY

TIME : 30 MINUTES

MAX.MARKS : 20

SECTION – A

(20x1=20)

Answer all the questions:

I Choose the correct answer:

- The number of ways of distributing two indistinguishable objects in two boxes is
(a) 4 (b) 9 (c) 3 (d) 6
- Particles with zero and integral spin require their overall wave functions to be symmetric are called
(a) Bosons (b) Maxwellons (c) Fermions (d) Photons
- In a bimolecular reaction, the change in rate constant, k_2 , with ionic strength of the solution is called _____ effect.
(a) primary isotope (b) secondary isotope
(c) secondary kinetic salt (d) primary kinetic salt effect
- The unit of rate of chemical reaction at the electrode surface is
(a) $\text{mol m}^2 \text{s}^{-2}$ (b) $\text{mol m}^{-2} \text{s}^{-2}$ (c) $\text{mol m}^{-2} \text{s}^{-1}$ (d) $\text{mol}^2 \text{m}^{-2} \text{s}^{-1}$
- The relation between the change in surface tension and the composition of a surface was derived by
(a) Tafel (b) Gibbs (c) Harkins (d) Langmuir

II Fill in the blanks:

- The number of system in a particular state is called _____.
- ^{19}F nucleus is a _____.
- A reaction which proceeds at an accelerating rate is called _____.
- Electrodes that have high exchange current density for a given reaction are said to be _____.
- _____ adsorption isotherm is quite successful to explain the chemisorption process.

III State whether the following statements are true or false:

11. A process which proceeds spontaneously in an isolated system with a decreasing entropy is called a fluctuation.
12. Pressure of a electron gas is one-third of the electron density.
13. If the activation entropy is positive, the activated complex is more disordered in comparison with the reactants.
14. The efficiency of the fuel cell is increased by the use of porous electrode.
15. Physical adsorption is characterized by high heats of adsorption.

IV. Match the following:

- | | |
|---|---------------------------------|
| 16. Lagrange's undetermined multiplier, $\beta =$ | (a) unimolecular reactions |
| 17. Dissipation function | (b) electrical double layer |
| 18. Lindemann's theory | (c) $1/kT$ |
| 19. Gouy-Chapman | (d) surface catalysed reactions |
| 20. Langmuir-Hinshelwood | (e) $T\theta$ |

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PAPER : ADVANCED PHYSICAL CHEMISTRY

TIME : 2½ HOURS

MAX.MARKS : 80

SECTION – B

(5 x 8 = 40)

Answer any five questions:

1. (a) What is partition function? Give its significance.
(b) Calculate the translational partition function for oxygen molecule at 27°C and at 1atm.
2. Derive the expression for entropy in terms of partition function.
3. Discuss the effect of temperature on reaction rate.
4. Write notes on potential energy surfaces.
5. The cell Zn(Hg)/ZnSO₄. 7H₂O/Hg₂SO₄(s), Hg(sat.), has a temperature coefficient of -0.00148VK⁻¹ at 308K. Calculate ΔG, ΔH and ΔS at 308K at which the cell emf is 1.4062V.
6. Explain the Guoy-Chapmann model of electrical double layer.
7. Explain the Eley-Rideal mechanism of surface reactions.

SECTION – C

(2 x 20 = 40)

Answer any two questions:

8. a) Derive the expression for translational partition function. (6)
b) Compare Boltzmann, Bose-Einstein and Fermi-Dirac Statistics. (10)
c) Calculate the Fermi energy of Silver, whose density is 10.5X10³ Kgm⁻³, its atomic weight is 107 and the number of free electrons per cubic meter is 5.86 X 10⁻²⁸. (4)
9. (a) Write the Onsager reciprocity relation. How is it proved by using the principle of microscopic reversibility? (7)
(b) Write down the mechanism of H₂-Br₂ reaction and derive the rate expression for it. (7)
(c) Calculate the free energy of activation of a reaction at 300K if k = 1 X 10⁻³ mol dm³ s⁻¹. (6)

10. (a) Derive Butler-Volmer equation for an electrode process involving one electron transfer. (8)
- (b) Explain the working of Hydrogen-Oxygen fuel cell. (7)
- (c) 1 gram of charcoal adsorbs 100mL of 0.5M CH₃COOH to form a monolayer and thereby the molarity of CH₃COOH reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal is $3.01 \times 10^2 \text{ m}^2/\text{g}$. (5)

