M.Sc. CHEMISTRY Second Semester PHYSICAL CHEMISTRY-II (MSC - 204)

Duration: 3Hrs. Full Marks: 70

Part-A (Objective) =20 Part-B (Descriptive) =50

(PART-B: Descriptive)

Duration: 2 hrs. 40 mins. Marks: 50

Answer any four from Question no. 2 to 8 Question no. 1 is compulsory.

- 1. Calculate the packing efficiency of cubic closest packing. Show that the critical radius ratio for tetrahedral coordination is 0.225. (5+5=10)
- 2. Discuss the Michaelis-Menten mechanism and kinetics of enzyme catalysed reactions. How would you determine Michaelis constant K_m ? (8+2=10)
- Briefly mention the important postulates of conventional activated complex theory (cACT) and derive the rate constant of a gaseous bimolecular reaction in terms of thermodynamic formulations (cACT). (10)
- 4. i. Define phenomenological law. Prove that the direct phenomenological coefficients have always positive values for processes occurring simultaneously in the same system.
 - ii. Derive an expression for the rate of entropy production arising from heat interaction between two systems. (5+5=10)
- Define canonical, grand canonical and microcanonical ensembles. Derive an expression for the molecular vibrational partition function of an ideal diatomic gas.

(5+5=10)

- 6. What is meant by the terms *partition function*? Derive an expression for the equilibrium constant of an ideal gaseous mixture in terms of the partition functions of the reactants and the products. (2+8=10)
- 7. Drive the BET equation for multilayer adsorption stating important assumptions. (10)
- 8. What is the origin of charge on colloidal particles? What is meant by electrical double layer? Briefly discuss the factors that can affect the CMC in aqueous media.

 (2+3+5=10)

2017/06

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Duration: 20 minutes

Marks - 20

(PART A - Objective Type)

I. Choose the correct answer:

 $1 \times 20 = 20$

- i) The radius ratio in an ionic crystal lies between 0.732 and 1.0, the structure is:
 - (a) Triangular
 - (b) Tetrahedral
 - (c) Octahedral
 - (d) Cubic
- ii) The F-centre in alkali halides is defined as:
- (a) Hole trapped by a pair of anions
- (b) Electron trapped at anion vacancy
- (c) Two adjacent F-centre
- (d) Three adjacent F-centre
- iii) The Miller indices of crystal planes which cut through the crystal axes at (2a, -3b, -3c) is:
- (a) (322)
- (b) 233
- (c) (322)
- (d) (223)
- iv) Maximum packing efficiency is not possible in which arrangement (configurations)?
 - (a) BCC
 - (b) FCC
 - (c) HCP
 - (d) CCP
- v) The "grain boundary" defect in solids is a:
- (a) Point defect
- (b) Line defect
- (c) Plane defect
- (d) None above
- vi) The crystal defects (zero-dimensional) due to the aliovalent impurity in ionic solids cause:
 - (a) Decrease in density
 - (b) Increase in density
 - (c) No change in density
 - (d) Deviate the charge neutrality

- vii) The Miller indices (hkl) of a crystal plane can be obtained from:
- (a) The intercepts of the plane on crystal axes.
- (b) The reciprocal of the intercepts (as fractions).
- (c) The smallest three integers obtained from the fractions.
- (d) All the above steps.
- viii) What happens in a steady state?
 - (a) Product is being formed faster than reactants are consumed.
 - (b) Heat is evolved.
 - (c) The concentration of an intermediate is constant.
 - (d) The reaction terminates.
- ix) Based on the collision theory, the atoms at the top of the potential energy "hill" are called:
 - (a) Peak of the hill
 - (b) Activation energy
- (c) Transition state
- (d) Saddle point
- x) In absolute reaction rate theory, the activated complex:
- (a) Maintains equilibrium with reactants.
- (b) Behaves like normal molecule except the number of degrees of freedom.
- (c) Has fourth translation degree of freedom.
- (d) Obeys all above characteristics.
- xi) Langmuir isotherms holds at low pressure but fails at:
 - (a) High pressure
- (b) Low temperature
- (c) Intermediate pressure
- (d) Sub-zero temperatures
- xii) The presence of the double layer in colloids accounts for:
 - (a) Kinetic properties
 - (b) Electrical properties
 - (c) Optical properties
 - (d) Stability of colloids
- xiii) The relaxation time (τ) for the following reaction is:

$$A = \frac{k_1}{k_{-1}} = E$$

- $(a)^{\frac{1}{k_1+k_{-1}}}$
- $(b)^{\frac{1}{k_1-k_{-1}}}$
- $(c)^{k_1+k_{-1}}$
- $(d)^{k_1-k_{-1}}$

- xiv) Which one of the following statements is not true concerning enzyme catalysed reactions?
 - (a) Enzymes require optimum temperature.
 - (b) Enzymes become zwitter ionic at optimum Ph.
 - (c) Enzymes increase activation energy.
 - (d) Enzymes are highly specific in nature.
- xv) An example of a relaxation method of measuring rates is:
 - (a) Spectroscopic monitoring of product concentration
 - (b) Stopped flow technique
 - (c) Temperature jump experiments
 - (d) Measurement of spectral line widths
- xvi) In which technique, a short pulse of electromagnetic radiation is used to initiate the reactions?
 - (a) Pulse radiolysis
 - (b) Flash photolysis
 - (c) Stopped-flow method
 - (d) Temperature jump method
- xvii) In which statistics, the particles are considered distinguishable?
 - (a) Maxwell-Boltzmann
 - (b) Bose-Einstein
 - (c) Fermi-Dirac
 - (d) All above
- xviii) Adsorption takes place with:
 - (a) Decrease in enthalpy of the system.
 - (b) Increase in enthalpy of the system.
 - (c) No change in enthalpy of the system.
 - (d) First increase and then decrease in enthalpy of the system.
- xix) Laplace equation is given by:
 - (a) $p_{in} + p_{out} = \frac{2\gamma}{r}$
 - (b) $p_{in} p_{out} = \frac{27}{r}$
 - (c) $p_{out} + p_{in} = \frac{2}{r}$
- $(d) p_{in} + p_{out} = -\frac{2\eta}{r}$
- xx) The flux generated by the gradient of chemical potential is:

- (a) Heat flow
- (b) Charge flow
- (c) Mass flow
- (d) All of these



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