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REV-00
MSC/23/28

2014/01

M.Sc. CHEMISTRY
First Semester
Physical Chemistry
(MSC - 03)

Duration: 3Hrs. **Full Marks: 70**

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

(PART-B: Descriptive)

Duration: 2 hrs. 40 mins. **Marks: 50**

1. Answer the following questions: (any *five*) **2 × 5 = 10**

a) What do you mean by wave particle duality? Explain.

b) Discuss the effect of temperature on the surface tension of a liquid.

c) Define critical micellization concentration (CMC) of a surfactant. Discuss the micellization phenomena.

d) What is meant by excluded volume? Show that excluded volume, b is four times the actual volume of the gas molecules.

e) Derive the expression for the root mean square velocity from Maxwell's distribution for molecular velocities.

f) Discuss the role of zeta potential in floccullation of colloidal systems.

g) What do you mean by functionality of a monomer? What is the functionality of Tartaric acid?

2. Answer the following questions: (any *five*) **3 × 5 = 15**

a) Define linear operator. Show that the operator ∇^2 is linear.

b) Deduce Schrodinger wave equation.

c) Show that during adsorption of H_2 gas as hydrogen atoms on the surface of Ni, the adsorption isotherm becomes: $\theta = \frac{(K_p)^{\frac{1}{2}}}{[1+(K_p)^{\frac{1}{2}}]}$ where the symbols have their usual meanings.

d) For a 1.0 x 10^{-4} M aqueous solution of n-butanoic acid, $\frac{d\gamma}{dc}$ = -0.08 N m^2 mol^{-1}, at 25 °C, Using Gibbs adsorption equation, determine the surface excess of butanoic acid and also calculate the average surface excess of butanoic acid.

e) Explain the term coefficient of viscosity of a fluid. Show that the viscosity of a gas is independent on pressure.

f) For O_2 gas, the root mean square velocity at T_1, the average velocity at T_2 is equal to 2.5 x 10^3 m s^{-1}. Calculate T_1 and T_2.

g) Discuss the principal of osmometry for determination of molecular weight of a polymer.

3. Answer the following questions: (any *five*) **5×5 = 25**

a) State the condition of orthogonality and normalization of two wave functions and examine the orthogonality of the functions Ψ_1 = x and Ψ_2= x^2 over the interval $-K \leq x \leq K$, where K is a constant.

b) Define Hermitian operator. Prove that the eigen functions of a hermitian operator having different eigen values are orthogonal.

c) The following data have been obtained with the adsorption of nitrogen on active charcoal at 273 K at a series of pressures.

P (mm Hg)	3.93	12.98	22.94	34.01	56.23
v (ml/ gm)	0.987	3.04	5.08	7.04	10.31

Verify Langmuir isotherm and determine the values of the constants a and b.

d) Discuss briefly BET theory of multilayer adsorption. Write the BET equation and explain the terms involved in the equation.

e) Use the van der Waals equation of state to calculate the pressure exerted by exactly 1 mol of gaseous ammonia, NH_3, held at a temperature of 1000 K in a vessel of volume 2.50 dm^3. The values of the van der Waals parameters for ammonia are a = 4.225 atm dm^6 mol^{-2} and b = 3.71 × 10^{-2} dm^3 mol^{-1}.

f) Discuss the origin of charge on colloidal particles. Describe briefly the electrical properties of colloids.

g) Discuss the kinetics of free radical chain polymerisation.

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(The figures in the margin indicate full marks for the questions)

Duration: 20 minutes **Marks – 20**

PART A- Objective Type

1. Select and put '√' mark on the appropriate answer: 1×20= 20

1) An orbital is:
   (a) a circular tract of an electron in an atom
   (b) a one electron wave function
   (c) an observable property of the system
   (d) a hermitian operator

2) As per the uncertainty principle, $\Delta x . \Delta p_x$ is equal to
   (a) H (b) $h/2\pi$ (c) λ (d)zero

3) The wave function in quantum mechanics represents:
   (a) a state of a system (b) probability of the system
   (c) shape of the system (d) energy of the system

4) The lowest energy is equal to zero for:
   (a) the hydrogen atom
   (b) a rigid rotor
   (c) a harmonic oscillator
   (d) a particle in a three dimensional box

5) Among the following which one is not the correct expression for de-Broglie relationship:
   (a) $h = \lambda x p$
   (b) $\frac{h}{v} = \lambda x m$
   (c) $E_{kinetic} = \frac{hv}{2\lambda}$
   (d) $E_{kinetic} = \frac{2hv}{\lambda}$

6) Which of the following is NOT a correct assumption of Langmuir adsorption isotherm:
   (a) The solid surface is homogeneous and contains a fixed number of adsorption site
   (b) Each site can adsorb more than one molecule
   (c) The adsorbed gas behaves ideally in the vapour phase
   (d) There is no interaction between the adsorbed molecules

7) For a physisorption process which of the following statement is NOT correct?
   (a) There are van der Waals interaction between the adsorbate and adsorbent
   (b) The process predominates at low temperature
   (c) The process cannot proceed beyond a monolayer
   (d) The process is reversible

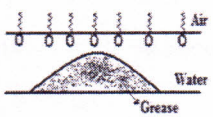
8) The excess pressure inside a liquid drop, ΔP is given as (Young-Laplace equation):

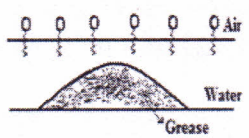
   (a) $\gamma\,(r_1 + r_2)$ $(b)\,\gamma\,(r_1 - r_2)$ $(c)\,\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ $(d)\,\gamma\,(\frac{1}{r_1} - \frac{1}{r_2})$

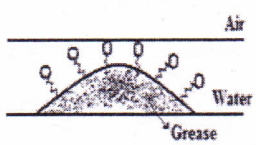
9) A surface active agent form aggregates in nonpolar medium, which is termed as:

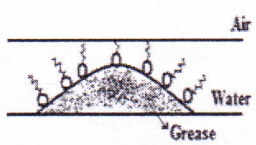
   (a) Micelles (b) Reverse micelles (c) Microemulsion (d) colloids

10) Which of the following describes the interaction of the surfactant molecule,  in a system composed of grease and water ?

(a) 

(b) 

(c) 

(d) 

11) The second virial coefficient of ammonia, NH_3, is -40.4 $cm^3\,mol^{-1}$ at 600 K. What does this imply about the nature of the interactions between the molecules at this temperature?
   (a) The interactions between molecules are attractive.
   (b) The interactions between molecules are negligible
   (c) Nothing. The value of the virial coefficient is unrelated to the molecular interactions
   (d) The interactions between the molecules are repulsive

12) If at same temperature and pressure, the densities for two diatomic gases are respectively d_1 and d_2, then the ratio of velocities of sound in these will be:

(a) $\sqrt{\frac{d_1}{d_2}}$ (b) $\sqrt{\frac{d_2}{d_1}}$ (c) d_1d_2 (d) $\sqrt{d_1d_2}$

13) The average speed of H_2, N_2 and O_2 gas molecules are in the order:

(a) $H_2 > N_2 > O_2$ (b) $O_2 > N_2 > H_2$ (c) $H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2$

14) The product PV of a gas has the same units as:

(a) Force (b) Force/area (c) Pressure (d) energy

15) In a van der Waals gas the term which accounts for intermolecular forces is:

(a) RT (b) V-b (c) $P + a/V^2$ (d) $(RT)^{-1}$

16) Dispersion of a liquid in a gas, a solid in water, and a liquid in a liquid are respectively known as:

(a) hydrosol, aerosol, emulsion (b) aerosol, hydrosol, emulsion
(c) emulsion, aerosol, hydrosol (d) hydrosol, emulsion, aerosol

17) The kinetic chain length, v is expressed as:

(a) $\frac{rate\ of\ initiation}{rate\ of\ propagation}$

(b) $\frac{rate\ of\ initiation}{rate\ of\ termination}$

(c) $\frac{rate\ of\ termination}{rate\ of\ propagation}$

(d) $\frac{rate\ of\ propagation}{rate\ of\ termination}$

18) The number-average molar mass ($\overline{M_n}$) and weight-average molar mass ($\overline{M_w}$) of a polymer are obtained respectively by:

(a) osmometry and viscosity measurements
(b) osmometry and light scattering measurements
(c) ultracentrifuge and viscosity measurements
(d) viscosity and light scattering measurements

19) Which of the following is the correct expression for intrinsic viscosity:

(a) $\frac{ln\eta_r}{c}$

(b) $\frac{ln\eta_{sp}}{c}$

(c) $\left(\frac{\ln \eta_{sp}}{c}\right)_{C\to 0}$

(d) $\left(\frac{\ln \eta_{sp}}{c}\right)_{C\to \infty}$

20) The relationship between degree of polymerisation, $\overline{D_p}$ and extent of reaction, p is given as:

(a) $\overline{D_p} = \frac{1+p}{1-p}$

(b) $\overline{D_p} = \frac{1}{1+p}$

(c) $\overline{D_p} = \frac{1}{1-p}$

(d) $\overline{D_p} = \frac{1}{(1-p)^2}$

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