

M. Sc. CHEMISTRY
FIRST SEMESTER
PHYSICAL CHEMISTRY - I
MSC - 104

Duration: 3 Hrs.

Marks: 70

Part : A (Objective) = 20

Part : B (Descriptive) = 50

[PART-B : Descriptive]

Duration: 2 Hrs. 40 Mins.

Marks: 50

[Answer question no. One (1) & any four (4) from the rest]

1. i. Using the relation $n_1 d\mu_1 = -n_2 d\mu_2$, 5
derive the Gibbs-Duhem-Margules equation $\frac{d\ln\gamma_1}{d\ln x_1} = \frac{d\ln\gamma_2}{d\ln x_2}$
ii. Derive three gas laws from kinetic gas equation.
How can you derive ideal gas equation from these three laws. Determine 3+1+1=4
the value of universal gas constant in SI unit.
2. i. State Heisenberg uncertainty principle and establish it with the help of 3
gamma ray microscope.
ii. Deduce Schrodinger time independent wave equation. 2
iii. State the condition of orthogonality of wave functions. Prove that if 1+2=3
the eigen functions of a Hermitian operator have different eigen values
they are orthogonal.
iv. Find the de Broglie wavelength of an electron when it is accelerated 2
through the potential difference of 100 volt.
3. i. For a binary mixture of ideal gases, derive the expressions for ΔG_{mix} 6
and ΔS_{mix} .

ii. For a real gas show that

$$\ln\left(\frac{f}{p}\right) = \int_0^p (z-1) d \ln p$$

(Note: In the above questions, the terms used have their usual meanings)

4. Derive Most probable velocity and Average velocity from Maxwell distribution law. Calculate the ratio between these two. 9+1=10

5. How can you determine viscosity of a gas from viscosity of liquid. Write the effect of temperature and pressure on viscosity 8+2=10

6. i. Define z-average molar mass. Is it greater or smaller than mass average molecular mass for a polydisperse system? 2

ii. Show that for a equimolar mixture of two substances 3
 $M_1 = \bar{M}_n + (\bar{M}_n \bar{M}_w - \bar{M}_n^2)^{0.5}$

$$M_2 = \bar{M}_w - (\bar{M}_n \bar{M}_w - \bar{M}_n^2)^{0.5}$$

iii. Equal masses of polymer molecules with $M_1=10000$ and $M_2=100000$ are mixed. Calculate \bar{M}_n and \bar{M}_w . 3

iv. Briefly discuss the practical significance of molecular weight of polymers. 2

7. i. Derive an overall rate expression for free-radical chain polymerization. 6

ii. What are chain transfer agents? Discuss their role and effect on molecular weight obtained in their presence. 4

8. i. Describe a method commonly employed for the determination of viscosity of a liquid. 5

ii. Write down the Schrodinger wave equation for a particle of mass 'm' confined in a one dimensional wall of length 'a' moving along x direction such that the potential 'V' is zero within the wall and $V = \infty$ outside the wall. Calculate the wave function and the energy of the particle. Define degeneracy. 1+2+1+1=5

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[PART-A : Objective]

Choose the correct answer from the following:

1×20=20

1. Which of the following function is acceptable as wave function?
 - a. $\Psi = x$
 - b. $\Psi = e^x$
 - c. $\Psi = \sin x$
 - d. $\Psi = \tan x$

2. Which is not an example of linear operator?
 - a. d/dx
 - b. d^2/dx^2
 - c. $\sqrt{\quad}$
 - d. x^2

3. The wave function in quantum mechanics represents
 - a. Energy of the system
 - b. A state of the system
 - c. Probability of a system
 - d. Operator

4. The degeneracy of quantum particle in a cubical box having energy three times the ground state energy is
 - a. 1
 - b. 2
 - c. 3
 - d. 6

5. The zero point energy of the Harmonic oscillator is
 - a. Zero
 - b. $\frac{1}{2}\hbar\omega$
 - c. $\hbar\omega$
 - d. $3/2\hbar\omega$

6. G is the Gibbs energy, then $\oint dG$ is
 - a. Equal to 0
 - b. Not equal to 0
 - c. Equal to 0 only at constant pressure
 - d. Equal to 0 only at constant temperature

7. For aqueous CaCl_2 solution
- $\gamma_{\pm} = \gamma_+^{1/3} \gamma_-^{2/3}$
 - $\gamma_{\pm} = \gamma_+^{1/3} \gamma_-^{1/3}$
 - $\gamma_{\pm} = \gamma_+ \gamma_-^{1/2}$
 - $\gamma_{\pm} = \gamma_+ \gamma_-$
8. On the basis of $dA = -PdV - SdT$, the correct thermodynamic relation is
- $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
 - $\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
 - $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$
 - $\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial V}\right)_T$
9. Which of the following is a partial molar property?
- $\left(\frac{\partial A}{\partial n_1}\right)_{V,T,n_2}$
 - $\left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_2}$
 - $\left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2}$
 - $\left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2}$
10. The enthalpy of a process is equal to the slope of the plot of
- G versus T
 - G/T versus 1/T
 - G/T versus T
 - G versus 1/T
11. Boyle's law is applicable in
- Isochoric process
 - Isothermal process
 - Isobaric process
 - Isotonic process
12. The mean kinetic energy of one gram-mole of a perfect gas at absolute temperature T is
- 1/2 KT
 - 1/2 RT
 - 3/2 KT
 - 3/2 RT
13. We have a jar 'A' filled with a gas characterized by parameter P, V and T. another jar 'B' filled with a gas with parameters 2P, V/2 and 2T, where symbols have their usual meanings. The ratio of the number of molecules of jar 'A' to those of jar 'B' is
- 1:1
 - 1:2
 - 2:1
 - 4:1
14. Mean free path of a gas molecule with collision diameter σ at given density is proportional to
- σ^0
 - σ
 - σ^2
 - 1/ σ^2
15. Following gases are kept at the same temperature. Which gas possesses maximum r.m.s. speed?
- Oxygen
 - Nitrogen
 - Hydrogen
 - Carbon dioxide
16. The relationship between degree of polymerization (DP) and number average molecular weight is
- $\bar{M}_n = DP$
 - $\bar{M}_n = DP \times M$
 - $\bar{M}_n = \frac{DP}{M}$
 - $\bar{M}_n = DP \times M^2$
17. The expression $(\eta_{sp}/c)_{c \rightarrow 0}$ is called as
- Relative viscosity
 - Reduced viscosity
 - Inherent viscosity
 - Intrinsic viscosity
18. The molecular weights obtained by measuring colligative properties
- \bar{M}_n
 - \bar{M}_w
 - \bar{M}_v
 - \bar{M}_z
19. Diisopropyl xanthate disulphide is associated in polymerization as
- Chain inhibitor
 - Chain modifier
 - Telogen
 - Initiator
20. In chain polymerization, which of the following is true?
- Identity of monomer retains
 - No byproduct is formed
 - Hybridization of C-atom changes
 - All the three

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