

M. Sc. CHEMISTRY  
FIRST SEMESTER  
PHYSICAL CHEMISTRY - I  
MSC - 103(OLD COURSE)

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  $\Delta G_{\text{mix}}$  6  
and  $\Delta S_{\text{mix}}$ .

ii. For a real gas show that

4

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

(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

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

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

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

- Which of the following function is acceptable as wave function?
  - $\Psi = x$
  - $\Psi = e^x$
  - $\Psi = \sin x$
  - $\Psi = \tan x$
- Which is not an example of linear operator?
  - $d/dx$
  - $d^2/dx^2$
  - $\sqrt{\quad}$
  - $x^2$
- The wave function in quantum mechanics represents
  - Energy of the system
  - A state of the system
  - Probability of a system
  - Operator
- The degeneracy of quantum particle in a cubical box having energy three times the ground state energy is
  - 1
  - 2
  - 3
  - 6
- The zero point energy of the Harmonic oscillator is
  - Zero
  - $\frac{1}{2}\hbar\omega$
  - $\hbar\omega$
  - $3/2\hbar\omega$
- G is the Gibbs energy, then  $\oint dG$  is
  - Equal to 0
  - Not equal to 0
  - Equal to 0 only at constant pressure
  - Equal to 0 only at constant temperature
- For aqueous  $\text{CaCl}_2$  solution
  - $\gamma_{\pm} = \gamma_+^{1/3} \gamma_-^{2/3}$
  - $\gamma_{\pm} = \gamma_+^{1/3} \gamma_-^{1/3}$
  - $\gamma_{\pm} = \gamma_+ \gamma_-^{1/2}$
  - $\gamma_{\pm} = \gamma_+ \gamma_-$
- On the basis of  $dA = -PdV - SdT$ , the correct thermodynamic relation is
  - $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
  - $\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
  - $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$
  - $\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial V}\right)_T$
- Which of the following is a partial molar property?
  - $\left(\frac{\partial A}{\partial n_1}\right)_{V,T,n_j}$
  - $\left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_j}$
  - $\left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_j}$
  - $\left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_j}$
- 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
- Boyl's law is applicable in
  - Isochoric process
  - Isothermal process
  - Isobaric process
  - Isotonic process
- The mean kinetic energy of one gram-mole of a perfect gas at absolute temperature T is
  - $1/2 KT$
  - $1/2 RT$
  - $3/2 KT$
  - $3/2 RT$



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Course : .....

Semester : ..... Roll No : .....

Enrollment No : ..... Course code : .....

Course Title : .....

Session : ..... 2017-18 ..... Date : .....

**Instructions / Guidelines**

- The paper contains twenty (20) / ten (10) questions.
- Students shall tick (✓) the correct answer.
- No marks shall be given for overwrite / erasing.
- Students have to submit the Objective Part (Part-A) to the invigilator just after completion of the allotted time from the starting of examination.

Full Marks	Marks Obtained
20	

Scrutinizer's Signature

Examiner's Signature

Invigilator's Signature

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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
  - a. 1:1
  - b. 1:2
  - c. 2:1
  - d. 4:1
14. Mean free path of a gas molecule with collision diameter  $\sigma$  at given density is proportional to
  - a.  $\sigma^0$
  - b.  $\sigma$
  - c.  $\sigma^2$
  - d.  $1/\sigma^2$
15. Following gases are kept at the same temperature. Which gas possesses maximum r.m.s. speed?
  - a. Oxygen
  - b. Nitrogen
  - c. Hydrogen
  - d. Carbon dioxide
16. The relationship between degree of polymerization (DP) and number average molecular weight is
  - a.  $\overline{M}_n = DP$
  - b.  $\overline{M}_n = DP \times M$
  - c.  $\overline{M}_n = \frac{DP}{M}$
  - d.  $\overline{M}_n = DP \times M^2$
17. The expression  $(\eta_{sp}/c)_{c \rightarrow 0}$  is called as
  - a. Relative viscosity
  - b. Reduced viscosity
  - c. Inherent viscosity
  - d. Intrinsic viscosity
18. The molecular weights obtained by measuring colligative properties
  - a.  $\overline{M}_n$
  - b.  $\overline{M}_w$
  - c.  $\overline{M}_v$
  - d.  $\overline{M}_z$
19. Diisopropyl xanthate disulphide is associated in polymerization as
  - a. Chain inhibitor
  - b. Chain modifier
  - c. Telogen
  - d. Initiator
20. In chain polymerization, which of the following is true?
  - a. Identity of monomer retains
  - b. No byproduct is formed
  - c. Hybridization of C-atom changes
  - d. All the three