

**M.Sc. 1st Semester Examination, 2019**

**CHEMISTRY**

*(Physical Chemistry)*

**PAPER – CEM-101**

*Full Marks : 40*

*Time : 2 hours*

*The figures in the right hand margin indicate marks  
Candidates are required to give their answers in their  
own words as far as practicable*

*Illustrate the answers wherever necessary*

**GROUP—A**

Answer any **four** questions of the following :  $2 \times 4$

1. Write down the dimension of wave function,  $\psi(x, y, z)$ . 2
2. If two operators  $\hat{A}$  and  $\hat{B}$  has same set of eigen-

*( Turn Over )*

functions, then which of the following relation is correct :

2

(i)  $[A, B] \neq 0$

(ii)  $[\hat{A}, \hat{B}] = 0$

(iii)  $[\hat{A}, \hat{B}] = 1$

(iv)  $\hat{A} = \hat{B} = 0$

3. In stretching of rubber band,

$$dG = Vdp - SdT + fdL$$

which of the following is true ?

2

(a)  $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial V}\right)_{P,L}$

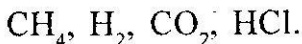
(b)  $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial T}\right)_{P,L}$

(c)  $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial V}{\partial T}\right)_{P,L}$

(d)  $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial P}\right)_{T,L}$

4. Which of the following statements is wrong ? 2
- (a) UV absorption is attributed to electronic transitions
  - (b) UV absorption provide information about valence electron
  - (c) IR absorption is attributed to transition between rotational energy levels of whole molecules.
  - (d) NMR spectrometers use radiofrequency electromagnetic radiation
5. The letters 'CHEMISTRY' are written separately one on each card. The nine cards are shuffled. Calculate the probability of obtaining the word 'chemistry'. 2
6. When should we apply rational system of activity to determine the activity co-efficient of a system ? 2
7. Distinguish between identical distinguishable and indistinguishable particle. 2

8. Identify the molecule whose rotational constant cannot be determined by IR spectroscopy. 2



### GROUP-B

Answer any **four** questions of the following :  $4 \times 4$

9. Find the constrained maxima of the function

$$f(x) = e^{-x^2 - y^2}$$

subject to the condition  $x + y = 1$ . 4

10. Normalized state  $\phi$  is constructed as a linear combination of ground state  $\psi_0$  and first excited state  $\psi_1$  with energies  $\frac{1}{2}$  and  $\frac{3}{2}$  respectively. If the average energy of the state  $\phi$  is  $\langle E \rangle = \frac{7}{6}$ , then calculate the probability of finding  $\psi_1$  in  $\phi$ . 4

11. A non-ideal gas follows the equation

$$P = \frac{RT}{V} \left[ 1 + \frac{B}{V} \right]$$

where 'B' is a function of temperature only.

Show that deviation of internal energy from that of ideal gas,

$$U - U_{\text{ideal}} = -\frac{RT^2}{V} \left( \frac{\partial B}{\partial T} \right)_V \quad 4$$

12. Arrange the following in order of increasing wave number of stretching vibration :

(i) C—H (alkane)

(ii) —O—H (alcohol)

(iii)  $\text{>C=O}$  (Ketone)

(iv) —C≡C— (alkyne)

Give proper justification. 4

13. What are the driving forces for the stabilization of nanoparticle synthesized in organic and aqueous medium? What are organosol and hydrosol? 2 + 2

14. Can  $\beta$  be negative? 4

15. The energies and degeneracies of the two lowest electronic states of atomic iodine are listed below :

<u>Energy/cm<sup>-1</sup></u>	<u>Degeneracy</u>
0	4
7603.2	2

What temperature is required so the 2% of the atoms are excited in the excited state ? 4

16. Define fugacity co-efficient and hence derive the relation

$$\ln \phi = \int_0^p \frac{z-1}{p} dp$$

where symbols have their usual meanings. 4

### GROUP-C

Answer any **two** questions of the following : 8 × 2

17. Show that time evolution of the expectation value of an operator  $\hat{D}$  of a system is given by the following expression,

$$\frac{d\langle D \rangle}{dt} = \frac{1}{i\hbar} \langle [D, H] \rangle.$$

(All the symbols have their usual significances. Assume  $\hat{D}$  has no explicit time dependence.)

Hence, obtain the time evolution of the average value of momentum for a one-dimensional system.

4 + 4

18. (a) A particle in a state  $\phi = \psi_1 + 3\psi_2$ , where  $\psi_1$  and  $\psi_2$  are the eigenfunctions of the Hamiltonian of the particle with eigenvalues  $E_1$  and  $E_2$  respectively. Obtain the average energy of the particle in the state  $\phi$ .

(b) Show that,

$$\left[ x^2, p_x^2 \right] = 4i\hbar p_x x - 2\hbar^2 \quad 4 + 4$$

19. Obtain an expression for the thermodynamic probability distribution of particles described by symmetric wave functions and arrive at the appropriate quantum statistical distribution law in terms of  $\beta$ .

8

20. (a) Derive the expression of molar entropy of a rigid diatomic rotor.
- (b) Calculate the translational partition function for benzene in a volume of  $1\text{m}^3$  at  $25^\circ\text{C}$ . 5 + 3
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