

## U.G. 5th Semester Examination - 2021

### CHEMISTRY

Course Code : BCEMDSHC1 [DSE 1]

Course Title : Advanced Physical Chemistry

Full Marks : 30

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.*

1. Answer any **ten** of the following questions:

1×10=10

- State the Lewis-Rendel statement related to 3rd law of thermodynamics.
- Write down Dulong-Petit's law.
- Calculate the molar residual entropy for carbon monoxide.
- Write down the Schrödinger equation for a three dimensional rigid rotator having bond length ' $r$ '.
- Calculate  $9!$  using Stirling approximation formula. Hence calculate % error involved therein.

- Write down the expression of partition function considering degenerate energy levels. Hence find its dimension.
- Find out the Miller indices for the crystal plane which cut through the respective crystallographic axes at  $(2a, 3b, c)$ , where  $a$ ,  $b$  and  $c$  are the primary intercepts on the axes.
- What is the lower limit of the interplanar spacing that can give observable diffraction pattern?
- Why melting points of crystalline substances are sharp?
- What is Laue equation?
- What is orbital?
- Comment on the shape of  $p_x$  orbital.
- What is equilibrium configuration in statistical thermodynamics?
- Why Barometric distribution occurs?
- Draw an approximate  $C_v$  vs  $T$  curve for a solid element disobeying Dulong-Petit law.

2. Answer any **five** of the following questions:

2×5=10

- Find out the smallest and largest separation between the atoms of an element having fcc structure with side length  $a$ .

b) A particle moving in a ring has  $\psi = \frac{1}{\sqrt{2\pi}} \cos 2\phi$  where  $0 \leq \phi \leq 2\pi$ . Calculate average value of angular momentum  $p_\phi$  where  $p_\phi = \frac{\hbar}{i} \frac{d}{d\phi}$ .

c) Evaluate the commutator:  $[l_x, l_y]$  where  $l_x$  and  $l_y$  represent  $x$  and  $y$  components of angular momentum respectively.

d) Consider that you have three distinguishable balls and you are going to distribute them into three compartments in all possible ways. Calculate the thermodynamic probability of each macrostates.

e) Explain with S-T diagram, the principle of cooling by isothermal magnetization followed by adiabatic demagnetization of paramagnetic substances.

f)  $e^{-a} = N / \sum e^{-\beta \epsilon_i}$ . Evaluate  $a$ .

g) Write down the expression for Hamiltonian operator for a  $n$ -electron atom. Mention the terms. 1+1

h) For an orthorhombic unit cell  $a = 0.7 \text{ \AA}$ ,  $b = 1.3 \text{ \AA}$  and  $c = 1.8 \text{ \AA}$ . Calculate  $d_{hkl}$ .

3. Answer any **two** from the following: 5×2=10

a) Find out the most probable radial distance of finding an electron in  $2p$  state of H-atom.

The radial wave function for the  $2p$  state of hydrogen atom is given by:

$$R_{2,1} = \frac{1}{\sqrt{3}} \left( \frac{1}{2a_0} \right)^{3/2} \left( \frac{r}{a_0} \right) e^{-r/2a_0} \text{ (where symbols}$$

have their usual meaning). Also find out the average radial distance of finding the electron from nucleus in  $2p$  state.  $2 \frac{1}{2} + 2 \frac{1}{2}$

b) i) State and explain one limitation of Nernst Heat Theorem.  $\frac{1}{2} + 1 \frac{1}{2}$

ii) Arrive at the expression for  $L_z$  in spherical polar coordinate system. 3

c) i) "Entropy is measure of randomness." Write its molecular interpretation and connect  $W$  with the explanation.  $2 \frac{1}{2}$

ii) A metal of atomic mass 63.5 CGS unit crystallizes in f-c-c pattern. Calculate its density.  $2 \frac{1}{2}$