2019

B.Sc. (Honours)

5th Semester Examination

CHEMISTRY

Paper - DSE-1T

Advanced Physical Chemistry

Full Marks : 40 Time : 2 Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

Group - A

1. Answer any *five* questions : 2×5=10

(a) State Steno's law of crystallography.

(b) K^+ and Cl^- ions have same scattering power — Justify.

(c) Determine the Miller indices of the planes that intersect the crystallographic axes (i) a, 2b, 2c and (ii) a, b, –c.

[Turn Over]

(d) MO is B.C.C, ρ = 10.3 gm/cc. Calculate (i) edge length (ii) d_{110} and d_{111} (M = 95.94 gm/mol)

(e) Which state function of the system is related to the maximum value of thermodynamic probability and how ?

(f) What is the no. of Microstates for 4 identical distinguishable particles in two states.

(g) State Planck's law (3rd law of thermodynamics).

(h) Describe the mechanism of electrical conductivity in conducting polymers.

Group - B

Answer any *four* questions : 5×4=20

2. (a) KCl has a fcc lattice. But from X-ray diffraction experiment it appears to be simple cubic — Explain. 3

(b) The density of NaCl is 2.17×10^3 kg/m^3 and (100) plane reflection using X-ray of wave length λ occurs at $\theta = 6°$. Calculate λ. 2

3. (a) Calculate the closest distance between the atoms placed in a fcc lattice. 1

(b) The element Po (at wt = 210) crystallizes in the cubic system. Bragg first order reflection using X-ray of wave length 0.154 nm occur at $\sin\theta$ values 0.225, 0.316 and 0.388 for reflection from (100), (110) and (111) planes (i) Determine whether the unit cell is S.C., B.C.C., F.C.C. (ii) Calculate 'a' (iii) Calculate density. 4

4. (a) The molecules of a gas have two energy states, zero and E and degeneracies g_1 and g_2 respectively. Write down the expression for molecular partition function. 2

(b) Consider 20 molecules divided equally between four non-degenerate energy levels (i) what is the thermodynamic probability (w) for this distribution? (ii) How does the value of w change if one molecule is removed from one level and added to another ? 3

5. (a) Consider a system of six distinguishable particles. One of the macrostates has the following distribution of particles :

Energy :	0ϵ	1ϵ	2ϵ	3ϵ	4ϵ
No. of Particles :	0	0	2	2	2

Calculate its thermodynamic probability. 2

(b) Calculate the difference in entropy between two macrostates I and II where six distinguishable particles are distributed in 3 different energy levels $(0, \in \text{and } 2 \in)$ in the following manner

Energy	0	$\in$	$2\in$
Macrostate – I	3	3	0
Macrostate – II	2	2	2

3

6. (a) State Dulong & Petit's law. 1

(b) What is the limitation of Einsteins model of Specific heat of solid ? 2

(c) The Debye's law has been found to be quite satisfactory in the case of many metallic systems specially for cubical monoatomic ones — Explain. 2

7. (a) What is the criteria for synthetic polymer formations ? 3

(b) Write short note on — Copolymerization. 2

Group - C

Answer any *one* question : 10×1=10

8. (a) Derive Barometric distribution formula from Boltzmann energy distribution. 4

(b) Calculate the total number of Microstates of the distribution of three distinguishable particles in two boxes. 2

(c) Calculate the rotational partition function for N_2 molecule at 27°C temperature. The internuclear distance of N_2 is 109.76 pm. 2

(d) Suppose a molecule has two energy levels $\epsilon_1 = 0$ and $\epsilon_2 = kT$. Calculate — (i) the partition function and (ii) ration of the number of molecules in the two levels [K = Boltzmann constant and T is the temperature in Kelvin] 2

9. (a) An element occurs in two forms α and β. α has FCC and β has BCC with 'a' values 3.68Å and 2.92Å respectively. (i) Calculate the percentage of shrinkage of volume when α is converted to β and (ii) Calculate the ratio of densities. 3

(b) Why does crystal not show 5 fold, 7 fold axis of symmetry ? Explain. 3

(c) What is meant by Tetrahedral and Octahedral voids ? 2

(d) For which (111) planes do you expect the intensities to be less, those containing Na or those containing Cl^- atoms only in NaCl ? 2
