2025

M.Sc. 1st Semester Examination

CHEMISTRY

Paper : CEMC403X0

(Physical Chemistry-I)

Full Marks : 50 Time : Two 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

Answer any ***four*** questions : 2×4=8

1. Distinguish between $_2He^4$ and $_2He^3$ on the basis of statistical mechanics.

2. 'Statistical parameters are multiplicative in nature'. — Justify.

3. (a) What is the best composition of a mixture of a ternary system?

   (b) State the Castellan's definition of 'molality'. 1+1

4. Show that the frequency of a rigid diatomic molecule increases with the increase in rotational quantum number.

P.T.O.

5. $\hat{A}$ is a Hermitian operator of a quantum mechanical system and it does not commute with its' Hamiltonian operator, $\hat{H}$. Let ψ_1 and ψ_2 are the eigen function of $\hat{A}$ and $\hat{H}$ respectively. Evaluate the following integrals,

(i) $\left\langle \psi_1 \middle\| \left[\hat{A},\hat{H}\right] \middle\| \psi_1 \right\rangle$ and (ii) $\left\langle \psi_2 \middle\| \left[\hat{A},\hat{H}\right] \middle\| \psi_2 \right\rangle$

6. If $\hat{A}$ and $\hat{B}$ are the two Hermitian operators, then $\left[\hat{A},\hat{B}\right]$ is anti-Hermitian. — Explain.

Group - B

Answer any ***four*** questions : 4×4=16

7. Calculate the ratio of translational partition function of D_2 and H_2 at the same temperature and volume.

8. Derive the expression of molar entropy of a heteronuclear rigid diatomic rotor.

9. How would you measure the activity of a volatile solute for practical system?

10. Rotational constant and fundamental vibration frequency of HBr are 10 cm^{-1} and 2000 cm^{-1} respectively. Find the rotational constant and fundamental vibrational frequency for DBr.

11. Consider a particle of mass M constrained to move in a frictionless string of radius *a* with its centre at the origin in XY plane. Write down the Hamiltonian of the system. Obtain its energy and write down its time dependent wave function.

12. Identify which of the following is not Hermitian — Justify your answer.

(i) $\frac{\hbar}{i}\frac{\partial}{\partial x}$

(ii) $i\frac{\partial^2}{\partial x^2}$

(iii) $\frac{d^2}{dx^2}$

Group - C

Answer any *two* questions : 8×2=16

13. What do you mean by thermodynamic probability? Derive the expression for the thermodynamic probability distribution of particles described by symmetric wave function and hence arrive at the appropriate quantum statistical distribution law. 1+7

14. (a) Explain what is meant by fugacity co-efficient and derive its expression for a real gas.

(b) The energies and degeneracies of the two lowest electronic states of atomic Iodine are listed below :

Energy/cm^{-1}	Degeneracy
0	4
7603.2	2

P.T.O.

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

15. Deduce Schwartz inequality. $\hat{D}$ and $\hat{F}$ are two non-commutating operator which obey the following relation, $[D, F] = iG$.

Hence deduce,

$$\sigma_D.\sigma_F \geq \frac{|\langle G \rangle|}{2}$$

(Symbols have their usual significances)

16. Write down the steps and the rate of each step for a unimolecular photophysical process. Hence deduce the following relation,

$$K_{ISC} = \frac{1}{\tau_f}\left(\frac{1-\phi_f}{\phi_f}\right)$$

Given, $\phi_p + \phi_f + \phi_{ISC}^T = 1$

(Symbols have their usual significances)

Internal Assessment : 10 marks