

CHEMISTRY — HONOURS

Paper : CC-11

(Physical Chemistry - 4)

Full Marks : 50

The figures in the margin indicate full marks.

*Candidates are required to give their answers in their own words
as far as practicable.*

Answer **question no. 1** and **any eight** questions from the rest.

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

1×10

- (a) Write down the normalised wave function for 1s orbital of a hydrogen atom, $R_{10}(r)$, mentioning all the terms.
- (b) State whether L^2 and L_x can be determined simultaneously and precisely and why.
- (c) State the equal a priori principle of statistical mechanics.
- (d) State why Simpson's rule is often called parabolic rule.
- (e) State why least square method is often called 'Regression Analysis'.
- (f) If Q_1 is the canonical partition function for 10cc of He and Q_2 is that for 50cc of He, at 25°C and 1 atm pressure, find $\ln\left(\frac{Q_1}{Q_2}\right)$.
- (g) If you are to use a trial wave function of the form $\varphi(x) = (1 + c\alpha x^2)e^{-\alpha x^2/2}$, where $\alpha = \left(\frac{K\mu}{\hbar^2}\right)^{1/2}$ and c is a variational parameter to calculate the ground state energy of a harmonic oscillator, what do you think the value of c will come out to be? Why?
- (h) Express the Hamiltonian operator for a hydrogen molecule in atomic units.
- (i) Find the number of microstates for the distribution of 4 indistinguishable particles in 5 boxes.
- (j) Justify or criticise— "Third law of thermodynamics is applicable only to perfect crystals".
- (k) In the VB treatment of hydrogen molecule what are the three types of integrals involved?
- (l) For a reaction at temperature T , $\Delta G = a + bT + cT^2$. Using Nernst Heat Theorem, find the expression of 'b'.

2. Calculate the value of $\langle r \rangle$ for the $n = 2, l = 1$ state and the $n = 2, l = 0$ state of the hydrogen atom. Are you surprised by the answers? Explain 5

$$\text{Given : } \Psi_{200} = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0} \right)^{3/2} \cdot \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$\Psi_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(\frac{r}{a_0} \right) e^{-r/2a_0} \cdot \cos\theta, \text{ where } a_0 \text{ is the Bohr radius.}$$

$$\text{Int.} = \int_0^{\infty} r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}$$

3. If ψ_a and ψ_b are two atomic orbitals of a diatomic molecule that are allowed to mix to form molecular orbital, show that LCAO – MO method leads to the secular determinant :

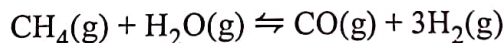
$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{bb} - E \end{vmatrix} = 0.$$

What are the expressions for the quantum mechanical integrals, H_{aa} , H_{ab} , S_{ab} ? What do they signify? 5

4. Use a trial wave function of the form $\phi(r) = re^{-\alpha r}$ with α is a variational parameter to calculate the ground-state energy of a hydrogen atom. Compare in terms of percentage the value arrived at by you with the exact value. 5

$$\text{Given : Int.} = \int_0^{\alpha} r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}.$$

5. Consider the chemical reaction described by the equation :



at 300K. If 1.00 bar of $\text{CH}_4(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are introduced into a reaction vessel, the pressures at equilibrium obey the equation

$$\frac{p_{\text{CO}} \cdot p_{\text{H}_2}^3}{p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}}} = 26.$$

Solve this equation using Newton-Raphson method up to four significant figures. Consider the initial guess of p_{CO} as 0.5. 5

6. (a) State the basic difference between Trapezoidal rule and Simpson's rule and in this context comment on the statement : "Simpson's rule yields more accurate result than the Trapezoidal rule".

- (b) Using the given data table, find out the most accurate value for $\int_{-0.6}^{+0.3} f(x)dx$.

x	-0.6	-0.5	-0.4	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
f(x)	4	2	3	8	4	-2	2	3	5	8

3+2

7. Write the \hat{L}^2 operator in spherical polar coordinates for a rigid rotator. Compute the value of $\hat{L}^2 Y(\theta, \phi)$

for $Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1)$. Show if the function be an eigenfunction of \hat{L}^2 .

5

8. (a) Explain the principle of adiabatic demagnetization using a suitable labelled diagram.

- (b) Calculate the relative number of microsates in water with respect to ice at 273K.

(ΔH_{fusion} for ice = 6.008 KJmol⁻¹ at 273K and 1 bar)

3+2

9. (a) Obtain the barometric formula from the Boltzman distribution, mentioning the assumptions involved. Show graphically the decrease of barometric pressure with altitude for air at temperature T and indicate the half-height, the height for the pressure to decrease by a factor of two.

- (b) How would you describe an ensemble whose systems are one-litre containers of water at 298K?

3+2

10. Suppose there are two energy levels in a system, $\epsilon_0 = 0$ and $\epsilon_1 = kT$ with degeneracy 3 and 1 respectively. Calculate :

- (a) the partition function

- (b) the ratio of number of molecules in the two levels

- (c) the same ratio at an infinitely high temperature

- (d) the same ratio at an infinitely high temperature if degeneracy of the levels gets reversed.

5

11. (a) What do you mean by classical turning point in a simple harmonic oscillator? Make an estimate of the positions of classical turning points, say, x_1 and x_2 (in the ground state of a harmonic oscillator), using proper arguments.

- (b) Determine the probability of finding a classical harmonic oscillator in the classically forbidden region for $v = 0$ (ground state).

3+2

$$\text{Given : } \psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \cdot e^{-\frac{\alpha x^2}{2}}$$

$$\text{Int.} = \int_1^{\infty} e^{-z^2} dz = 0.1394.$$

X(5th Sm.)-Chemistry-H/CC-11/CBCS

(4)

12. (a) Starting from $U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$, show that $G - G(0) = -kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V}\right)_T$,

where Q is the canonical partition function and other terms having usual significance.

(b) In case of indistinguishable independent gas molecules, show that $G - G(0) = -nRT \ln \left(\frac{q}{N}\right)$, where

q be the molecular partition function.

3+2

13. (a) Show that $\hat{H}\psi = -\frac{m_e e^4}{32\epsilon_0^2 h^2} \psi$ for a $2p_0$ state of a hydrogen atom,

where $\psi_{2p_0} = \frac{1}{(32\pi)^{1/2} a_0^{5/2}} \cdot r \cdot e^{-r/2a_0} \cos\theta$

$$a_0 = \frac{\epsilon_0 h^2}{\pi m_e e^2}$$

(b) Compare the LCAO-MO and VB treatments of H_2 .

3+2
