2022

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 $ln\left(\dfrac{Q_1}{Q_2}\right)$.

   (g) If you are to use a trial wave function of the form $\varphi(x) = \left(1 + c\alpha x^2\right)e^{-\alpha x^2/2}$, where $\alpha = \left(\dfrac{K\mu}{\hbar^2}\right)^{1/2}$ 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'.

Please Turn Over

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

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

$\psi_{210} = \dfrac{1}{\sqrt{32\pi}} \left(\dfrac{1}{a_0} \right)^{3/2} \left(\dfrac{r}{a_0} \right) e^{-r/2a_0} \cdot \cos 0$, where a_0 is the Bohr radius.

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

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 :

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

What are the expressions for the quantum mechanical integrals, H_{aa}, H_{ab}, S_{ab}? What do they signify?
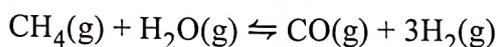
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4. Use a trial wave function of the form $\varphi(r) = r e^{-\alpha r}$ with α is a variational parameter to calculate the ground-state energy of a hydrogen atom. Compare in terms of percentage the value arrived at by you with the exact value.

5

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

5. Consider the chemical reaction described by the equation :

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

at 300K. If 1.00 bar of $CH_4(g)$ and $H_2O(g)$ are introduced into a reaction vessel, the pressures at equilibrium obey the equation

$$\dfrac{p_{CO} \cdot p_{H_2}^3}{p_{CH_4} \cdot p_{H_2O}} = 26.$$

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

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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 $\hat{L^2}Y(\theta, \varphi)$ for $Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}}\left(3\cos^2\theta - 1\right)$. 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 microslates 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 $\epsilon_i = kT$ 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

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

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

Please Turn Over

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

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

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

q be the molecular partition function. 3+2

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

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

$a_0 = \dfrac{\epsilon_0 h^2}{\pi m_e\, e^2}.$

(b) Compare the LCAO-MO and VB treatments of H_2. 3+2

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