Birla Institute of Technology & Science, Pilani (Pilani Campus)

MIDSEM EXAMINATION, SECOND SEMESTER 2022-23

Course Title: General Chemistry | Course No. CHEM F111 | Duration: 90 min.

3rd May 2023 | **CLOSED BOOK** | Maximum Marks: 90

Instructions to the students:

- Do not do rough work on question paper.
- Do not use pencil for writing answer.
- Answer all parts of a question together.
- *Useful data (notations have usual meanings): $k = 1.38 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$, $c = 3 \times 10^8\ ms^{-1}$; $m_e = 9.11\times10^{-31}$ kg; $h = 6.626\times10^{-34}$ Js; $R_H = 109677\ cm^{-1}$; 1 amu = 1.66×10^{-27} kg; $a_0 = 52.9$ pm, 1eV = 1.6×10^{-19} J.*

Q1. (a) What is the speed of an electron emitted by Li, if light having a frequency of $4.77\times10^{15}\ s^{-1}$ is absorbed, given that the work function of Li is 2.9 eV? **[3]**

(b) Calculate the de Broglie wavelength of (i) a 1000 kg automobile traveling at 100 km/h, and (ii) an electron traveling at 1% of the speed of light. Based on the result comment on the applicability of the quantum concept. **[5]**

(c) Consider an electron having a one-dimensional wavefunction $\sqrt{2}\sin\pi x, 0 \le x \le 1$. Calculate (i) normalization constant, and (ii) probability that the electron is in the first half of the range, from $x = 0$ to 0.5. **[2+3]**

(d) Write out the operator $\hat{A}^2$ when $\hat{A}$ is defined as $\frac{d}{dy} + y^2$. **[3]**

(e) Consider a particle of mass m. (i) Determine the average momentum, $\langle p \rangle$, for the ground state when confined in a one-dimension box of length L and show step-by-step calculations. (ii) Write all the associated wavefunctions when the energy of the particle is $\frac{27h^2}{8mL^2}$ for three-dimensional cubical box of length L. **[2+4]**

Q2. (a) The spherical harmonic function, $Y_{l,m}(\theta,\phi)$ is an eigen function of $\hat{L}_x^2 + \hat{L}_y^2$ operator. Find its corresponding eigen value in terms of l, m_l, and $\hbar$ (Symbols l, m_l, and $\hbar$ have usual meaning). **[4]**

(b) A radial wavefunction of hydrogen atom is given below, where $\rho = \frac{2Zr}{a_0}$, a_o is the Bohr radius and r is the radial variable.

$$\frac{1}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(4\rho - \frac{\rho^2}{3}\right)e^{-\frac{\rho}{6}}$$

(i) Identify the orbital corresponding to this wavefunction and calculate the energy (**in eV**) of an electron in this orbital? **[2 + 2]**

(ii) Find the number of radial and angular nodes, and the location(s) of the radial node(s) in terms of a_0. **[2 + 2]**

(iii) Depict the radial wavefunction plot and the radial density distribution plot of the orbital, clearly labeling both the X and Y-axes. **[2 + 2]**

(c) The normalized ground state wavefunction of hydrogen is provided below, where a_0 is the Bohr radius.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}\ a_0^{3/2}}\ e^{(-r/a_0)}$$

(i) Calculate the average of $1/r$ for an electron in the ground state. **[3]**

(ii) Calculate the probability for the electron to be confined in a sphere of radius $r = a_0$. **[4]**

Q3. (a) (i) Derive all the possible singlet term symbols for the configuration p^1d^1, and (ii) write the total number of states that will be observed for each term symbol. **[8]**

(b) Find the lowest energy term symbol for the ground state of Mn^{2+} ion (At. no. 25) **[3]**

(c) (i) For the species N_2^{2-} and O_2^{2-}, write the MO electronic configuration as per the convention taught in the course.

(ii) Calculate the bond orders for these species. **[2 + 2 = 4]**

(d) Fill up the following table by drawing appropriate pictures for bonds formed by overlapping of two p-orbitals. **[4]**

Orbitals / Bond	Bonding, show g or u	Antibonding, show g or u
σ–bond		
π–bond		

(Note: Answer by drawing above table in answer-sheet)

(e) Determine the value of the normalization constant for the bonding MO of a hydrogen molecule. Given, the value of the overlap integral (S) between the atomic orbitals φ_{1s_A} and φ_{1s_B} is 0.59, where φ_{1s_A} and φ_{1s_B} are the normalized atomic orbitals of H-atoms concerned. **[3]**

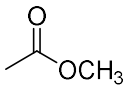
Q4. (a) In the rotational Raman spectrum of a $^{19}F_2$, the displacement from exciting line ($\bar{\nu}_{ex.}$) is represented by $\Delta\bar{\nu}_{rot} = (10.68J \pm 16.02)$ cm^{-1}. Calculate (i) rotational constant, B (ii) moment of inertia, I and (iii) bond length of the molecule. [**7]**

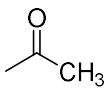
(b) Calculate the ratio of population of molecules in the J = 1 and J = 0 rotational levels for $^{12}C^{16}O$ (assume it as a rigid rotor) at 25 °C (given that **I** = 1.45 ×10^{-46} kg m^2). **[4]**

(c) The wavenumber of the fundamental vibrational transition for $^{79}Br^{81}Br$ is 323.2 cm^{-1}. Calculate the force constant of the bond. **[4]**

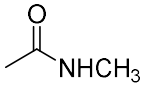
(d) The transmittance of 5.28 ppm aqueous solution of $K_2Cr_2O_7$ (MW = 294.18/mol) in a 1.00 cm cell at 350 nm is 42.5%. Calculate its molar absorptivity at this wavelength. **[4]**

(e) Arrange the following molecules (A-D) in the increasing order of C=O stretching frequencies. **[2]**

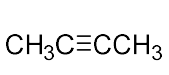

A

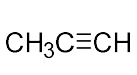

B

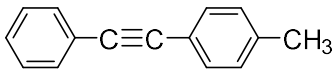

C


D

(f) Which of the following molecules (A-C) will not show a band corresponding to carbon-carbon triple bond stretching frequency in the IR spectra? Explain, why? **[2]**


A


B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