Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
I Semester 2017-2018

Subject: GENERAL CHEMISTRY CHEM F111 **Mid-Semester Examination (Closed Book)**
Max. Marks: 90 **Duration: 90 minutes** **Date: October 11, 2017**

NOTE: There are FIVE questions in all. Attempt all the questions. Start answering each question on a fresh page and answer all parts of the question together. Pencil should not be used. Symbols have usual meanings. Do not scribble on the question paper.

USEFUL DATA: $c = 3 \times 10^8$ m/s; $m_e = 9.109 \times 10^{-31}$ kg; 1 amu $= 1.66 \times 10^{-27}$ kg; $a_0 = 0.529$ Å; $h = 6.626 \times 10^{-34}$ Js; $k = 1.38 \times 10^{-23}$ J.K^{-1}; $R_H = 109680$ cm^{-1}; $\int Sin^2(ax)\,dx = \frac{1}{2}x - \frac{Sin(2ax)}{4a} + Constant$

Q1. (a) A wavefunction for a particle in 1D box of length L is $\text{Sin}\frac{n\pi x}{L}$; $0 \le x \le L$.

(i) Calculate the normalization constant and write the normalized wavefunction. **[3+1]**

(ii) Determine the maximum probability density of the particle when it is present at n = 1 level. At what value of x, the probability density of this particle will fall to 50% of the maximum value. **[3]**

(iii) Determine the value(s) of x at which nodes will appear in wavefunction corresponding to n = 3 level for the particle. **[2]**

(b) An electron is confined in a square box of side 1Å. Determine the degeneracy of first two energy levels of the electron. What will be the energy difference between the second and fourth energy levels? **[2+3]**

(c) The threshold wavelength for potassium metal is 564 nm. What is its work function? What is the kinetic energy of the electrons ejected if radiation of wavelength 410 nm is used? **[4]**

Q2. (a) The radial and angular parts of wavefunction demonstrating a particular orbital of hydrogen atom is given by **[2x4=8]**

$$R(r) = \left(\frac{4}{81\sqrt{6}}\right)\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}\left(\frac{6zr}{a_o} - \frac{Z^2r^2}{a_o^2}\right)e^{-\frac{Zr}{3a_o}} \qquad Y(\theta,\phi) = \sqrt{\left(\frac{3}{4\pi}\right)}\,sin\theta sin\phi$$

(i) Write the complete wavefunction and identify this orbital.
(ii) Calculate the value of orbital angular momentum of an electron present in this orbital.
(iii) Write the number of radial nodes and its position in terms of a_0 for this orbital.
(iv) Determine the energy of this atom (in Joule only) in the given state.

(b) If the wavefunction for helium (electronic configuration $1s^2$) is represented by $\psi_{He(1,2)} = (1/\sqrt{2})[(1s_1, \alpha)(1s_2, \beta) - (1s_1, \beta)(1s_2,\alpha)]$, where α and β are electronic spin functions. Mathematically prove whether this wavefunction is symmetric or antisymmetric. **[4]**

(c) One of the terms of p^2 electronic configuration is ^3P, calculate its degeneracy and write down the term symbol(s) of the level(s) associated with this term. Mention the term symbol of ground state level of this term. **[6]**

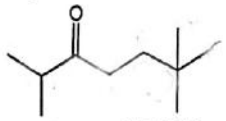
Q3. (a) Calculate the relative population in the J = 1 level w.r.t. the ground level considering B = 2 cm^{-1} at 300K. For a molecule with comparatively lesser mass, what would be the consequence of relative population? **[3+2]**

(b) State the gross selection rule for activity in vibrational Raman spectroscopy. Identify the Raman active and inactive normal mode(s) of vibration for CO_2. Justify your answer. **[1+3]**

(c) For CH_3NHCH_3 molecule, calculate the stretching frequency of ^{14}N-^1H bond in cm^{-1} where the force constant of the bond is 620 N m^{-1}. What will be the difference observed when $CH_3CH_2NH_2$ compared with CH_3NHCH_3 in the same region of IR spectrum and why? **[4+2]**

(d) Calculate the concentration of a solution with UV-transmittance of 20% recorded in a cell of 2.5 cm thickness (molar absorption coefficient = 12000 dm^3/mol. cm^{-1}). **[3]**

Q4. (a) Determine the number of signals expected in ^{1}H NMR and ^{13}C NMR spectra of the following aliphatic ketone. Also, label the most de-shielded carbon only in ^{13}C NMR. **[2+2+1]**



(b) When the ^{1}H-NMR spectrum of acetone is recorded on an instrument operating at 60 MHz, a single sharp resonance at δ 2.1 ppm is seen. **(i)** How many hertz downfield from TMS does the acetone resonate? **(ii)** If the ^{1}H-NMR spectrum of acetone was recorded at 100 MHz, what would be the chemical shift (δ)? **[3+2]**

(c) A sweet-smelling compound with the molecular formula $C_{10}H_{12}O_3$ was isolated from synthetic perfume. Using the IR and NMR (^{1}H & ^{13}C) spectral data: IR 1725 cm^{-1}; ^{1}H-NMR: δ 8.0 (2H, doublet), 6.9 (2H, doublet), 4.3 (2H, quartet), 3.8 (3H, singlet) 1.4 (3H, triplet); ^{13}C NMR: δ 166, 163, 132, 123, 114, 61, 55, 14. **[1+4+3]**

(i) Identify the bond corresponds to stretching frequency 1725 cm^{-1}

(ii) Propose the structure of unknown compound.

(iii) Assign δ values (chemical shift) for different protons of the compound.

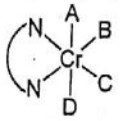
Q5. (a) For the C_2 and O_2 molecules, fill the table given below: **[4+2+2]**

Molecule	Arrange the following molecular orbitals $1\pi_g$, $1\pi_u$, $2\sigma_g$ in the increasing order of energy	What will be the magnetic behavior of the molecule?	The bond dissociation energy will.....upon addition of one electron
C_2			
O_2			

(b) **(i)** For octahedral Rh(III) complexes having the general formula $Rh(NH_3)_xCl_3$, complete the following table: **[2+2]**

x	No. of mole of AgCl precipitated on addition of excess of $AgNO_3$	Number of ions produced in solution
5		
3		

(ii) For the optically active isomer of $[CrCl_3(en)H_2O]$. Identify A, B, C, D in the given structure. **[2]**



(c) Arrange the following complexes in the increasing order of Δ_o. (Atomic number; Ti = 22; Co = 27; Rh = 45; Ir = 77) **[4]**

(i) $[Ti(H_2O)_6]^{3+}$, $[Ti(en)_3]^{3+}$, $[TiCl_6]^{3-}$ **(ii)** $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$

.....***GOOD LUCK***.....