Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
I Semester 2016-2017

CHEM F111 GENERAL CHEMISTRY
Mid-Semester Examination (Closed Book)

Max. Marks: 90 **Duration: 90 minutes** **Date: 07th October 2016**

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: $\sigma = 5.6697 \times 10^{-8}$ Wm^{-2}K^{-4}; b = 2.9 mmK; c = 3×10^{8} m/s; Mass of electron = 9.109×10^{-31} kg
1 amu = 1.66×10^{-27} kg; $a_0 = 0.529$ Å; h = 6.626×10^{-34} Js; R = 8.314 JK^{-1}mol^{-1}; 1 bar = 101.3 kPa

Standard integral: $\int \sin^2 bx\, dx = \frac{x}{2} - \frac{1}{4b}\sin 2bx$; 1Å = 10^{-10} m; 1 nm = 10^{-9} m

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Q. 01. (a) An average human body has a surface area of 0.1 m^2. Assuming human body behaves like a black body, calculate **power** emitted by this body at 37 °C ? **[3]**

(b) A linear conjugated molecule of length, *L*, can be approximated using the **particle in a one-dimensional box**. The wavefunction corresponding to one of the energy levels is given by $\psi = \sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}; \quad 0 \le x \le L$

(i) Write the **number of node(s)**, if any, present in the energy level corresponding to the given wavefunction.

(ii) Evaluate **probability** of finding the electron described by the above wavefunction within *0.4L* to *0.5L*.

(iii) If the length, *L*, of the molecule is 12Å, calculate the **wavelength (in nm)** of the electromagnetic radiation required to excite the electron from $n = 5$ to $n = 6$ level. **[1+4+4]**

(c) A particle of mass, *M*, moving in a **two-dimensional ring** of radius, *r*, is associated with **zero potential energy** and is represented by a wavefunction $\psi_m(\phi) = e^{im\phi}$; where *m* is rotational quantum number:

(i) Write down the expression of **Hamiltonian operator** (in polar coordinates).

(ii) Determine the **magnitude of kinetic energy** associated with this particle when it is present in the **ground energy level**; given that the moment of inertia, *I*, is 4×10^{-42} kg m^2.

(iii) Normalize the wavefunction, $\psi_m(\phi)$, and determine the **value** of **normalization constant**. **[1+2+3]**

Q. 02. (a) The expression of a particular orbital of a hydrogenic atom (B^{x+}) is,

$$\psi = \frac{1}{4(2\pi)^{1/2}}\left(\frac{3}{a_0}\right)^{3/2}\left(\frac{3r}{a_0}\right)e^{-3r/2a_0}\cos\theta$$

(i) Fill up the following table on the basis of the above information (**Answer the question in the tabular format by drawing table in your answersheet as given below**): **[5]**

Atomic Symbol (*B*)	Atomic charge (*x*)	*n*	*l*	$\lvert m_l \rvert$

(ii) Write the expressions for **Coulomb potential energy** and **total energy** corresponding to this orbital. **[2]**

(iii) Determine the numbers of **radial** and **angular node(s)**, if any, present in this orbital. **[2]**

(b) Determine the **electronic configuration** for an atom belonging to **2nd period** of the periodic table with the **ground state term symbol** $^4S_{3/2}$. **[4]**

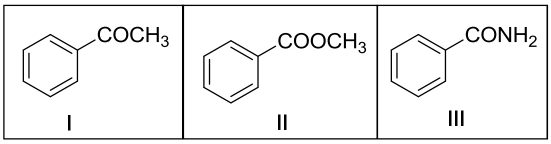
(c) Calculate the **most probable radius** at which an electron will be found when it occupies 1s orbital with radial distribution function, $P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$ of a hydrogenic atom, O^{7+} in **Angstrom unit (Å)**. **[5]**

Q. 03. (a) Calculate the **spacing** between the 3rd and 6th spectral lines (in cm^{-1}) in the **rotational spectrum** of $^{1}H^{35}Cl$ molecule having bond length of 0.127 nm. **[6]**

(b) IR spectra of two pairs of compounds: (i) [$CH_3C{\equiv}N$ and $CH_3C{\equiv}CCH_3$], and (ii) [$C_6H_5CH_2NH_2$ and $C_6H_5CH_2CONH_2$] are given to you. Write the distinguishable IR band(s) for each given pair of compounds. **[4]**

(c) The force constant for HF molecule is 9.7×10^2 N m^{-1}. Calculate the **wavenumber (in cm^{-1})** of IR radiation to excite the molecule from ***n* = 0 to *n* = 1**, where *n* is the vibrational quantum number. **[4]**

(d) Arrange the following compounds (**I**, **II** and **III**), in order of **decreasing** $\bar{\upsilon}_{C=O}$ stretching frequency. Give reasons for the order chosen. **Explanation for each compound is required**. **[4]**



Q. 04. (a) A compound $C_8H_{18}O_2$ with a strong broad IR absorption band at 3293 cm^{-1} exhibits peaks at δ 1.22 (12H, singlet), 1.57 (4H, singlet) and 1.96 (2H, broad singlet) in ^1H-NMR spectrum. The proton decoupled ^{13}C NMR of this compound consists of three lines resonating at δ 29.4, 37.8 and 70.5. **Identify the structure of compound** and **assign given chemical shift values of ^1H-NMR** for different group of protons. **[8]**

(b) A NMR signal is appearing 120 Hz downfield from TMS in an instrument operating at 300 MHz. (i) What is signal's **chemical shift** (δ)? (ii) What would be its **chemical shift** if the spectra is recorded in an instrument operating at 100 MHz? **[4]**

(c) Complete the following table by writing all the information for compound **[A]** in given format at one place. **(Answer the question in the tabular format by drawing table in your answersheet as given below)** **[1+2+1+2]**

Compound **[A]**	Number of peaks in ^1H NMR	Label the most de-shielded protons	Multiplicity of each peak in ^1H NMR	Number of peaks in proton decoupled ^{13}C NMR
$CH_3OCH_2OCH_2CH_3$				

Q. 05. (a) Reduction of Fe(III) oxide by carbon is presented as, $2Fe_2O_3(s) + 3C(s) \longrightarrow 4Fe(s) + 3CO_2(g)$; Using the data provided in the table given below, determine: (i) $\Delta_rH^{\varnothing}_{298}$, (ii) $\Delta_rS^{\varnothing}_{298}$, (iii) $\Delta_rG^{\varnothing}_{298}$, and (iv) estimate the **minimum temperature** at which the reaction becomes **spontaneous** at **1 bar** pressure. **[2+2+2+2]**

	Fe_2O_3 (s)	**C (s)**	**Fe (s)**	**CO_2 (g)**
$\Delta_fH^{\varnothing}_{298}$ ($kJmol^{-1}$)	-824.2	0	0	-393.5
$S^{\varnothing}_{298}$ ($JK^{-1}mol^{-1}$)	87.4	5.7	27.3	213.7

(b) The normal boiling point of a solvent is 80 °C and its $\Delta_{vap}H$ = 30.8 $kJmol^{-1}$. Assuming that $\Delta_{vap}H$ is independent of temperature in the temperature range and that the vapor behaves ideally, calculate its boiling point at 5 kPa. **[3]**

(c) The mechanism of Br^--catalyzed aqueous reaction, $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br^-} C_6H_5N_2^+ + 2H_2O$, is described below,

$Step\ 1: H^+ + HNO_2 \xrightarrow{k_1} HNO_2^+$

$Step\ 2: HNO_2^+ \xrightarrow{k_{-1}} H^+ + HNO_2$

$Step\ 3: HNO_2^+ + Br^- \xrightarrow{k_2} ONBr + H_2O$

$Step\ 4: ONBr + C_6H_5NH_2 \xrightarrow{k_3} C_6H_5N_2^+ + H_2O + Br^-$

(i) Identify the reaction intermediates, I_1 and I_2; **(ii)** Determine the rate of the reaction, $r = \frac{d}{dt}[C_6H_5N_2^+]$

(iii) Determine: $\frac{d}{dt}[I_1]$ and $\frac{d}{dt}[I_2]$; **(iv)** Determine the expression of ***r*** using Steady State Approx. **[1+1+2+3]**