Birla Institute of Technology and Science, Pilani (Pilani Campus)
COMPREHENSIVE EXAMINATION, SECOND SEMESTER 2022-23

Course Title: General Chemistry | Course No. CHEM F111 | Duration: 120 min.
12th July 2023 | **OPEN BOOK** | Maximum Marks: 80

Name:…… **ID…….**

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.

Q1. (a) What will be the power (**in Watts**) radiated (due to flow of electric current) by the surface of a cylindrical object of length 10.0 cm and radius 0.10 mm that is heated to 3000 K. Neglect the power emitted from the surfaces at the two end of the object. **[4]**

(b) Assume the carbon allotrope C_{32} as a rigid sphere (having radius 2.5Å) and the electrons of the molecule as being confined to the surface of the sphere. The wavelength of light necessary to cause a transition of an electron from state l to $l+1$ is 127 nm. Calculate the value of l. **[6]**

(c) When an electric discharge is passed through a particular sample of gaseous Li^{2+} ion, it produces the electromagnetic spectrum corresponding to the lowest frequency in the Paschen series. What will be the energy (**in Joule**) required to produce Li^{3+} ion from the above irradiated sample? **[4]**

(d) What will be the de Broglie wavelength of an electron accelerated from rest through a potential difference of 1000 kV? **[4]**

(e) Evaluate angular momentum (P_ϕ) of a particle on a ring with $\Psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$. **[2]**

Q. 2 (a) In the rotational spectrum of $^{79}Br^{19}F$, there are equally spaced lines that are 0.714 cm^{-1} apart. Identify the levels involved in the most intense rotational transition at temperature 27 °C. **[4]**

(b) Which type of rotational spectroscopy would you use to determine the pure rotational spectrum of H_2? Considering the bond length of H_2 is 0.074 nm, calculate the spacing of the pure rotational transition lines in the rotational spectrum of H_2. **[5]**

(c) The bond length and force constant for $^1H^{35}Cl$ are found to be 127.5 pm and 516.3 Nm^{-1}, respectively. Calculate the zero-point energy and energy of the fundamental vibration band (**both in cm^{-1}**). **[3]**

(d) Match the following molecules to their characteristic IR peaks. **[4]**

Molecules	$PhCH_2CH_2CHO$ **A**	$PhCH_2CH_2CO_2H$ **B**	$PhCH_2CO_2CH_3$ **C**	$PhCOCH_2CN$ **D**
ν/cm^{-1}	1730, 3300 (br)	1684 and 2200	1740, 1160, and 1257	1725, 2850 and 2730

(e) The hydration energy ($\Delta H_{hyd.}$) of Cr^{2+} ion is – 460 kcal/mole (1 kcal/mole = 350 cm^{-1}) when it forms the $[Cr(H_2O)_6]^{2+}$ complex. The crystal field splitting energy of $[Cr(H_2O)_6]^{2+}$ is 13900 cm^{-1}. Calculate hydration energy ($\Delta H_{hyd.}$) when there is no crystal field stabilization. **[4]**

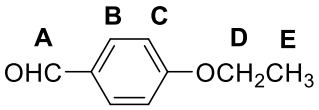
Q. 3 (a) Calculate the additional stabilization energy for both *Z*-in and *Z*-out in $[Cr(NH_3)_6]^{3+}$ complex (*Show the energy calculation steps clearly*). Based on the additional stabilization energy calculation comment on the possibility of Jahn-Teller distortion in $[Cr(NH_3)_6]^{3+}$ complex. **[3]**

(b) Complex $[TiF_6]^{3-}$ exhibits mild Jahn-Teller distortion, but this effect on the nature of its electronic spectrum is pronounced significantly as a broad peak. Justify the observation with proper labeling of d-orbitals. **[3]**

(c) 1 mL of a 0.1 M metal solution and 1 mL of a 0.3 M ligand solution were mixed. The final concentration of the metal complex (ML_3) was 0.05 M. Calculate the overall stability constant (β_3) of the complex? **[3]**

PTO

(d) For compound given below, complete following table (*Draw table in the answer sheet*).



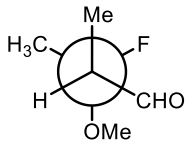
[4]

Most shielded proton in the ^{1}H NMR spectrum:	Integration of the peak for proton **B:** Multiplicity of the peak for proton **B:**	Integration of the peak for proton **D:** Multiplicity of the peak for proton **D:**	Number of peaks in proton decoupled ^{13}C-NMR spectrum.

(e) (i) A 250 MHz ^{1}HNMR spectrum of a compound shows two peaks, one at a frequency 510 Hz higher than that of the reference compound (TMS) and the other at a frequency 280 Hz lower than that of the reference compound. What chemical shifts would be assigned to these two peaks? **[4]**

(ii) The nuclear magnetic moment of ^{31}P is equal to 1.1305 nuclear magnetons, *i.e.*, 1.1305 μ_N. Calculate its magnetogyric ratio and the g-factor. **[3]**

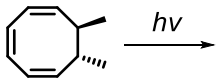
Q4 (a) Convert following Newman projection to Fischer projection (with most oxidized carbon at vertically top position). Assign the absolute configuration (R/S) to each chiral center. **[2+1]**



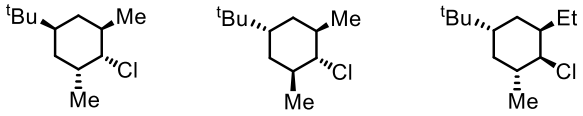
(b) (i) Which one of the following dienes (**A** and **B**) would react faster on heating them individually at same temperature with acrylaldehyde (CH_2=CHCHO). Provide explanation for your choice in 1-2 sentences. **[1+1]**

A **B**

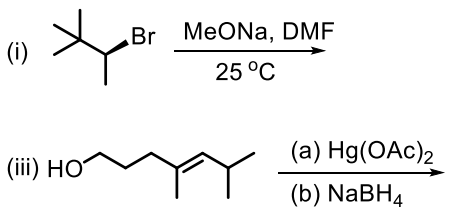
(ii) Write product(s) of the following electrocyclization reaction. **[2]**



(c) State whether the chlorides (**X**, **Y** and **Z**) given below would yield an alkene on heating with sodium ethoxide. If yes, write the structure of the corresponding alkene(s). **[5]**



(d) Provide structure of the major product(s) with appropriate stereochemistry (if applicable) of the following reactions. **[8]**



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