

This question paper contains 4+1 printed pages]

HPAS (Main)—2016

CHEMISTRY

Paper I

Time : 3 Hours

Maximum Marks : 100

Note :— Attempt *Five* questions in all. Question No. 1 is compulsory. *All* parts of a question must be answered in continuation at one place.

1. (a) What is super acid ? Give *one* example. The reaction of super acid with neopentane, CMe_4 gives an intermediate **A** which rearranges to product **B** and CH_4 . Identify **A** and **B**. 7
- (b) The solution of KMnO_4 is deeply coloured while solution of Mn(II) salts are almost colourless. Explain. 7
- (c) Show that the function $f(x, y, z) = \cos ax, \cos by, \cos cz$ is an eigen function of the Laplacian operator, ∇^2 . 6
2. (a) The plot of ionic radius versus number of *f* electrons of trivalent lanthanides showed a dip at Gd(III) . Explain. 7

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- (b) List the differences between first row transition metals and lanthanides. 7
- (c) Calculate the electronic partition function of chlorine atom assuming that the energies of first and higher excited states are very large. 6
3. (a) The first line in the rotation spectrum of carbon monoxide has a frequency of 3.8424 cm^{-1} . Calculate the rotational constant and the C-O bond length in carbon monoxide. 7
- (b) Calculate the pressure exerted by $2 \text{ dm}^3 \text{ mol}^{-1}$ of ethane at 27°C if it follows van der Waals equation. $a = 5.489 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0638 \text{ dm}^3 \text{ mol}^{-1}$. 7
- (c) Explain the bonding in Zeise's using Dewar Chatt and Duncanson (DCD) model. An appropriate orbital overlap picture is essential. 6
4. (a) A molecule AB_2 has the following IR and Raman spectra data. Discuss the molecular structure and assign the observed lines to molecular vibrations :

Frequency (cm^{-1})	IR	Raman
3,750	Very Strong	
3,650	Strong	Strong, Polarized
1,595	Very Strong	

(b) The densities of liquid water and water vapour at its normal boiling point are 0.958 and 5.98×10^{-4} kg dm^{-3} respectively and the change in the entropy of vaporization is $108.99 \text{ JK}^{-1}\text{mol}^{-1}$. Calculate the change of pressure for the change in temperature by two degrees. 7

(c) $[(\eta^3\text{-allyl})\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ (A) does not react with nucleophile, Nu. However, complex A upon reaction with NOBF_4 affords products B which upon reaction with Nu affords product C. Identify products A, B and C. What lesson one learns from these reactions ? 6

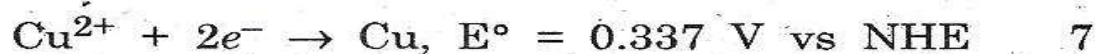
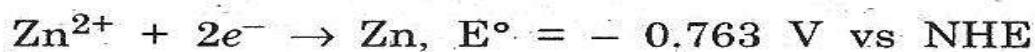
5. (a) Explain the spin state and electronic configuration of Fe(II) in myoglobin and oxygen bound myoglobin. 7

(b) Draw and explain the O_2 binding graph for haemoglobin. Explain cooperativity effect exhibited by haemoglobin which is absent with myoglobin. 7

- (c) What valuable information can be obtained from a knowledge of heats of reactions ? 6
6. (a) How many isomers are possible for (i) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and (ii) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$. Draw their structures. 7
- (b) The effective magnetic moment of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is about 3.20 BM. Is it higher or lower or equal to the $\mu_{\text{spin-only}}$? Provide an explanation. 7
- (c) Express the universal gas constant "R" in different units for one mole of an ideal gas. 6
7. (a) Calculate the ionic strength of a solution containing 0.3 molal NaCl and 0.02 molal Na_2SO_4 and 0.08 molal KCl. 7
- (b) Write the spontaneous reaction in the galvanic cell



and calculate the standard E.M.F. of the cell and free energy change using the following standard electrode potentials :



(c) Explain the following IR data :

Complex	$\nu(\text{CO}), \text{cm}^{-1}$	
$[\text{Mn}(\text{CO})_6]^+$	2090	
$\text{Cr}(\text{CO})_6$	2000	
$[\text{V}(\text{CO})_6]^-$	1860	6

8. (a) Calculate the bond order of CO molecule. 7

(b) 50% of a substance decomposes in 5 minutes. How much of it would decompose in 20 minutes, if the reaction is of the second order ? 7

(c) The ^{13}C NMR spectrum of $\text{Fe}(\text{CO})_5$ revealed one signal for CO carbon while its IR spectrum revealed two bands for CO moiety. Explain 6

$N = 6.022 \times 10^{23}/\text{mol}; C = 12 \text{ g/mol}; O = 15.994 \text{ g/mol}; R = 0.0821 \text{ dm}^3 \text{ atm mol}^{-1}\text{K}^{-1}$
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