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

P.T.O.

(*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 dm^3 mol^{-1} of ethane at 27°C if it follows van der Waals equation. a = 5.489 dm^6 atm mol^{-2}, b = 0.0638 dm^3 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 : 7

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 $JK^{-1}mol^{-1}$. Calculate the change of pressure for the change in temperature by two degrees. 7

(*c*) $[(\eta^3\text{-allyl})Mo(\eta^5\text{-}C_5H_5)(CO)_2]$ **(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*) $[Co(en)_2Cl_2]Cl$ and (*ii*) $[Co(NH_3)_5(NO_2)]Cl_2$. Draw their structures. 7

(*b*) The effective magnetic moment of $[Ni(NH_3)_6]^{2+}$ is about 3.20 BM. Is it higher or lower or equal to the $\mu_{spin\text{-}only}$? 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

$$^{-}Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu^{+}$$

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

$Zn^{2+} + 2e^{-} \rightarrow Zn$, $E^{\circ} = -0.763$ V vs NHE

$Cu^{2+} + 2e^{-} \rightarrow Cu$, $E^{\circ} = 0.337$ V vs NHE 7

(c) Explain the following IR data :

Complex	ν(CO), cm^{-1}
$[Mn(CO)_6]^+$	2090
$Cr(CO)_6$	2000
$[V(CO)_6]^-$	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 $Fe(CO)_5$ revealed one signal for CO carbon while its IR spectrum revealed two bands for CO moiety. Explain 6

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