Seat No. : _____

AP-118

May-2016

M.Sc., Sem.-II

407 : Chemistry (Inorganic Chemistry)

Time : 3 Hours] **[Max. Marks : 70**

1. Answer the following questions :

   (a) For benzene molecule, find out electron density, charge density and π-bond order.

   [Given : $\Psi_1=\frac{1}{\sqrt{6}}(p_1+p_2+p_3+p_4+p_5+p_6)$, $\Psi_2=\frac{1}{\sqrt{12}}(2p_1+p_2-p_3-2p_4-p_5+p_6)$,

   $\Psi_3=\frac{1}{2}(p_2+p_3-p_5-p_6)$] **7**

   OR

   Discuss Walsh diagram for XH_2 type of the molecule.

   (b) (i) Explain the effect of Bent's rule on the bond angle on the different fluoromethanes.

   (ii) Explain VSEPR theory in short. **7**

   OR

   Write short note on band theory of solids and femi level.

2. Answer the following questions :

   (a) Write the different steps involved in working out the molecular orbitals in AB_6 type molecule. **7**

   OR

   In a molecule AB_5 (D_{3h}), central atom A has s, p and d orbitals. What are the orbitals available on A which will form σ bonds with B.

   (b) In a molecule $[M(CO)_4L_2]$ (D_{4h}), find out the symmetries of stretching vibrations only for CO. Assign which will be IR active and which will be Raman active. Will there be any coincidence ? **7**

   OR

Assign the shape and point group of the following AB_3 type molecules with the help of their IR and Raman spectra :

Molecule	IR cm^{-1}	Raman cm^{-1}
PCl_3	192, 260, 485, 510	190, 261, 486, 515
ClF_3	320, 365, 435, 525, 700, 750	322, 365, 435, 525, 702, 750
BF_3	480, 690, 1450	480, 888, 1454

3. Answer the following questions :

(a) Write a note on metal arene complexes. **7**

OR

Discuss in detail, transition metal-butadiene compounds.

(b) Discuss the stability of Metal-Carbon bond in organometallic ocmpounds. **7**

OR

Write a note on activation of small organic molecules by organo-metallic compounds. (Discuss any four).

4. Answer **three** of the following questions :

(a) Give the criteria to recognize outer sphere reaction and examples of such reactions. **7**

OR

Describe the effect of ions, effect of nucleophile and effect of temperature on reaction mechanism.

(b) Define 'Electron tunnelling' and derive Marcus Equation. **7**

OR

Write a note on unstable (unusual) oxidation states.

5. Answer the following questions in short : **14**

(1) According to Bent's rule, more electronegative substituent prefer hybrid orbital having which character ?

(2) Give one example of a molecule of the type AX_3E_1 according to VSEPR theory.

(3) Why the VSIP of electrons of 2s orbital in nitrogen atom is lower than that of oxygen atom ?

(4) In SCF method, why the columbic term (J) is double ?

(5) How many active vibrations will be there in a non-linear molecule.

(6) Name the d orbital used in σ-bonding in AB5 (D3h) type of molecule.

(7) How would you distinguish between IR and Raman vibrations if a molecule possess centre of symmetry.

(8) In a molecule $[M(CO)_3L_3](C_3v)$, the symmetries of stretching vibrations are $A_1 + E$. How many bands will be active in both i.e. IR and Raman.

(9) Define Hapticity.

(10) Write a structure of Zeise's salt.

(11) $[MoCl_2(\eta^5 - C_5H_5)_2] + C_2H_2 \rightarrow$

(12) Complete the reaction : D $- [Os(dipy)_3]^{2+} + L - [Os(dipy)_3]^{3+} \rightarrow$ _____.

(13) Give the name of process which produces hydrated electrons.

(14) Does reaction rate always increase as the free energy change becomes more negative ?

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SOME CHARACTER TABLE

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v\ (yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, R_y	xz
B_2	1	–1	–1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	–1	R_z	
E	2	–1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	–1	1	1	–1	R_z	
E′	2	–1	0	2	–1	0	(x, y)	$(x^2-y^2, 2xy)$
A''_1	1	1	1	–1	–1	–1		
A''_2	1	1	–1	–1	–1	1	z	
E″	2	–1	0	–2	1	0	(R_x, R_y)	(xy, yz)

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	R_z	
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1		x^2-y^2
B_{2g}	1	–1	1	–1	1	1	–1	1	–1	1		xy
E_g	2	0	–2	0	0	2	0	–2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z	
B_{1u}	1	–1	1	1	–1	–1	1	–1	–1	1		
B_{2u}	1	–1	1	–1	1	–1	1	–1	1	–1		
E_u	2	0	–2	0	0	–2	0	2	0	0	(x, y)	