Ex/BESUS/ PGC-202/10

M.Sc. (Applied Chemistry} 2nd Semester Examination, 2010

Inorganic Chemistry-II

(PGC-202)

Time : 4 hours **Full Marks : 100**

Use *separate answerscript for each group.*

GROUP-A

(Answer any SIX questions.)

1. a) What is Lande splitting factor (gj) ? Derive an expression for it.

   b) Starting from Van Vleck equation, derive an expression for the magnetic susceptibility of a molecule for which the ground state has J = J], the first excited state has J = Jj +1 and energy difference between them is comparable to kT. 5+5

2. a) Discuss the principles of determination of magnetic susceptibility determination by Guoy method.

   b) What is Larmor's precision? Using Larmor's precision, how can you calculate molar diamagnetic susceptibility? 5 +5

3. a) The ground state of Co(II) in tetrahedral coordination environment is ^{4}**A2,** yet the magnetic moment of tetrahedral Co(II) complexes are much higher than that calculated using spin only formula—explain

   b) The electronic spectral studies on transition metal complexes of CO and F indicates that the former is a strong field and the latter a weak field ligand - explain with the help of partial MO diagram. 5 +5

4. Show that the crystal field potential from a square planar arrangement includes contribution from $\mathbf{Y2}^{0}$, $\mathbf{Y4}^{0}$ and $\mathbf{Y4*}^{4}$ but potential from an octahedron includes contribution from $\mathbf{Y4}^{0}$ and $\mathbf{Y**}^{4}$ but not from $\mathbf{Y2}^{0}$. Given

   $Y_{2}^{\circ} = (5/8)*(3\cos^{2}e - 1)\text{-}(2TC)\text{-}^{w}$
   $Y_{4}^{\circ} = (9/128)*(35\cos^{4}0 - 30\cos^{2}6 + 3)\text{-}(2n)**$
   $Y_{4}^{\pm 4} = (315/256)^{,A}\sin^{4}0\text{-}(2n)'^{w}e^{\pm 44}$

5. Calculate the energy of five d-orbitals under tetrahedral crystal field potential. Given

V_{Ict} =- (392/729)*(270*(zer^4/a^5)[Y_4° + (5/14)*(Y/ + YV^4)] and

Vod - (49/1**8V*(2itAw**V)[Y_4° + (5/14)^w(Y_4^4 + Y^)]

$$\int_0^{\pi}\Theta_2^{0*}\Theta_4^{0}\Theta_2^{0}\sin\theta d\theta = 18^{1/2}/7$$

$$\int_0^{\pi}\Theta_2^{1*}\Theta_4^{0}\Theta_2^{1}\sin\theta d\theta = -8^{1/2}/7$$

$$\int_0^{\pi}\Theta_2^{2*}\Theta_4^{0}\Theta_2^{2}\sin\theta d\theta = 2^{1/2}/7$$

$$\int_0^{\pi}\Theta_2^{2*}\Theta_4^{4}\Theta_2^{2}\sin\theta d\theta = 35^{1/2}/7$$

10

6. A transition metal octahedral complex with d^2 electronic configuration shows three spin allowed transitions with energies 17,200,25,200 and 36,000 cm"^{1}, respectively - assign them using Orgel diagram. Correlate transitions in terms of *Dq* and the Racah parameter *B'* and calculate the 10Z)q. 10

7. Show the splitting of five d-orbitals under the influence of point group symmetry Z)$_4$h and ***Cj***$_v$.

Given character tables for subgroup D$_4$ and ***dv***

D_t	E	$2C_4$	C_2	$2C_2$	$2C_2$
Ai	I	1	I	1	1
A_2	1	1	1	-1	-1
*i	I	-1	1	1	-1
B_2	1	-1	1	-1	\
E	2	0	-2	0	0

c»	E	c_2	$a_v(xz)$	
A>	1	1	1	1
A_2	1	I	-I	-I
Bx	1	-1	1	-1
B_2	1	-1	-1	1

10

GROUP-B

[Answer anu FOUR questions.)

8. a) Explain why

   (i) Rh H(Co)(PPh$_3$)$_3$ is more active hydroformylation catalyst than Rh$_4$(Co)$_{12}$.

   (ii) Co H (Co)$_3$(PBu$_3$) improves the linear to branch ratio than Co$_2$(Co)$_8$ during hydroformylation of alkene.

   b) Discuss the catalytic cycle for the hydroformylation of alkene using Co$_2$ (Co)$_8$ catalyst. 5+5

9. a) Point out the main feature of Rh H (Co)(PPh_3) as alkene hydogenation catalyst over Rh CI (PPh_3)$_3$. Explain the steps involved in the hydrogenation of alkene using the former complex as catalyst.

   b) What is Synthesis gas? How is Synthetic Gasolene made from Synthesis gas? 6+4

10. a) Justify that the oxidation of ethylene to acetaldehyde using Palladium (II) catalyst is further enhanced by Copper (II).

    b) Explain how Rh-catalyst Carboxylation of methanol to acetic acid is coupled with HI ^ H_20 cycle. 5+5

11. a) Base hydrolysis of $[Co(NH_3)_5CI]^{*2}$ is very fast while the complex $[Co(CN)_5Cl]^{-3}$ is not hyoVolysed by base. Explain with mechanism.

    b) You want to enhance the rate of replacement of the anionic ligand by H_20 in each of the following complexes, and can choose to do this by adding either a strong acid, a strong base or Ag^+. Which would be effective in each case and why?

    (i) $[Co(H_2NMe)_5\text{-}ON0_2]^{+2}$

    (ii) $[Co(Py)_5Br]^{+2}$

    (iii) $[Co(Ph)_5OMe]^{+2}$. 4+6

12. a) Design two-step syntheses of <u>Cis</u>- and <u>trans</u>- $[PtCl_2(N0_2)(NH_3)]$ starting from $[PtCl_4]^{"2}$.

    b) How does each of the following modifications affect the rate of a square planar complex substitution reaction?

    (i) Changing a <u>tans</u>- ligand from H to CI,

    (ii) Changing the leaving group from CI to I,

    (iii) Adding a bulky substituent to a <u>Cis</u>- ligand,

    (iv) Increasing the positive charge on the complex. 4+6