Chem 341
Inorganic Chemistry
Final Exam, Fall 2000

NAME: _____

- Calculators and model sets are the only aids allowed for this exam. Character tables and a periodic table are provided at the end of the exam (feel free to separate and keep in front of you).

- Partial marks will be rewarded where applicable, so be sure to show all your work and explain your answers.

- **Choose six of the following nine questions. Each question is worth 18 marks, and there is a bonus question worth 6 marks, for a maximum possible score of 114 (but the exam will be out of 108). Distribute your time accordingly.**

- Duration: 2 hours.

- **Check the boxes below to indicate the questions you want graded.**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Mark									

Some potentially useful constants:

$h = 6.626 \times 10^{-34}$ J·s

$c = 3.00 \times 10^{8}$ m·s^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$e = 1.602 \times 10^{-19}$ C

$F = e \cdot N_A = 9.649 \times 10^{4}$ C·mol^{-1}

$m_p = 1.673 \times 10^{-27}$ kg

$m_e = 9.109 \times 10^{-31}$ kg

$k = 1.381 \times 10^{-23}$ J K^{-1}

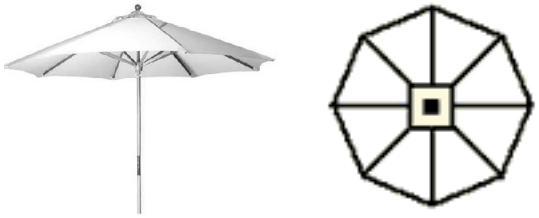
$\pi \simeq 3.1416$

e = the natural number $\simeq 2.718$

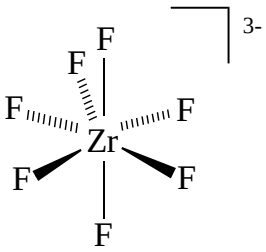
$R = 0.08206$ L·atm·K^{-1}·mol^{-1} $= 8.314$ J·K^{-1}·mol^{-1} $= 8.314$ V·C·K^{-1}·mol^{-1}

1. Give the point groups of the following (note: the point group is not necessarily in the given character tables) [3 marks each]:

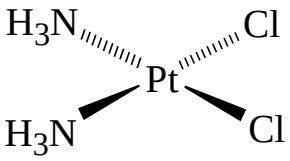
(a) 8-sided Patio Umbrella (note: there is no hook on the end of a patio umbrella; the top view is shown on the right)



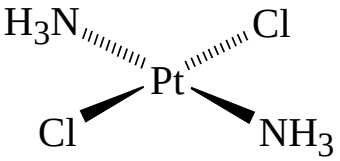
(b) $[ZrF_7]^{3-}$, pentagonal bipyramidal



(c) *cis*-$Pt(NH_3)_2Cl_2$, square planar



(d) *trans*-$Pt(NH_3)_2Cl_2$, square planar



(e) Camaro Z-28 (exterior only)

(f) Camaro Z-28 (exterior only) with a flat tire

2. The molecule with simple formula N_2F_2 has several isomers; two of these isomers have central nitrogens, with a terminal fluorine on each nitrogen.

(a) For the *cis* isomer [3 marks each part, 9 marks total]:

(i) Show the Lewis Dot Diagram (include formal charges, if any)

(ii) What is the point group?

(iii) How many IR bands and Raman bands would you expect if $\Gamma_{vib} = 3A_1 + A_2 + 2B_2$?

(b) For the *trans* isomer [3 marks each part, 9 marks total]:

(i) Show the Lewis Dot Diagram (include formal charges, if any)

(ii) What is the point group?

(iii) How many IR bands and Raman bands would you expect if $\Gamma_{vib} = 3A_g + A_u + 4B_u$?

3. (a) Wilkinson's and Zeigler-Natta are two catalysts that involve the conversion of C=C bonds to C-C bonds. Describe, as fully as possible, the catalytic cycle for one of these industrially important complexes, indicating all steps involved. [9 marks]

(b) Sketch an approximate, but representative, reaction profile (free energy versus reaction coordinate) for an uncatalyzed and catalyzed reaction, if the rate-determining step of the reaction involves [3 marks each, 9 total]:

(i) Association (ii) Dissociation (iii) Interchange

4. (a) Define and give one example of isolobality. [3 marks]

(b) Using Wade's Rules, predict the structures of the following clusters [3 marks each, 15 total]:

(i) $C_4B_4H_8$

(ii) $C_4BH_5Fe(CO)_3$

(iii) $Rh_4(CO)_{12}$

(iv) $Fe_2Rh_2(CO)_{12}$

(v) B_3H_9

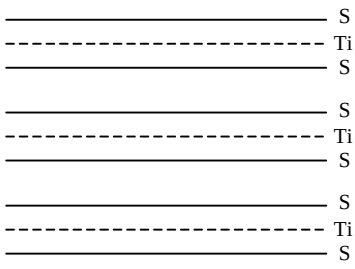
5. (a) Give the stoichiometric formulae of the following solids [3 marks each, 9 total]:

(i) The fluorite structure of calcium fluoride, which consists of a ccp lattice of cations, with anions in all of the tetrahedral interstitial sites.

(ii) The antifluorite form of potassium selenide, where a ccp lattice of anions has all of its tetrahedral sites occupied by cations.

(iii) The body-centered cubic structure of cesium chloride, where Cl^- anions define a simple cubic lattice and Cs^+ occupies the centres of the unit cells.

(b) Titanium disulfide is a layered material, where sulfurs define an hcp lattice. The titaniums occupy all the octahedral holes of alternate layers of the hcp lattice (see figure, right). What is intercalation, and what is the main reason that titanium disulfide may be used as a lithium battery via intercalation? [2 marks]



(c) Describe the process of doping an insulator to make render it semiconducting. Give an example, using band diagrams. [7 marks]

6. (a) For each of the following pairs of acids, circle the stronger acid. [3 marks]

(i) $[V(H_2O)_6]^{3+}$ or $[Nb(H_2O)_6]^{3+}$

(ii) $[Cu(H_2O)_6]^{2+}$ or $[Cu(H_2O)_6]^{3+}$

(iii) H_2SO_4 or H_2CO_3

(b) Write the equilibrium for the one of the above aqua-acids in water. [3 marks]

(c) The following redox reaction between two coordination complexes occurs via an outer sphere mechanism:

$$[Co(NH_3)_5Cl]^{2+} + [Ru(NH_3)_6]^{2+} \Leftrightarrow [Co(NH_3)_5Cl]^{+} + [Ru(NH_3)_6]^{2+}$$

(i) What can be said about the mechanism, reactants and the rate of electron transfer in this reaction? [3 marks]

(ii) Give the name of either the reactants or products for the above redox reaction. [2 marks]

(iii) Give the mechanistic details if the redox reaction occurred instead via an inner sphere mechanism. [3 marks]

(d) What is disproportionation and comproportionation of the oxidation state of a metal? Why does this phenomenon occur, and use Frost Diagrams in your answer. [4 marks]

7. Using ligand field theory and the MO diagrams for octahedral complexes given below, account for the order of the spectrochemical series, with respect to each of the three types of ligands. Describe the chemistry involved in the metal-ligand interaction for each type. Give two examples of each type of ligand, and indicate which of the two will give the larger LFSE value. [15 marks]

σ-donor π-donor π-acceptor

(b) Why is ligand field theory a better account of the properties of transition metal complexes, as compared to that predicted by crystal field theory? [3 marks]

8. (a) Account for the fact that boron trifluoride is monomeric, whereas boron trihydride can, and prefers to, dimerize. [3 marks]

(b) Predict the geometries of the following molecules using VSEPR theory [3 marks each, 9 total]:

(i) XeF_6 (ii) ClF_3 (iii) H_3NO (note: this is not HNO_3!)

(c) Give the MO diagram for N_2^{2+} and O_2^{2+}; fill in the electrons, and indicate the magnetic properties, HOMO, LUMO and bond order for each molecule. [6 marks]

9. (a) Briefly discuss the formulae and structures of the mononuclear and binuclear carbonyl complexes of the first row transition metals. [9 marks]

(b) Carbon rings with extended pi systems are common ligands in inorganic chemistry. Give three examples of complexes that contain this type of ligand, and include the electron count of the complex. [6 marks]

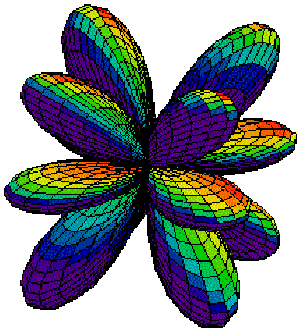
(c) Explain why $Cr(CO)_6$ is stable, while $Cr(NH_3)_6$ is not. [3 marks]

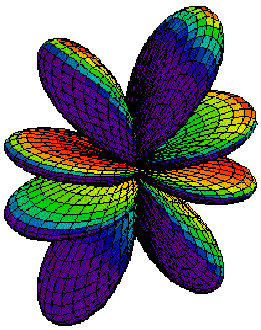
Bonus Question [6 marks]

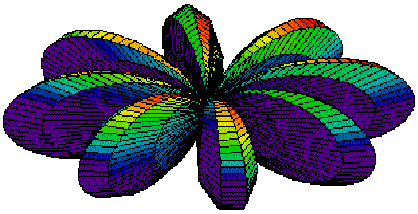
B1. How many g-orbitals are there for a given quantum number? [1 mark]

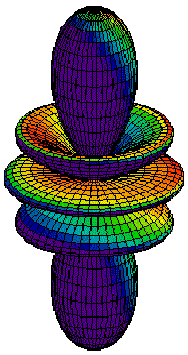
B2. Give the set of quantum number for each of the 5g orbitals. [3 marks]

B3. For each of the 5g-orbitals below, how many radial nodes and angular nodes are there? [2 marks]









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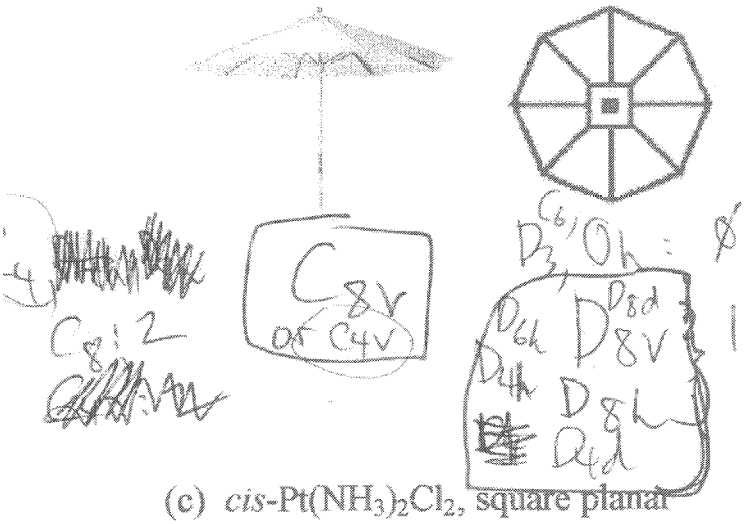

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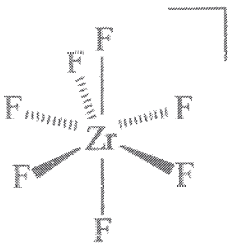

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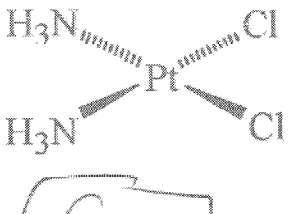

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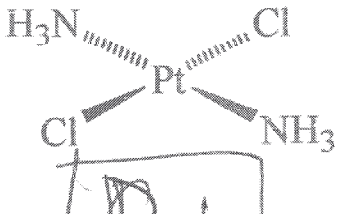

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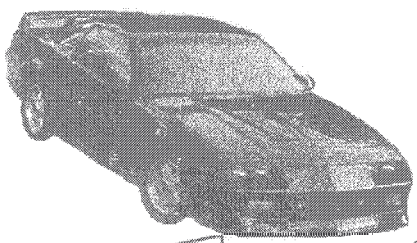

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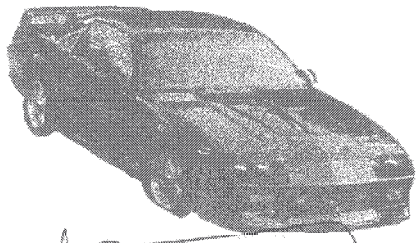

10+14 = 24e⁻

2. The molecule with simple formula N_2F_2 has several isomers; two of these isomers have central nitrogens, with a terminal fluorine on each nitrogen.

(a) For the *cis* isomer [3 marks each part, 9 marks total]:

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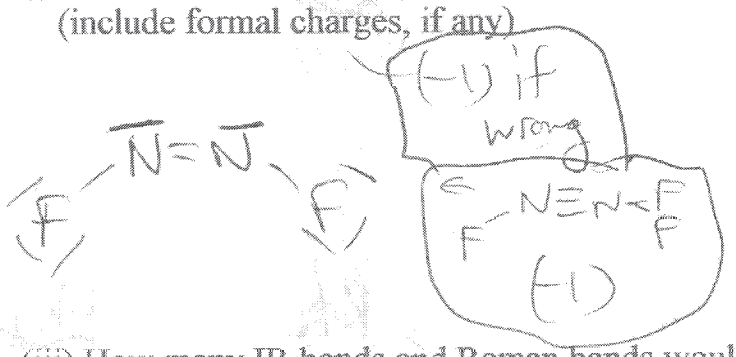


C_{2v}

C_2 : 1

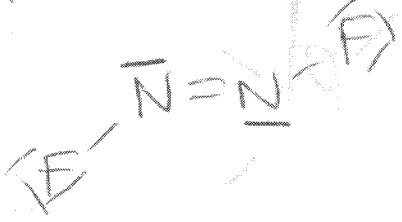
(iii) How many IR bands and Raman bands would you expect if $\Gamma_{vib} = 3A_1 + A_2 + 2B_2$?

5 IR, 6 Raman

(b) For the *trans* isomer [3 marks each part, 9 marks total]:

(i) Show the Lewis Dot Diagram (include formal charges, if any)

(ii) What is the point group?



C_{2h}

C_{4h} : 1 ½

D_{2h} : 2

C_2 : 1

(iii) How many IR bands and Raman bands would you expect if $\Gamma_{vib} = 3A_g + A_u + 4B_u$?

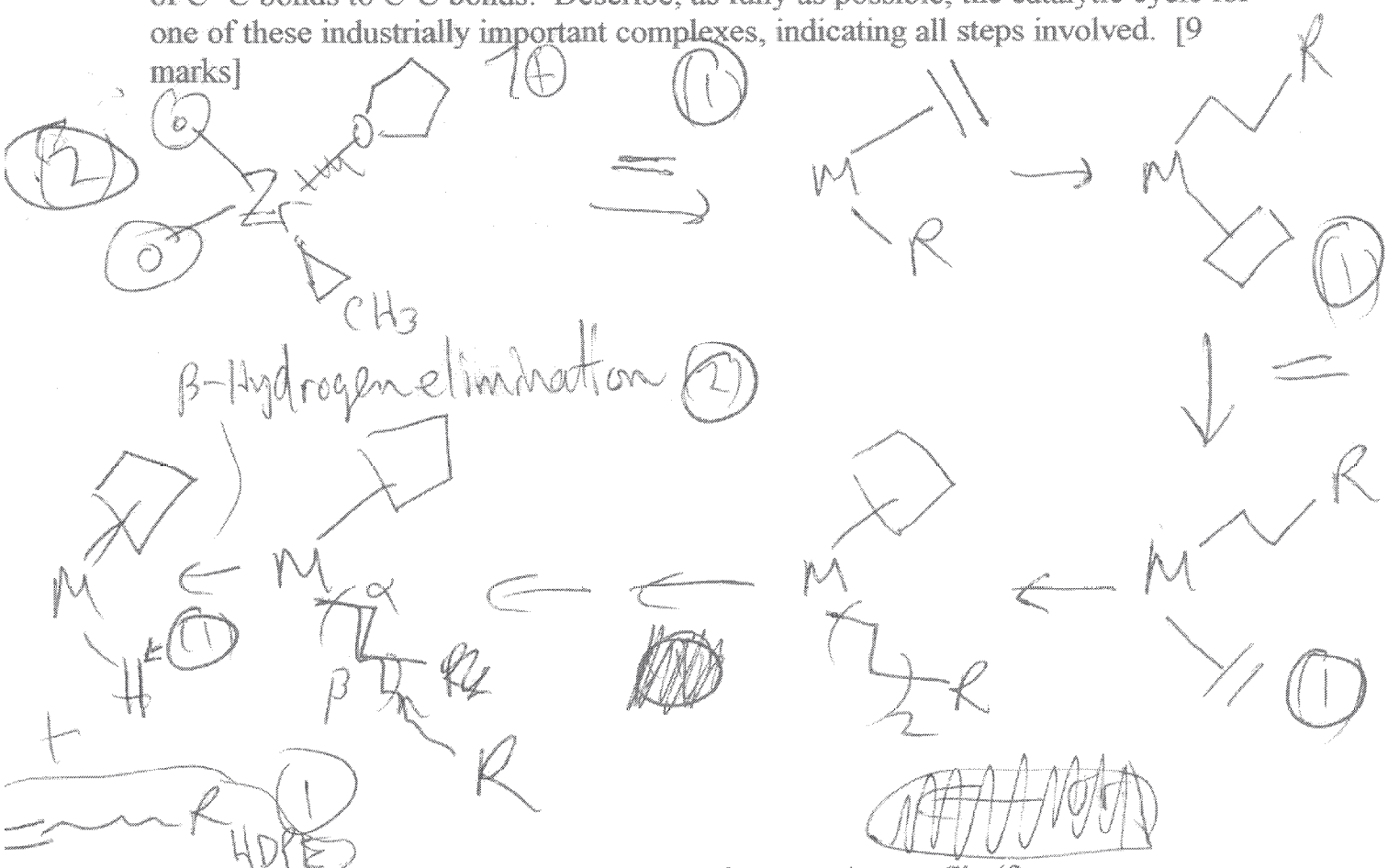
should be 2!

5 IR, 3 Raman

4 ± 4 : 2 marks
IR Raman

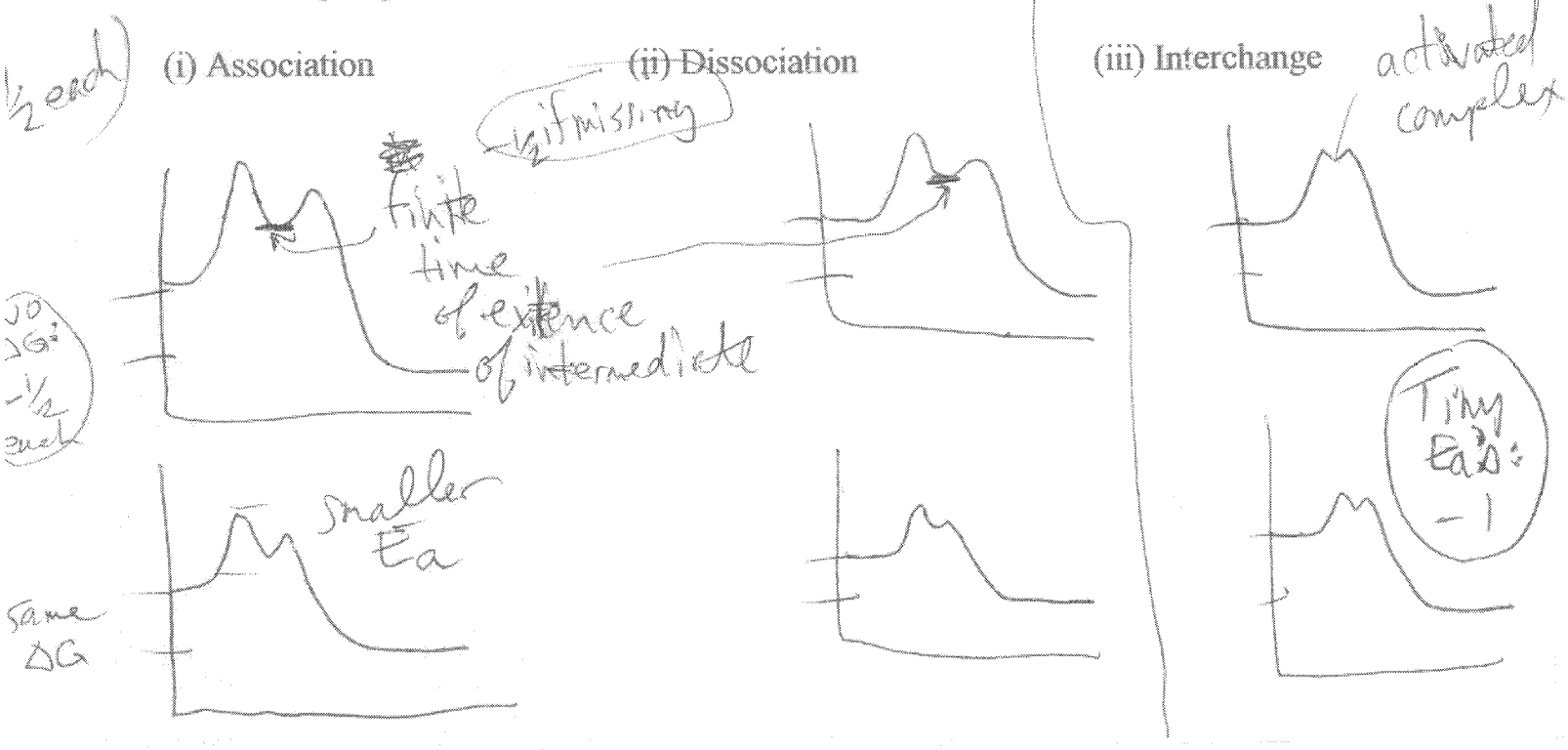
3 ± R ±
5 Raman : 1
or 4

3. (a) Wilkinson's and Zeigler-Natta are two catalysts that involve the conversion of C=C bonds to C-C bonds. Describe, as fully as possible, the catalytic cycle for one of these industrially important complexes, indicating all steps involved. [9 marks]



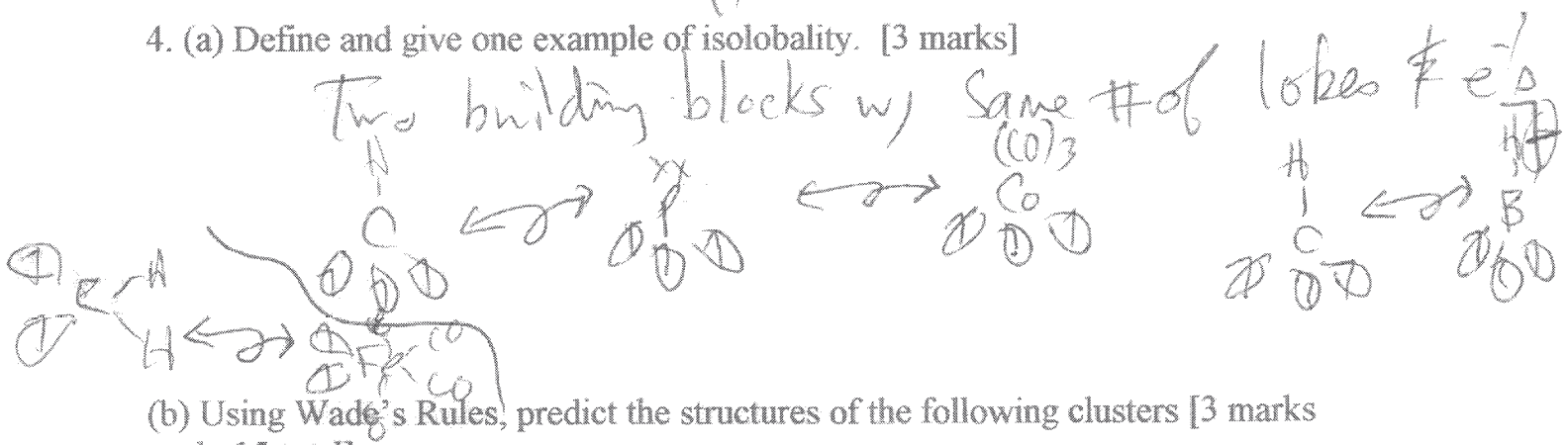
(b) ~~Sketch~~ an approximate, but representative, reaction profile (free energy versus reaction coordinate) for an uncatalyzed and catalyzed reaction, if the rate-determining step of the reaction involves [3 marks each, 9 total]:

(i) Association (ii) ~~Dissociation~~ (iii) Interchange



4. (a) Define and give one example of isolobality. [3 marks] 1/2 each

Two building blocks w/ same # of lobes & e⁻



(b) Using Wade's Rules, predict the structures of the following clusters [3 marks each, 15 total]:

(i) $C_4B_4H_8$

n=8

16 + 12 − 8 = 20e⁻

10 pairs, n+2

nido, based on 9-vertex polyhedron w/ one vertex missing

(ii) $C_4BH_5Fe(CO)_3$

n=6

16 + 3 − 5 + 8 + 6 − 12 = 16e⁻

8 pairs, n+2 pairs

nido, PBP (7-vertex polyhedron) missing one vertex

(iii) $Rh_4(CO)_{12}$

n=4

36 + 24 − 48 = 12e⁻

6 pairs, n+2

nido, TBP missing one vertex

(iv) $Fe_2Rh_2(CO)_{12}$

n=4

16 + 18 + 24 − 48 = 10e⁻

5 pairs, n+1

closo, ~~tetrahedral~~

(v) B_3H_9

n=3

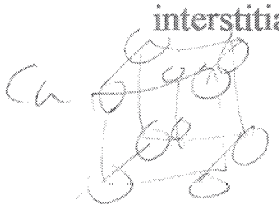
9 − 3 + 6 = 12e⁻

6 pairs, n+3

arachno, TBP missing two vertices

5. (a) Give the stoichiometric formulae of the following solids [3 marks each, 9 total]:

(i) The fluorite structure of calcium fluoride, which consists of a ccp lattice of cations, with anions in all of the tetrahedral interstitial sites.



Ca: $8\times\frac{1}{8}+6\times\frac{1}{2}$ = 4

F = 8×1

CaF_2

Ca_4F_8 −1/2

(ii) The antifluorite form of potassium selenide, where a ccp lattice of anions has all of its tetrahedral sites occupied by cations.

Se: 4

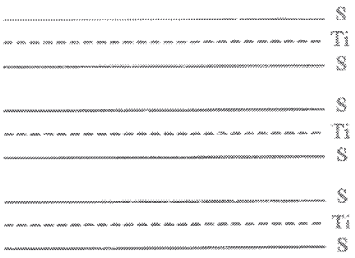
K: 8×1

K_2Se

(iii) The body-centered cubic structure of cesium chloride, where Cl^- anions define a simple cubic lattice and Cs^+ occupies the centres of the unit cells.

CsCl

(b) Titanium disulfide is a layered material, where sulfurs define an hcp lattice. The titaniums occupy all the octahedral holes of alternate layers of the hcp lattice (see figure, right). What is intercalation, and what is the main reason that titanium disulfide may be used as a lithium battery via intercalation? [2 marks]



cations into lattice, e^- into CB

empty space b/w alternate sulfur layers

(c) Describe the process of doping an insulator to make render it semiconducting. Give an example using band diagrams [7 marks].

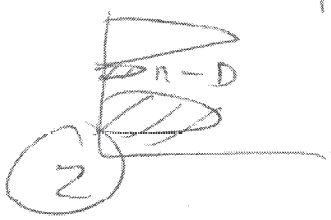
metal (1/2)

Impurity introduction, ~10^{-9} conc^n.

w/ one more or one less e^-, creates new band (1½)

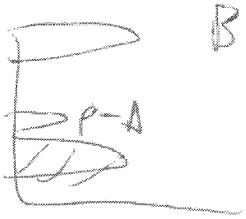
(3)

eg:



P or As into Si (2)

(2)



Bor Al into Si

6. (a) For each of the following pairs of acids, circle the stronger acid. [3 m

(i) $[V(H_2O)_6]^{3+}$ or $[Nb(H_2O)_6]^{3+}$

(ii) $[Cu(H_2O)_6]^{2+}$ or $[Cu(H_2O)_6]^{3+}$

(iii) H_2SO_4 or H_2CO_3

(b) Write the equilibrium for the one of the above aqua-acids in water. [3 mar

$[M(H_2O)_6]^{n+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{(n-1)+} + H_3O^+$

or $[M(H_2O)_6]^{n+} \rightleftharpoons [M(H_2O)_5(OH)]^{(n-1)+} + H^+$

(c) The following redox reaction between two coordination complexes occurs vi an outer sphere mechanism:

$[Co(NH_3)_5Cl]^{2+} + [Ru(NH_3)_6]^{2+} \Leftrightarrow [Co(NH_3)_5Cl]^{+} + [Ru(NH_3)_6]^{3+}$ X 3+

(i) What can be said about the mechanism, reactants and the rate of electron transfer in this reaction? [3 marks]

- Coord # do not change
- Fast e⁻ transfer
- Rate = k[A][B]
- Reactants do not bond/"Interchange"

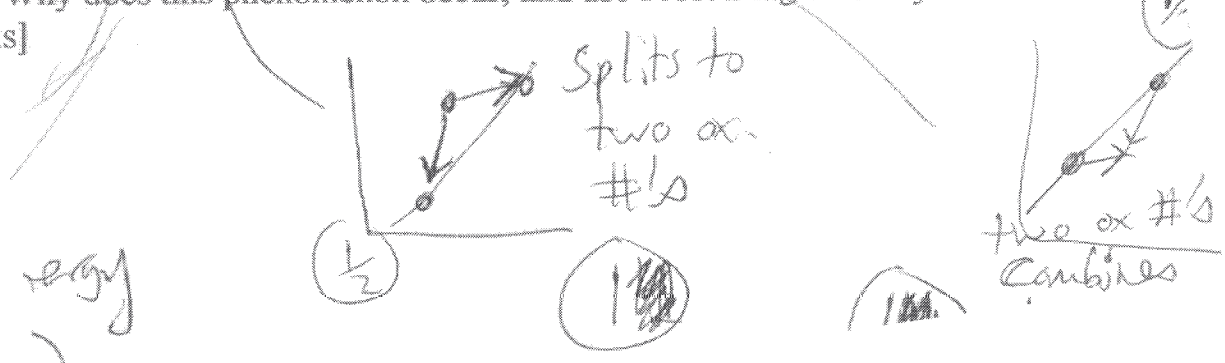
) Give the name of either the reactants or products for the above redox reaction. marks]

pentaamminechlorocobalt (III)
hexaammine ruthenium (II)
" (II)
" (III)

Give the mechanistic details if the redox reaction occurred instead via an inner re mechanism. [3 marks]

- Reactants bond
- e⁻ hops via M–L–M intermediate
- Coord #'s change
- Slower e⁻ transfer

hat is disproportionation and comproportionation of the oxidation state of a Why does this phenomenon occur, and use Frost Diagrams in your answer. ks]



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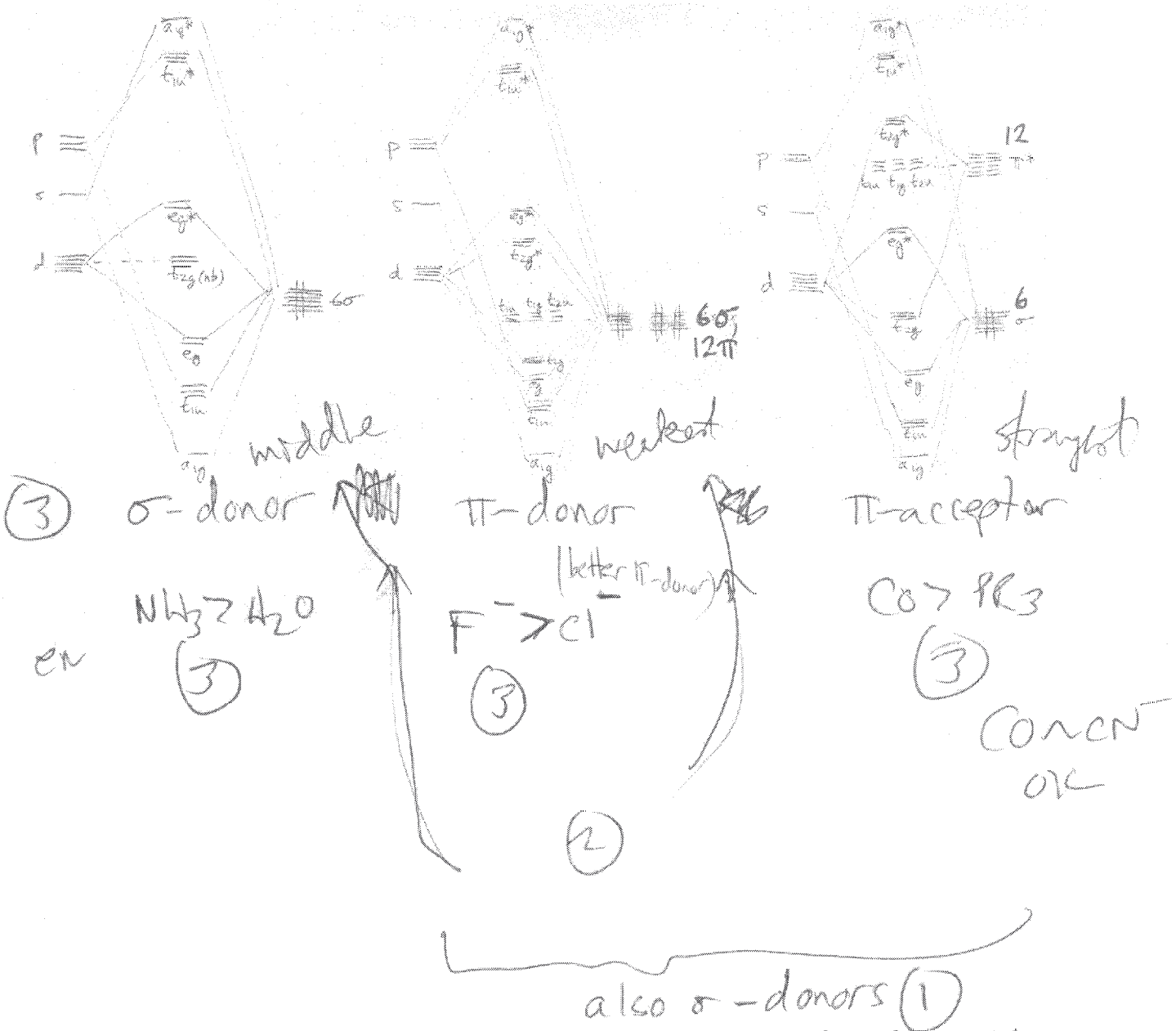

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L's not point -ve charges
Takes into account orbital overlap
(Better measure of Δ_o)

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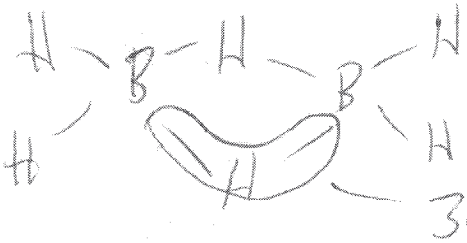
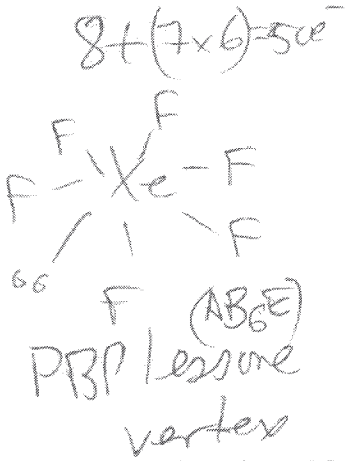
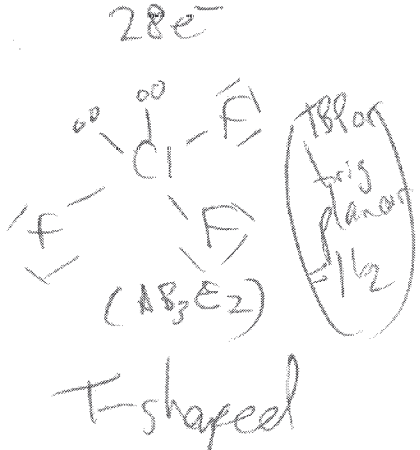


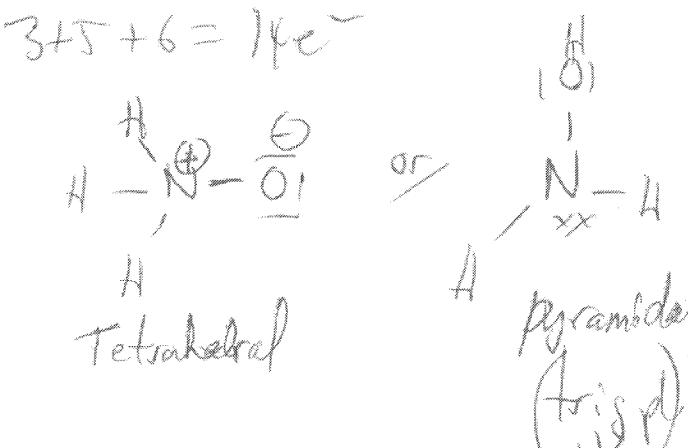
Can't occur for BF_3

(b) Predict the geometries of the following molecules using VSEPR theory [3 marks each, 9 total]:

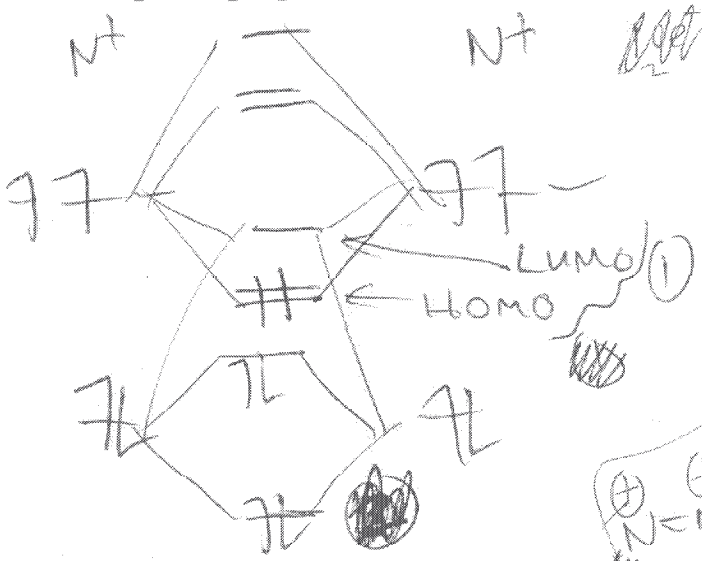
(i) XeF_6 (ii) ClF_3 (iii) H_3NO (note: this is not HNO_3!)

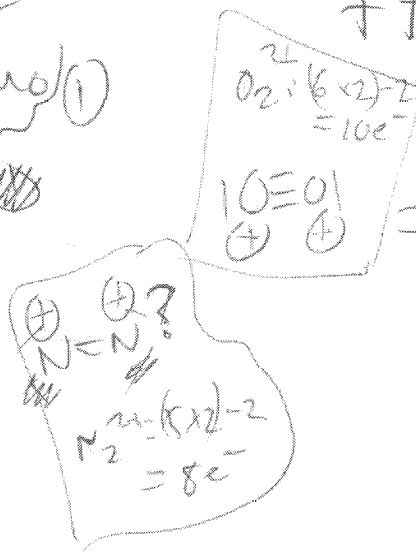


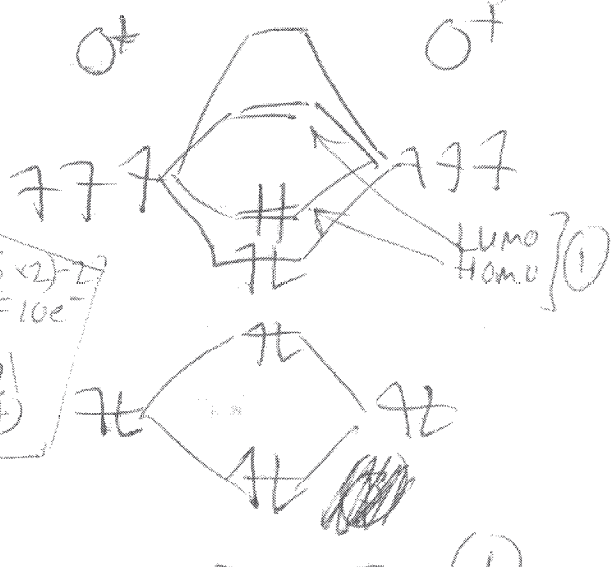




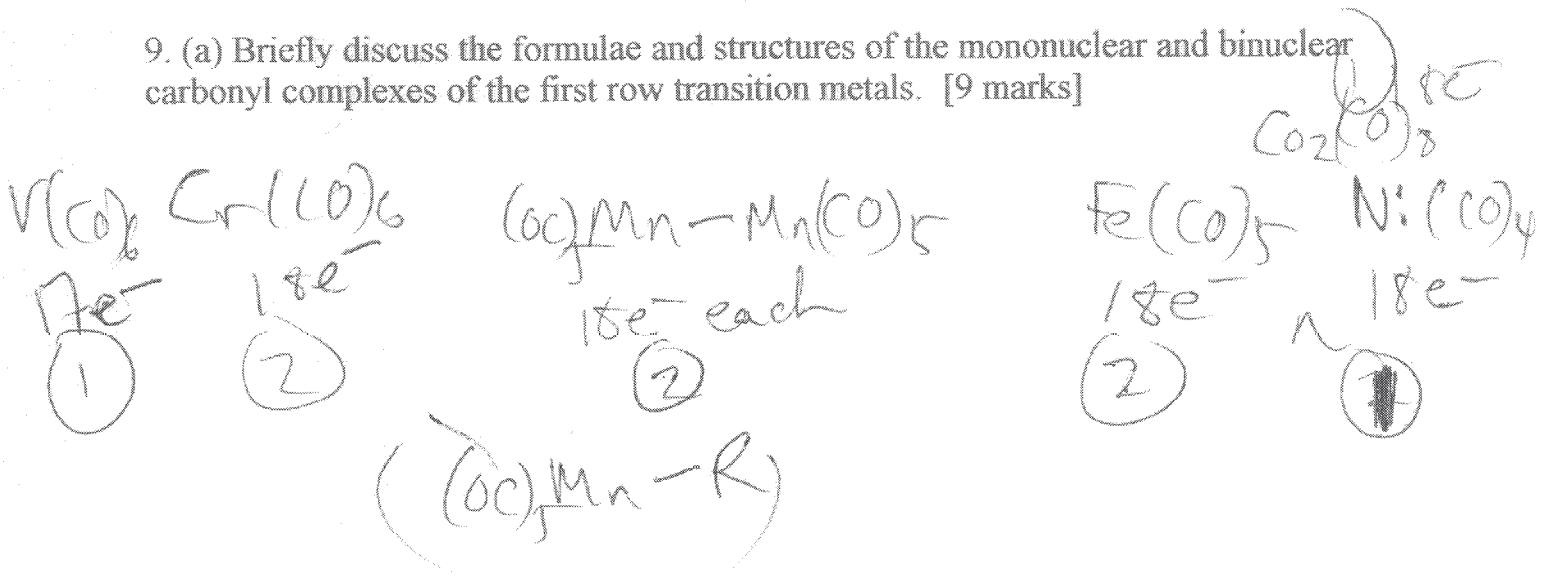
(c) Give the MO diagram for N_2^{2+} and O_2^{2+}; fill in the electrons, and indicate the magnetic properties, HOMO, LUMO and bond order for each molecule. [6 marks]



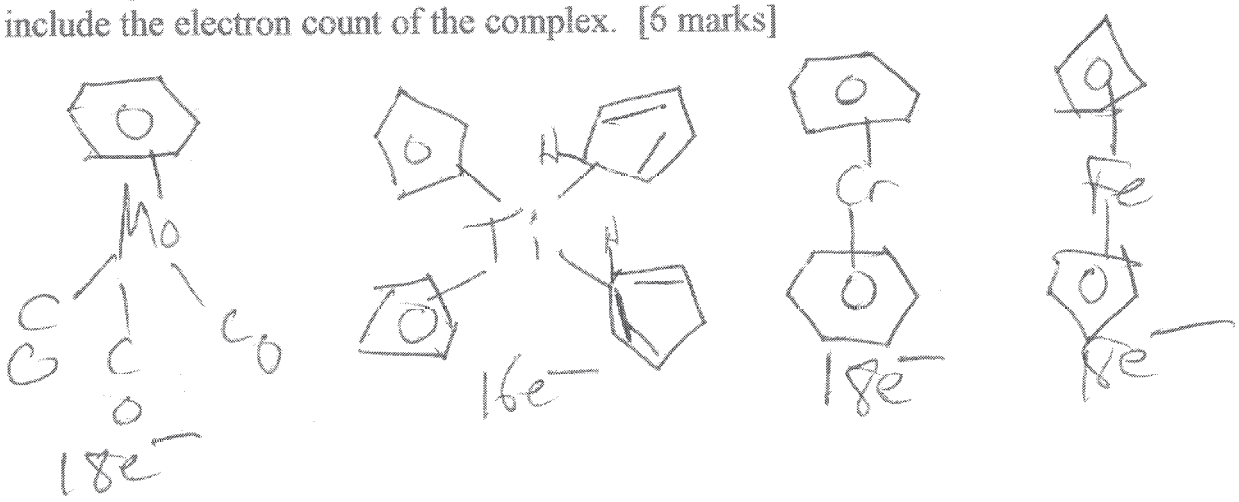




9. (a) Briefly discuss the formulae and structures of the mononuclear and binuclear carbonyl complexes of the first row transition metals. [9 marks]



(b) Carbon rings with extended pi systems are common ligands in inorganic chemistry. Give three examples of complexes that contain this type of ligand, and include the electron count of the complex. [6 marks]



(c) Explain why $Cr(CO)_6$ is stable, while $Cr(NH_3)_6$ is not. [3 marks]

$4s^2 3d^4$

π*-backbonding, relieves e⁻ density on Cr (1/2)

σ-donor, Cr already Ø-valent. (1/2)

Bonus Question [6 marks]

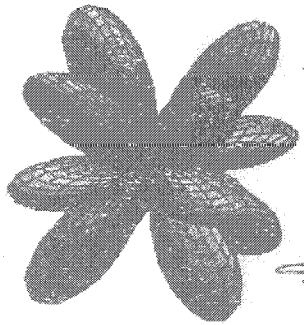
B1. How many g-orbitals are there for a given quantum number? [1 mark]

9

B2. Give the set of quantum number for each of the 5g orbitals. [3 marks]

n	l	m_l
5	4	-4
5	4	-3
5	4	-2
⋮	⋮	⋮

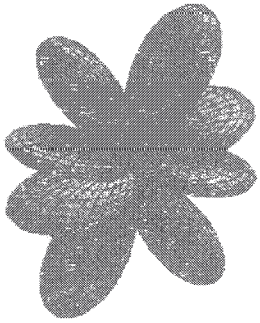
B3. For each of the g-orbitals below, how many radial nodes and angular nodes are there? [2 marks]



$n-l-1$

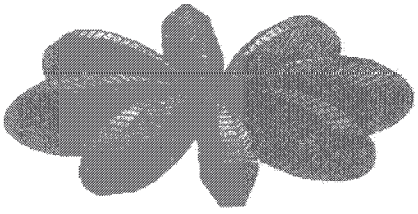
$= 5-4-1$

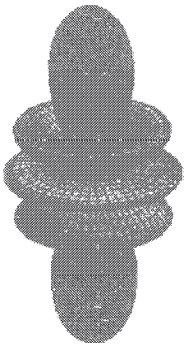
$= 0$ radial nodes

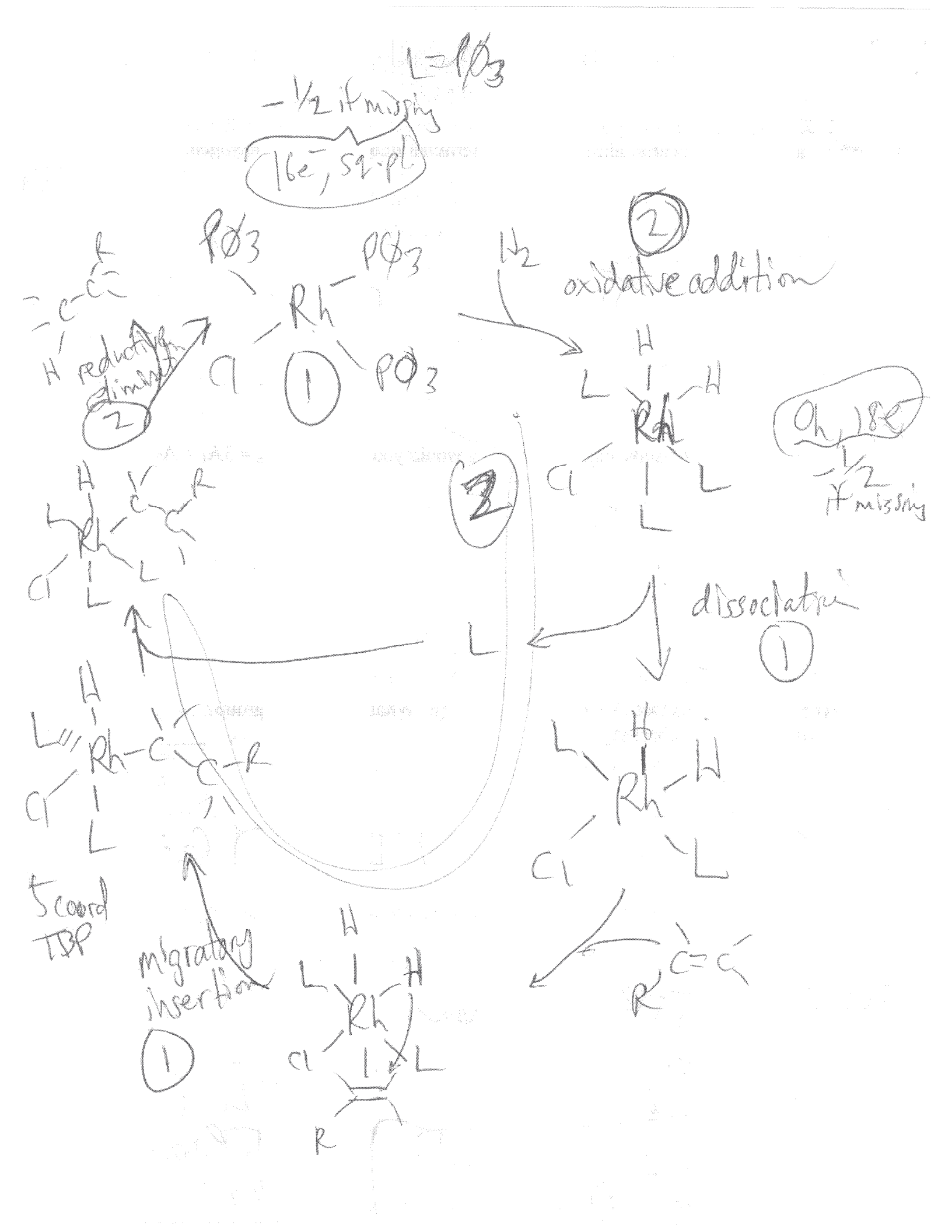


$l = 4$

angular nodes






L = PØ3
- ½ if missing
16e, sq-pl
PØ3
PØ3
Rh
Cl
PØ3
1
H2
2
oxidative addition
reductive elimination
2
H
L
Rh
Cl
L
L
Oh, 18e
- ½ if missing
2
dissociation
1
L
H
L
Rh
Cl
L
5 coord TBP
migratory insertion
1
H
L
Rh
Cl
L
R
H
L
Rh
Cl
L
C=C
R