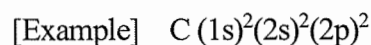


Inorganic Chemistry I
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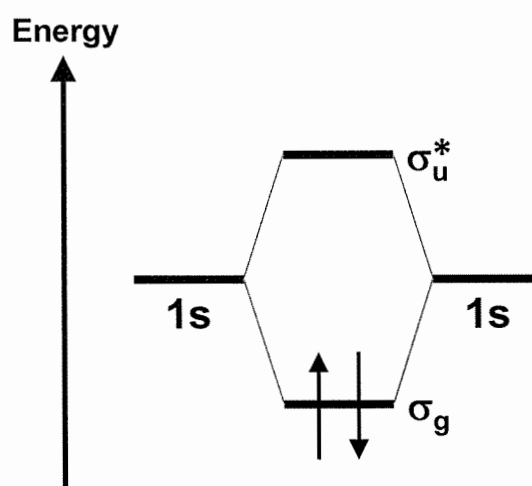
I – a Answer the following questions regarding halogens.

(1) Write down the ground state electronic configurations for chlorine (Cl) and bromide (Br<sup>-</sup>) according to the example.



(2) Draw the molecular orbital energy level diagram for F<sub>2</sub> molecule and add electrons in the diagram, according to the example.

[Example]



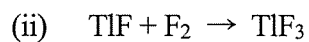
Molecular orbital energy level diagram for H<sub>2</sub> molecule

(3) Arrange four hydrogen halides (HF, HCl, HBr, and HI) in decreasing order of the boiling point. Also, explain the reason of the trend briefly.

I – b Consider the structures of the following molecule and ions, (i) ~ (iii), based on the valence-shell electron pair repulsion (VSEPR) model, and draw the structures with showing spatial arrangement of each atom clearly. In case that the central atom has lone-pair electrons, show the direction of each lone pair in the structure. Also, answer the point group for each molecule or ion, (i) ~ (iii).

- (i) NF<sub>3</sub>
- (ii) PF<sub>6</sub><sup>-</sup>
- (iii) XeF<sub>5</sub><sup>-</sup>

I – c Answer the questions regarding the following reactions, (i) ~ (iii).



(1) Which reactant acts as an acid in the reaction (i),  $\text{SnCl}_2$  or  $\text{CsCl}$ ? Also, which term best describes the acid, Brønsted-Lowry acid or Lewis acid?

(2) Give the oxidation numbers of all the metallic atoms in the reactions (ii) and (iii).

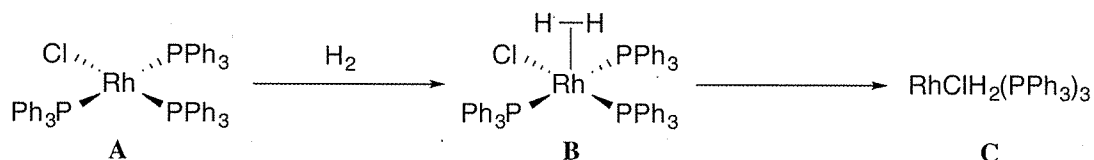
(3) Some *p*-block metals with high atomic numbers, such as tin, thallium, and lead, tend to form ions and compounds whose oxidation number is two less than the number of valence electrons. This phenomenon is called inert pair effect. Account for the reason of the effect briefly.

## Inorganic Chemistry II

II – a Answer the number of the CO ligands ("n" in each molecular formula) to satisfy the 18-electron rule for the organometallic complexes listed below [(i)~(v)]. Show how you count the number of electrons in each organometallic complex. All the organometallic complexes listed below are monomers. Here,  $C_6H_6$  = benzene and  $(C_5H_5)^-$  = cyclopentadienyl.

- (i)  $Cr(CO)_n$
- (ii)  $Fe(CO)_n$
- (iii)  $HMn(CO)_n$
- (iv)  $W(\eta^6-C_6H_6)(CO)_n$
- (v)  $Rh(\eta^5-C_5H_5)(CO)_n$

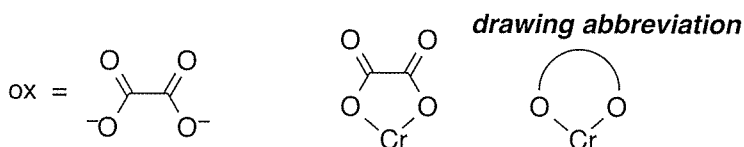
II – b The coordination of a hydrogen molecule to the complex **A** generates the complex **B**. The oxidative addition of a hydrogen molecule gives the complex **C**. Answer the following questions regarding these reactions.



(1) Answer the formal oxidation state of Rh and the number of electrons according to the 18-electron rule for the complexes **A**, **B**, and **C**.

(2)  $^1H$  and  $^{31}P$  NMR measurements indicate that the complex **C** has two kinds of Rh-H and two kinds of Rh-P in a different environment. Draw the most probable structure that is expected from these observations. Show the equivalent  $PPh_3$  ligands among the three  $PPh_3$  ligands.

II – c Draw all of the possible stereoisomers for the  $[Cr(Cl)_2(ox)_2]^{3-}$  complex. Explain the relationship between these stereoisomers. Here, the ox ligand may be abbreviated as follows, when you draw stereoisomers.



II –d Answer the following questions regarding tetrahedral complexes.

(1) Five  $d$ -orbitals of a metal ion in a tetrahedral crystal field are split into two groups. Draw the  $d$ -orbital energy level diagram and label each  $d$ -orbital ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{z^2}$ , and  $d_{x^2-y^2}$ ).

(2) The  $[\text{Ni(II)Cl}_4]^{2-}$  complex is tetrahedral. Answer the electron configuration of  $d^8$  Ni(II) ion according to the example shown below. In case of degenerate electron configurations, you can answer one of them. Answer the total spin quantum number ( $S$ ).

[Example]  $(d_{xy})^n(d_{yz})^n(d_{zx})^n(d_{z^2})^n(d_{x^2-y^2})^n$  ( $n = 0, 1, 2$ )

(3) In contrast to  $(3d)^8$  Ni(II) complexes,  $(4d)^8$  complexes such as Pd(II) and  $(5d)^8$  complexes such as Au(III) tend to adopt a square planar geometry. Explain the reason for this briefly.

II –e Answer the following questions regarding the ligand field theory.

(1) Answer all of the possible ligands that are classified into ①  $\pi$ -donor ligands and ②  $\pi$ -acceptor ligands from the following seven ligands.



(2) Draw the orbital interaction between a CO ligand and a metal ion, and explain briefly the reason why the CO ligand functions as a  $\pi$ -acceptor ligand.

(3)  $\pi$ -Acceptor ligands increase the ligand-field splitting parameter  $\Delta_{\text{O}}$  in the octahedral ligand field. Explain the reason for this briefly, using the  $d$ -orbital energy level diagrams to illustrate the changes induced by the  $\pi$  bonding.