

## Inorganic Chemistry I

[ Total 2 pages ]

I – a

Read the following sentences and answer the questions.

Structures of molecules with covalent bonds are determined by hybridizing the atomic orbitals such as s, p, d orbitals, *etc.* For example, the electron configuration of C atom ( $Z = 6$ ) is  $[\text{He}](2s)^2(2p)^2$ , and the electron configuration of  $\text{CF}_4$  molecule is  $[\text{He}](2s)^2(2p)^6$  by taking one electron from each F atom. Because  $\text{CF}_4$  adopts  $sp^3$  hybridization, the molecule shows a tetrahedron structure.

( 1 ) Answer the number of p orbitals associated with a given principal quantum number. Draw the electron distributions of the p orbitals when the principal quantum number is 2.

( 2 ) Answer the electron configuration of the B atom in  $\text{BF}_3$  molecule, and the hybridized orbital and the structure of the  $\text{BF}_3$ . The atomic number of B atom is  $Z = 5$ .

( 3 ) Answer the number of d orbitals associated with a given principal quantum number. Answer the smallest principal quantum number that accommodates d orbitals and draw the electron distributions of the d orbitals at this principal quantum number.

( 4 ) Answer the electron configuration of the Ti atom in  $\text{TiCl}_4$  molecule, and the hybridized orbital and the structure of the  $\text{TiCl}_4$ . The atomic number of Ti atom is  $Z = 22$ .

( 5 )  $[\text{NiCl}_4]^{2-}$  shows a tetrahedron structure, and  $[\text{Ni}(\text{CN})_4]^{2-}$  shows a square planar structure. Answer the reason for such different structures by considering the electron configurations. The atomic number of Ni atom is  $Z = 28$ .

I – b

Answer what you know about the following. Schematic diagrams may also be used.

( 1 ) n-type and p-type semiconductors.

( 2 ) X-ray diffraction and its use.

I – c

Water ( $\text{H}_2\text{O}$ ) becomes ice when cooled below 273 K ( $0^\circ\text{C}$ ) under 1 atm. The crystals exhibit hexagonal space group, with lattice constants  $a = 0.453 \text{ nm}$  and  $c = 0.741 \text{ nm}$ ; the density of ice at 1 atm 273 K is  $0.917 \times 10^6 \text{ g/m}^3$  and the Avogadro number  $6.02 \times 10^{23}$ . Answer the following questions.

( 1 ) Answer how many water molecules are contained in a unit cell of ice crystals. Note that the calculation formula should be given.

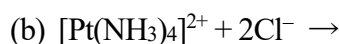
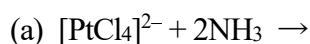
( 2 ) Illustrate the positions of the water molecules that are nearest neighbours in the tetrahedral structure, distinguishing between oxygen and hydrogen, respectively. Note that covalent and hydrogen bonds should be shown.

## Inorganic Chemistry II

【Total 2 pages】

II – a Answer the following questions concerning metal complexes.

(1) Answer the following chemical reaction products, giving their stereoscopic structures.



(2)  $[\text{Fe}(\text{en})_2\text{Cl}_2]^+$  (en: ethylenediamine) has three isomers.

(a) Draw all the structures of the three isomers. Use the description of en, as given in the right figure for simplicity.

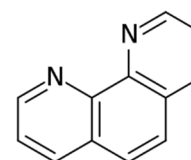
Description  
of en



(b) Assuming that the three isomers are isolated, explain how the three isomers are identified when the infrared absorption spectra, the Raman scattering spectra, and circular dichroism spectra are recorded.

(3)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  shows a weak absorption with a molar absorption coefficient of  $\sim 5 \text{ L/mol}\cdot\text{cm}$  at 493 nm, while  $[\text{Fe}(\text{phen})_3]^{2+}$  (phen: phenanthroline) exhibits a strong absorption with a molar absorption coefficient of  $\sim 11,000 \text{ L/mol}\cdot\text{cm}$  at 510 nm.

Molecular structure  
of phen



(a) Answer the name of the weak absorption of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .

(b) Answer the name of the strong absorption of  $[\text{Fe}(\text{phen})_3]^{2+}$ .

(c) Answer the reason why the absorption of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is weak while the one of  $[\text{Fe}(\text{phen})_3]^{2+}$  is strong.

(d) Is the corresponding absorption of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  more intense than the one of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  at 493 nm? Answer together with the reason.

II – b Answer the following questions about carbonyl complexes.

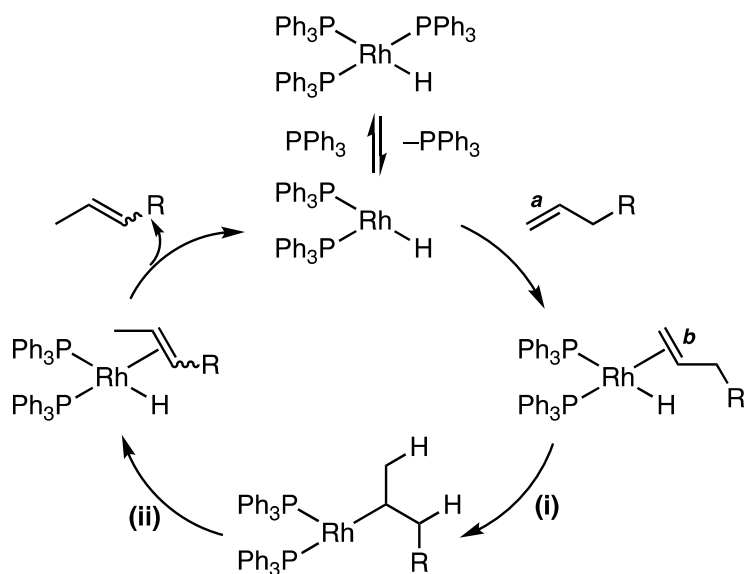
- ( 1 ) Answer the formal oxidation number and number of valence electrons (based on 18-electron rule) of each of the following complexes.



- ( 2 ) Answer the magnetic property (paramagnetic or diamagnetic) of each of the following complexes. Explain why.



II – c Answer the following questions about catalytic reactions. (Ph = phenyl)



- ( 1 ) Choose the names for reactions (i) and (ii) from the following list.

transmetalation	oxidative addition	insertion	cycloaddition
$\beta$ -hydride elimination	reductive elimination		

- ( 2 ) Which C=C bond length is longer, *a* or *b*? Explain why.