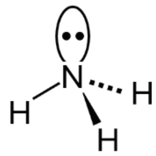
Inorganic Chemistry I

I-a Answer the following questions based on VSEPR (Valence Shell Electron Pair Repulsion) theory.

(1) Explain, with reasons, whether the H–O–H bond angle in a water molecule is larger or smaller than the central angle of a regular tetrahedron (109.5°). You may use figures for explanation.

(2) Show the three-dimensional structures for molecules and ions (a)–(c), following the example in the figure on the right. Include lone pairs if present.



(a) : BF_4^- (b) : SF_4 (c) : XeF_4

(3) The point group (Schönflies symbol) of the NH_3 molecule is C_{3v}. Similarly, answer the point groups (Schönflies symbols) for each of the molecules and ions (a)–(c).

I-b Answer the following questions regarding analytical measurements of compositions and crystal structures in solids.

(1) In X-ray photoelectron spectroscopy (XPS), the sample is irradiated with X-rays of a defined energy, and the emitted photoelectrons are detected. Explain how the detected photoelectrons are utilized for elemental identification and quantification in about 40 words.

(2) When XPS measurements were carried out on a Si single crystal stored in air, C and O were also detected in addition to Si. Explain the reason in about 30 words.

(3) For precise structural analysis of the LiH crystal, neutron diffraction is more suitable than X-ray diffraction. Explain why X-ray diffraction is less suitable for the LiH crystal in about 50 words.

(Continued on the next page)

I-c Read the sentences below and answer the following questions.

Graphite and diamond are (a) of carbon. In graphite, carbon atoms have (b) hybrid orbitals, forming entirely layered (c) lattices. Regarding the interactions between atoms, (d) bonds dominate within layers, whereas (e) interactions dominate between layers. In contrast, in diamond, carbon atoms have (f) hybrid orbitals, forming three-dimensional (g) networks.

In boron nitride (BN), the alternating arrangement of boron and nitrogen atoms allows for structural formations similar to those of graphite and diamond. Although hexagonal boron nitride (h-BN) exhibits graphite-like layered structures, *h-BN is an insulator, in contrast to the high conductivity of graphite. Furthermore, the diamond-like crystal structure observed in cubic boron nitride (c-BN) is known as the (h) structure.

(1) Choose the most appropriate word for (a)–(h) from the list below. Each word can be used only once.

List: allotropes, isotopes, sp^3, sp^2, sp, tetrahedral, octahedral, body-centered-cubic, hexagonal-closed-packed, honeycomb, rock-salt, zinc-blende, wurtzite, cesium-chloride, covalent, ionic, van der Waals, coordinate

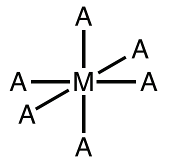
(2) Regarding the *underlined part, explain the reason for the high conductivity of carbon in about 20 words. In addition, explain the reason for the insulating property of h-BN in about 30 words.

(The end)

Inorganic Chemistry II

II-a Answer the following questions concerning metal complexes.

(1) Draw the six isomers of octahedral $MA_2B_2C_2$ complexes, where the two of each of three types of monodentate ligands A, B, and C are coordinated to the metal center M. The structure should be drawn as shown on the right.



(2) Answer the questions about the ionic radius of transition metal ions in metal complexes.

(a) Generally, for the same metal atom, the ionic radius decreases as the oxidation number increases (ex. Fe^{I}, Fe^{II}, and Fe^{III}). Briefly explain why.

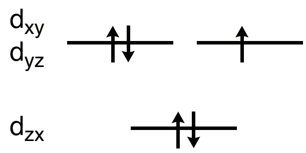
(b) Generally, for the same period with the same oxidation number (ex. Mn^{II}, Fe^{II}, and Co^{II}), the ionic radius generally decreases as the atomic number increases. Briefly explain why.

(3) Choose the appropriate word to fill in the blank in the following sentences. For (e) and (g), choose from the list of words below, and for the others, choose from the words in the box.

Thiocyanate ligand SCN^{-} tends to coordinate with Cr^{3+} and Co^{3+} ions on the [(a) S / N] atom side, whereas the coordination to Ag^{+} and Cd^{2+} ions tends to occur on the [(b) S / N] atom side. This phenomenon is understood as the HSAB (Hard and Soft Acids and Bases) rule. Relatively [(c) hard / soft] acids such as Cr^{3+} and Co^{3+} ions tend to be coordinated with [(d) small / large] atoms due to [(e)] interactions, while Ag^{+} and Cd^{2+} ions are [(f) hard / soft] acids, and [(g)] interactions are dominant in forming coordinate bonds, so they tend to be coordinated with [(h) small / large] atoms.

List: van der Waals, orbital, hydrophobic, electrostatic

(4) $[Fe(CN)_6]^{3-}$ complex shows an octahedral structure, and central Fe^{3+} ion consists of five 3d electrons. Draw the electronic configuration of 3d electrons according to the example shown on the right.



(5) $[NiCl_4]^{2-}$ complex shows a tetrahedral structure, whereas $[Ni(CN)_4]^{2-}$ shows a square planar structure. Draw the electronic configuration of 3d orbitals and answer the reason. Answer which metal complex shows paramagnetism with the reason.

(Continued on the next page)

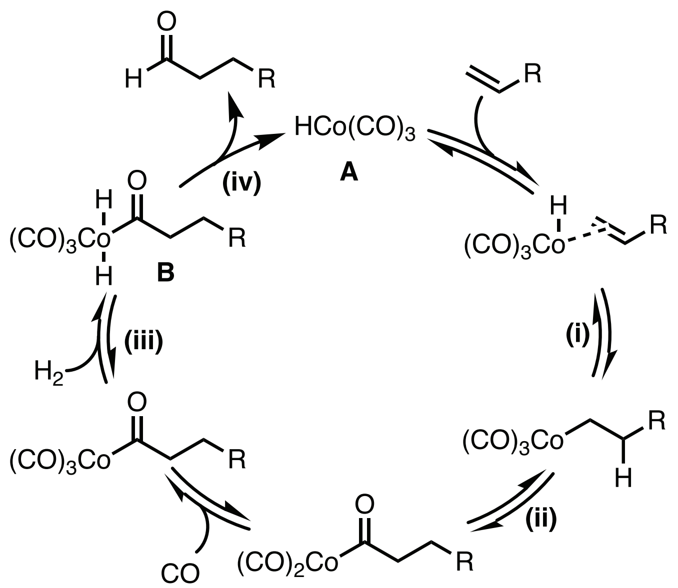
II-b Answer the following questions concerning metal complexes.

(1) There is a large difference in the stability of the complexes Cp_2Fe and Cp_2Co. Based on the 18 electron rule, explain which complex is less stable, and what redox reaction is likely to occur in the unstable complex.

Cp = cyclopentadienyl

(2) Draw the structures of metal complexes $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$, which satisfy the 18 electron rule.

II-c Answer the following questions of catalytic reactions. (R = an organic functional group)

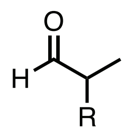


(1) Choose the suitable name for each reaction **(i)**, **(ii)**, **(iii)**, and **(iv)** from the following list. Each name can be used more than once.

List: transmetalation, oxidative addition, insertion, cycloaddition, *β*-hydride elimination, reductive elimination, coordination

(2) For complexes **A** and **B**, answer the formal oxidation number of each transition metal and the number of valence electrons based on the 18-electron rule.

(3) In this catalytic reaction, compound **C** (shown on the right) can also be obtained as a side product. Draw the reasonable reaction mechanism to produce **C**.



C

(The end)