

Graduate School Entrance Examination for 2016

(Department of Chemistry)

Specialized Subject

Examination Time: 13:00 ~ 16:30

Total Available Score: 350 points

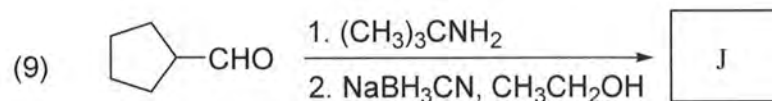
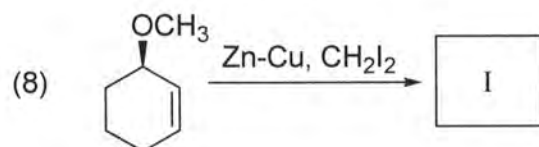
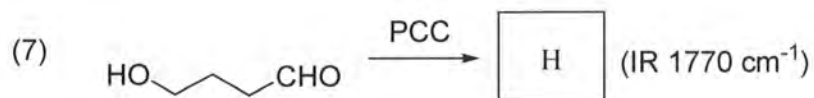
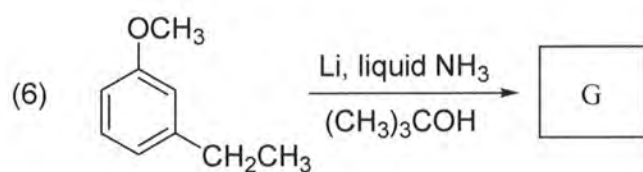
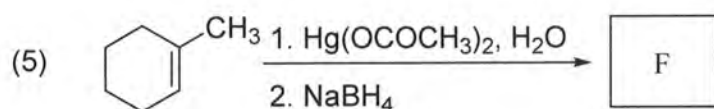
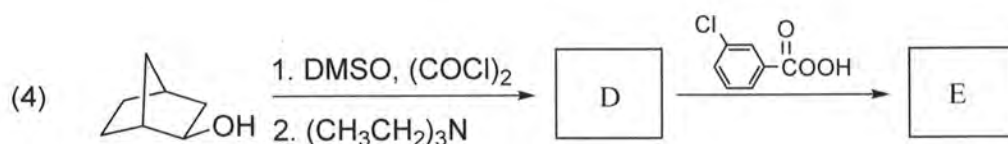
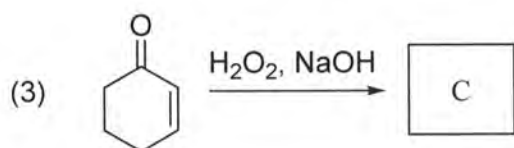
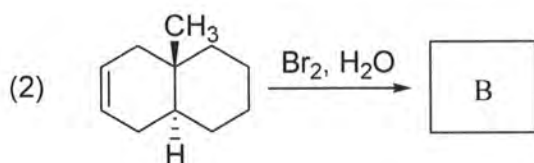
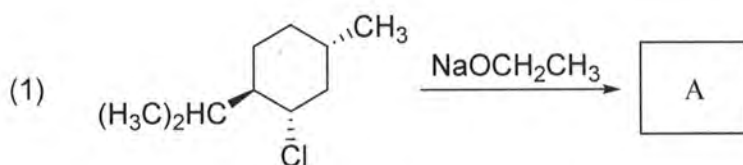
< INSTRUCTIONS >

- (1) Make sure you have received one problem booklet and eight answer sheets.
Each problem booklet consists of eight questions written in Japanese and their English version.
The contents of the Japanese version and the English version are the same.
Choose seven among eight of the following problems and answer them.
Write your answers on the appointed answer sheet.
A problem number is fixed on each answer sheet beforehand.
Raise your hand immediately if any of the contents are different from what you expected.
- (2) Fill in each answer sheet with your seat number and your name by all means.
- (3) In terms of problem numbers **3 ~ 8**, you can use the back side of each answer sheet.
- (4) Write a big X on the answer sheet of the problem you don't select.

(worksheet)

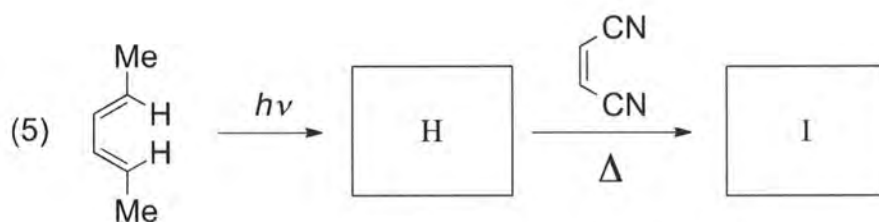
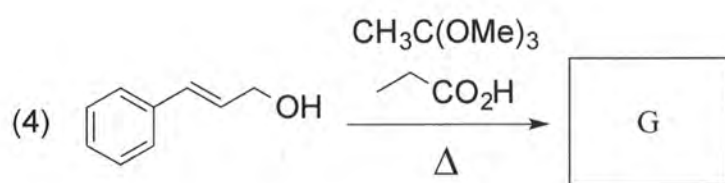
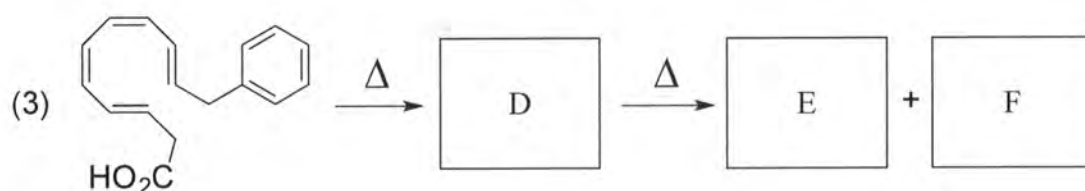
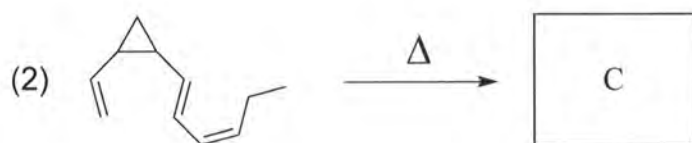
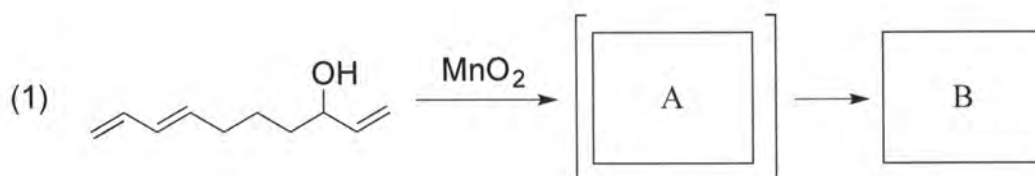
1 Give the structure of the major product expected from each of the following reactions (1) ~

(9). Be sure to show stereochemistry clearly where necessary.



(worksheet)

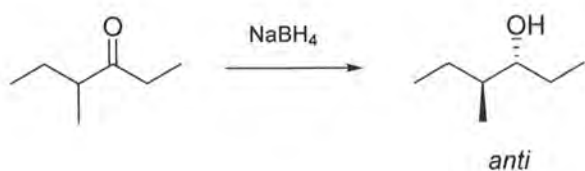
2 Indicate the structure and stereochemistry of the major product to be expected in the following reactions (1) ~ (5).



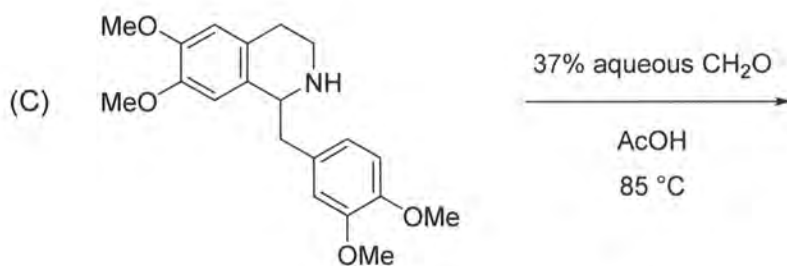
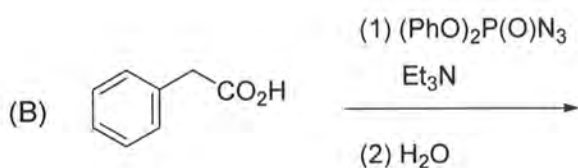
(worksheet)

3 Answer the following questions:

- (1) The *anti* diastereoisomer was formed as the major product in the following transformation. Explain your reasoning for the outcome. Use Newman projections to support your answer.



- (2) Propose the products of the transformations shown below (A ~ C). Additionally, provide a detailed mechanism to rationalize the outcome.



(worksheet)

4 Answer the following questions:

(1) An ideal gas of n mol undergoes an isothermal reversible expansion at temperature T K from an initial volume V to a final volume $2V$. Calculate heat q , internal energy change ΔU , enthalpy change ΔH , entropy change ΔS , Helmholtz energy change ΔA , and Gibbs energy change ΔG in the isothermal reversible expansion, where a gas constant is R .

(2) Answer the following questions for heat capacity.

(a) Show the definitions of heat capacity at constant pressure C_p and heat capacity at constant volume C_v in partial differential form.

(b) Show that

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \quad (i)$$

using the definitions of heat capacity and a total differential equation of $U(T, V)$.

(c) Show that $C_p - C_v = nR$ for an ideal gas using the expression (i) above.

(3) Show that

$$TV^{\gamma-1} = \text{constant}$$

$$PV^{\gamma} = \text{constant}$$

for an adiabatic reversible change of an ideal gas, where $\gamma = C_p/C_v$. Assume that C_v is independent of temperature.

(worksheet)

5 Answer the following questions:

(1) Answer the following questions about the helium atom:

- (a) Show the appropriate wave function of the ground state $\psi(1,2)$ in terms of spin and spatial parts. Explain why the wave function should be expressed like this. Note that $1s(\mathbf{r}_1)\alpha(\sigma_1)$ means an alpha electron occupying 1s atomic orbital.
- (b) Determine the normalization coefficient of $\psi(1,2)$, where 1s atomic orbitals are normalized. Show steps to solve the problem.
- (c) Suppose that the following equations hold.

$$I_j = \int d\mathbf{r}_j \phi^*(\mathbf{r}_j) \left[-\frac{1}{2} \nabla_j^2 - \frac{2}{r_j} \right] \phi(\mathbf{r}_j).$$

$$J_{12} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi^*(\mathbf{r}_1) \phi(\mathbf{r}_1) \frac{1}{r_{12}} \phi^*(\mathbf{r}_2) \phi(\mathbf{r}_2).$$

Show that the ground-state energy of the helium atom can be expressed as $E = I_1 + I_2 + J_{12}$.

- (d) What terms and levels (expressed as 1D) can arise from the ground state and $2p^2$ excited configuration, respectively?

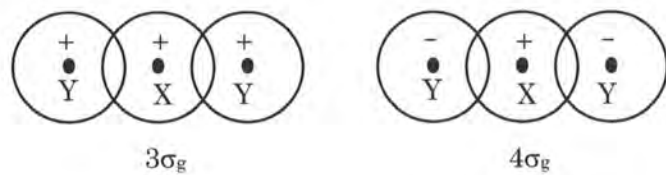
(2) Answer the following questions for the bonding in polyatomic molecules.

- (a) The four p_z atomic orbitals of carbon atoms of 1,3-butadiene form π molecular orbitals

$$\psi_i = \sum_{j=1}^4 c_{ij} p_{zj}. \text{ Write down the secular determinant for 1,3-butadiene using } H_{ij} = \int p_{zi}^* \mathbf{H} p_{zj} d\tau,$$

$$S_{ij} = \int p_{zi}^* p_{zj} d\tau, \text{ and the energy } E.$$

- (b) Find energies of π molecular orbitals using the Hückel approximations with three digits of significant figures. The substitution $x = (\alpha - E)/\beta$ is applicable. In the Hückel approximations, $H_{ii} = \alpha$ and $H_{ij} = \beta$ (for adjacent carbon atoms) are used as the energy and the resonance integrals, respectively.
- (c) We can draw schematic pictures for the molecular orbitals of a linear XY_2 molecule. For example, the $3\sigma_g$ and $4\sigma_g$ molecular orbitals can be represented as



Draw a schematic representation of the $2\sigma_u$, $1\pi_u$, $2\pi_u$, and $1\pi_g$ orbitals.

6 Answer the following questions concerning the CsCl-type crystal.

- (1) Figure 1 shows the schematic structure of the unit cell of the CsCl crystal. Answer the questions (a) and (b) concerning the structure X in which an identical atom is located on both the positions of the Cs^+ and Cl^- ions.

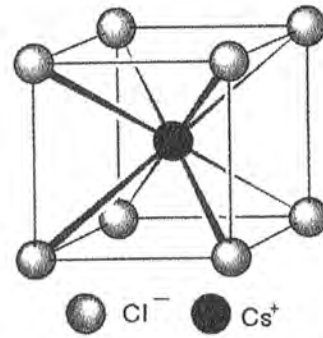


Figure 1. The schematic structure of the unit cell of the CsCl crystal.

- (a) Answer the name of the structure X.
- (b) When assuming that the identical atom is a true sphere, calculate the atomic packing factor of the structure X with three significant digits.
- (2) The density of the CsCl crystal is 3.99 g / cm^3 . Calculate the lattice constant of the unit cell of the CsCl crystal, a (pm), and the nearest distance between the Cs^+ and Cl^- ions, x (pm), with three significant digits. Use the atomic weights of the Cs and Cl atoms, 132.9 and 35.4, respectively, and Avogadro constant of $6.02 \times 10^{23} \text{ mol}^{-1}$.
- (3) The X-ray beam with wavelength of 154 pm is transmitted into the CsCl crystal. Calculate the reflection angle θ of the primary reflection from the (1 1 2) plane with three significant digits.
- (4) Derive the equation to obtain the crystal structure factor $F(hkl)$ of the CsCl crystal using the atomic scattering factors f_{Cs^+} and f_{Cl^-} and mirror indexes (h , k , and l), where f_{Cs^+} and f_{Cl^-} are the atomic scattering factors of the Cs^+ and Cl^- ions, respectively. Furthermore, using the obtained equation, show the observation condition (the extinction rule) of the X-ray diffraction of the CsCl crystal depending on the mirror indexes (h , k , and l).

Here, the crystal structure factor $F(hkl)$ of the X-ray diffraction from the (h k l) plane is obtained as follows:

$$F(hkl) = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

where f_j is the atomic scattering factor of atom j located at the lattice point (x_j , y_j , z_j).

- (5) Both the CsCl and CsI crystals belong to the same CsCl-type structure. Table 1 shows the intensities of the observed X-ray diffractions (I) from the ($h k l$) planes of the CsCl and CsI crystals. The mark "-" indicates that no X-ray diffraction was observed. Explain the reason why the observation results on the X-ray diffraction intensities are different from each other even though the CsCl and CsI crystals belong to the same structure.

Table 1. Intensities of the observed X-ray diffractions (I) from the ($h k l$) planes of the CsCl and CsI crystals.

$h k l$		1 0 0	1 1 0	1 1 1	2 0 0	2 1 0	2 1 1	2 2 0	3 0 0	3 1 0
Intensities of the X-ray diffractions (I)	CsCl	90	200	26	34	28	50	12	10	16
	CsI	-	220	-	40	-	66	16	-	20

- (6) In ionic crystals, each ion does not contact with the ions with the identical charge and is stabilized by being surrounded with as many ions with the opposite charge as possible. Therefore, we can predict the crystal structure types of ionic crystals from the coordination number and radius ratio (r/R) of the positive ion (radius: r) and the negative ion (radius: R). When the positive ion and the negative ion contact each other and the negative ions also contact each other, this radius ratio (r/R) is called as "the critical radius ratio". Answer the questions (a) and (b):

- (a) Calculate the critical radius ratios of both the CsCl-type structure and the NaCl-type structure (See Figure 2) with three significant digits.

- (b) Predict the crystal structures of NaBr, RbI and CsBr using the obtained critical radius ratios.

The ionic radiuses of ions are as follows;

Na^+ : 95 pm, Rb^+ : 148 pm, Cs^+ : 169 pm,

Br^- : 195 pm, I^- : 216 pm

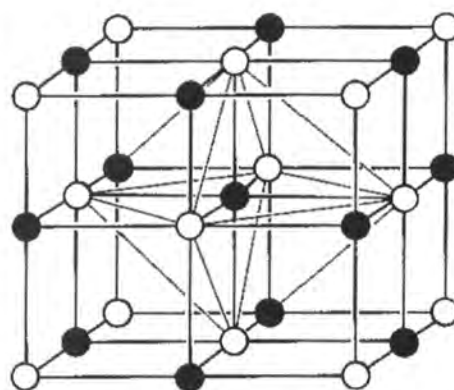
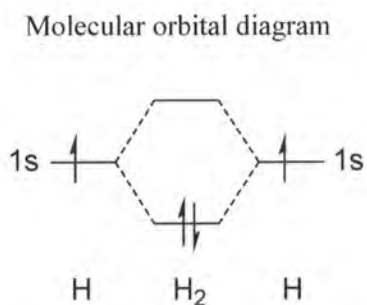


Figure 2. The schematic drawing of the unit cell of the NaCl-type structure.

7 Answer the following questions:

- (1) Which has a larger bond energy, O_2 or O_2^+ ? Explain the reason by describing the molecular orbital diagram of O_2 and the overlaps of atomic orbitals while referring to the example.

(Example)



Overlaps of atomic orbitals



- (2) Which has a larger bond energy, N_2 or N_2^+ ? Explain the reason by describing the molecular orbital diagram of N_2 in a similar way to question (1).
- (3) Which of the three single bonds between group 14 elements, C–C, Si–Si, and Ge–Ge bonds, has the greatest bond energy? And account for the reason.
- (4) Which of the three single bonds between group 16 elements, O–O, S–S, and Se–Se bonds, has the greatest bond energy? And account for the reason.
- (5) Which of the three double bonds between group 16 elements, O=O, S=S, and Se=Se bonds, has the greatest bond energy? And account for the reason.

(worksheet)

8 The first-row transition metals span from Sc (group 3) to Cu (group 11). Answer the following questions regarding complexes of these metals.

Sc Ti V Cr Mn Fe Co Ni Cu

- (1) Sketch all possible isomers of the octahedral complex $[\text{Co}(\text{gly})_2(\text{NH}_3)_2]^+$ (gly = $\text{H}_2\text{NCH}_2\text{COO}^-$). Suppose that gly is a bidentate ligand that binds through the nitrogen and oxygen atoms.

- (2) Consider ground state electronic structures of octahedral first-row transition metal complexes of the types: $[\text{MF}_6]^{3-}$ (**1**) and $[\text{M}(\text{CN})_6]^{3-}$ (**2**).
 - a) Which metal should give complex type (**1**) having the most unpaired electrons? Draw a qualitative crystal field splitting diagram for that metal.

 - b) Which metal should give complex type (**2**) having the most unpaired electrons? Draw a qualitative crystal field splitting diagram for that metal.

 - c) Which metals should give diamagnetic complex type (**2**)?

- (3) Although both of the four-coordinate complexes, $[\text{NiCl}_4]^{2-}$ (**3**) and $[\text{Ni}(\text{CN})_4]^{2-}$ (**4**), have the same number of d electrons, **3** is paramagnetic whereas **4** is diamagnetic.
 - a) Draw structural formulae for complex **3** and type **4**.

 - b) Draw qualitative crystal field splitting diagrams for **3** and **4**.

- (4) Consider first-row transition metal carbonyl complexes that have the generalized chemical formula $[\text{M}(\text{CO})_n]^{m-}$ ($n = 4, 5, 6$; $m = 0, 1, 2$) and attain the 18-electron rule.
 - a) Give chemical formulae for all complexes that meet the above criteria.

 - b) List the chemical formulae of $n = 4$ complexes in the order of decreasing CO stretching frequencies, and rationalize that order.

(worksheet)