2014
The Graduate School Entrance Examination
Chemistry
1:00 pm－3:00 pm

GENERAL INSTRUCTIONS

Answers should be written in Japanese or English.

1. Do not open the problem booklets, whether English or Japanese, until the start of the examination is announced.

2. Notify your proctor if you find any printing or production errors.

3. Answer all three problems in the problem booklet.

4. You are given three answer sheets. Use one answer sheet for each problem. You may use the reverse side if necessary.

5. Print your examinee number and the problem number in the designated places at the top of each answer sheet. The wedge-shaped marks on the top edge of the answer sheet represent the problem number you answer (P 1, P 2, P 3) on that sheet and also the class of the master's course (M) and doctoral course (D) applicants. At the end of the examination, follow your proctor's instructions and cut out carefully the two corresponding wedge marks on each sheet with a pair of scissors.

6. You may use the blank sheets of the problem booklet as working space and for draft solutions, but you must not detach them.

7. Any answer sheet with marks or symbols irrelevant to your answers will be considered invalid.

8. You may not take the booklet or answer sheets with you after the examination.

Examinee Number	No.

Write your examinee number in the space provided above.

Problem 1

I. The cubic diamond structure is shown in Figure 1.1. Avogadro's number is 6.02×10^{23} mol^{-1} and the atomic weights of C (carbon), O (oxygen) and Si (silicon) are 12.0, 16.0 and 28.1, respectively. Answer the following questions.

1. Give the number of atoms in the cell of the diamond structure shown in Figure 1.1 and the number of nearest-neighbor atoms of each atom.
2. The lattice constants a of C and Si with the diamond structure are 0.357 nm and 0.543 nm, respectively. Calculate the densities of C and Si. In addition, give the distance between nearest-neighbor atoms for C and Si. These answers should be written with two significant figures.
3. Diamond exhibits poor conductivity, while graphite is highly conductive. Describe the reason for the difference in about 50 words.
4. Single-crystalline pure silicon with the diamond structure is an intrinsic semiconductor. When B (boron) is doped at low concentration in the Si crystal, explain whether it becomes a p-type or an n-type semiconductor. In addition, describe its conduction mechanism using a schematic drawing of the electronic states.
5. For the B-doped Si of Question 4, draw a schematic illustration showing the temperature dependence of the carrier number, x, that contributes to conduction from very low absolute temperature to high temperature. The horizontal and vertical axes should be inverse temperature $1/T$ and $\log x$, respectively.
6. Give the chemical formula of the most stable oxide state of Si. Describe a method to determine whether complete oxidation of a pure Si crystal to the oxide has occurred.

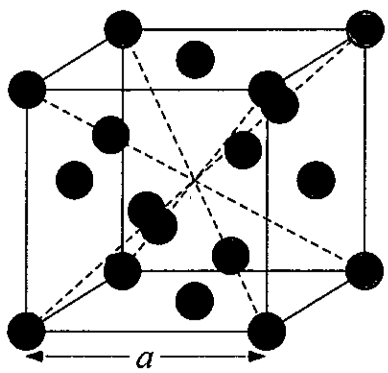


Figure 1.1 Diamond structure

II. The amount of ascorbic acid (vitamin C) in a soft drink is measured by redox titration. Answer the following questions. The influence of substances other than ascorbic acid in the soft drink can be neglected. The atomic weights of H (hydrogen), C (carbon), and O (oxygen) are 1.0, 12.0, and 16.0, respectively.

1. Ascorbic acid ($C_6H_8O_6$) is oxidized by the half-reaction shown in the formula (1). Give the chemical reaction for the redox reaction between ascorbic acid and iodine (I_2) as an oxidizing agent.

$$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^- \qquad (1)$$

2. To determine the precise iodine concentration, the redox titration is conducted using a standard solution of ascorbic acid containing starch as an indicator. Explain the color change at the end point.
3. When the concentration of standard ascorbic acid solution is 4.00×10^{-4} mol L^{-1}, and the volume of the solution is 10.00 mL, 0.80 mL of iodine solution is needed for the end point in the above titration. Show the equation for obtaining the iodine molar concentration, and give the molar concentration of the iodine solution.
4. A volume of 0.25 mL iodine solution is required for the complete oxidation of ascorbic acid in 10.00 mL of the soft drink. The iodine solution used in the titration is the same as in Question 3. Calculate the weight percentage of ascorbic acid in the soft drink. Assume that the density of the soft drink is 1.00 g cm^{-3}.
5. The ascorbic acid concentration also can be measured by other methods. Explain the separation principle of liquid chromatography in around 50 words.

Problem 2

I. Two different heat sources at temperatures T_1 and T_2 are used to operate a thermal engine by the following process. P_n represents the pressure of gas at each stage, and V_n represents the volume (n=1,2,3,4). The gas is an ideal gas and each stage is reversible. Answer the following questions.

	Initial state	Final state
First stage: isothermal expansion	(T_1, P_1, V_1)	(T_1, P_2, V_2)
Second stage: adiabatic expansion	(T_1, P_2, V_2)	(T_2, P_3, V_3)
Third stage: isothermal compression	(T_2, P_3, V_3)	(T_2, P_4, V_4)
Fourth stage: adiabatic compression	(T_2, P_4, V_4)	(T_1, P_1, V_1)

1. Draw a P–V diagram of the thermal engine relating pressure to volume. Then, show in the diagram the total work W_{total} performed by the engine to the outside.
2. Draw a T–S diagram of the thermal engine relating temperature to entropy. Then, show in the diagram the heat Q transferred from the heat source at the higher temperature and W_{total}.
3. Give an expression for η , the thermal efficiency of the thermal engine, using T_1 and T_2. Then, discuss the expression for η using the T–S diagram, which was drawn in Question 2.
4. For the case of using this thermal engine as a heat pump, give the coefficient of performance (COP) using T_1 and T_2. Then, when T_1 is constant, explain the dependence of the COP on T_2.

II. Many enzymatic reactions can be explained by the following mechanism. Here E is the enzyme, S is the substrate, ES is the bound state of the enzyme and substrate, P is the product, while k_a, k_b, and k_c are the rate constants for the respective reactions. Answer the following questions.

$$E + S \underset{k_b}{\overset{k_a}{\rightleftarrows}} ES \xrightarrow{k_c} P + E$$

1. Express $\frac{d[ES]}{dt}$ using [E], [S], [ES], k_a, k_b, and k_c.

2. Taking the total enzyme concentration to be $[E]_0 = [E] + [ES]$ and the constant to be $K_M = \frac{k_b + k_c}{k_a}$, show that the rate of formation of P is expressed by the equation below under a certain approximation,

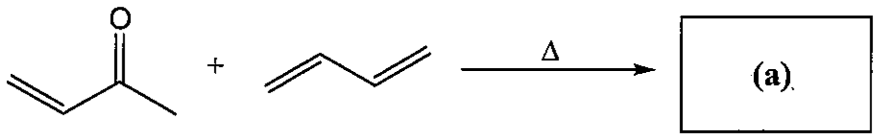
$$\frac{d[P]}{dt} = \frac{k_c[S][E]_0}{K_M + [S]}. \qquad (1)$$

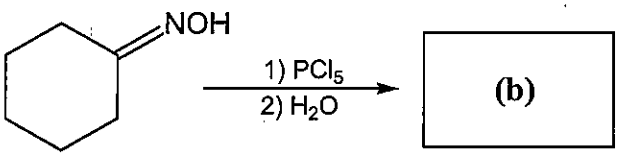
3. When a large excess of S exists, simplify equation (1) assuming that $K_M \ll [S]$, and briefly discuss the dependence of the rate of formation of P on the concentration of the substrate.

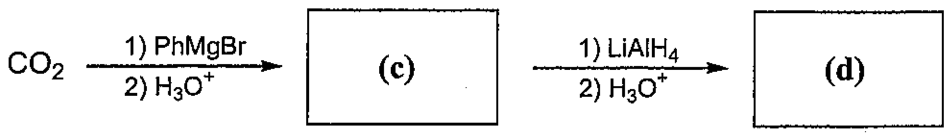
4. When K_M = 0.035 mol L^{-1} and [S] = 0.110 mol L^{-1}, the rate of formation of P is 1.15×10^{-3} mol L^{-1} s^{-1}. Calculate the rate of formation of P when a large excess of S exists.

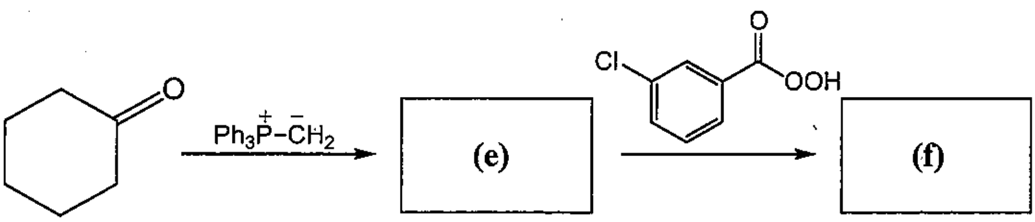
Problem 3

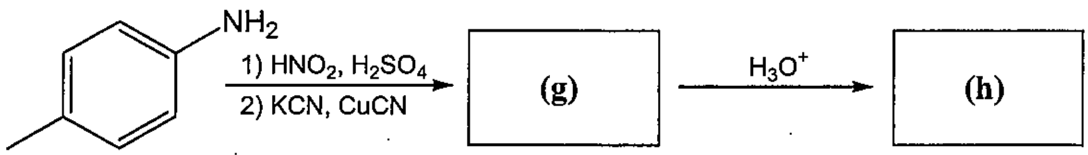
I. Draw the structural formulas of the major products (a)–(j) for the following reactions.

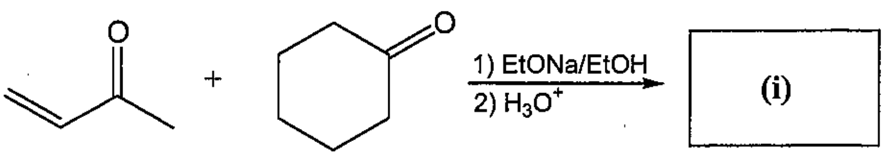


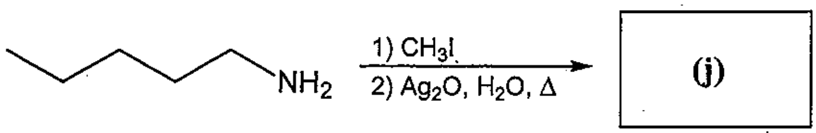




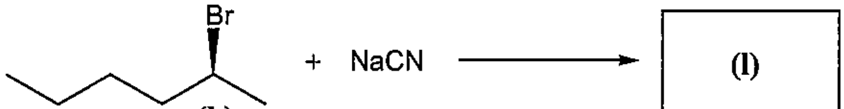




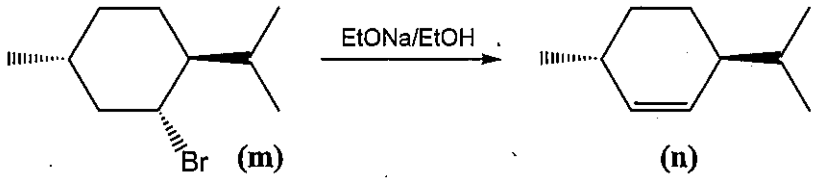




II. The S_N2 reaction of compound **(k)** with sodium cyanate produces compound **(l)** as a major product. The E2 reaction of compound **(m)** forms compound **(n)** as a major product. Answer the following questions.



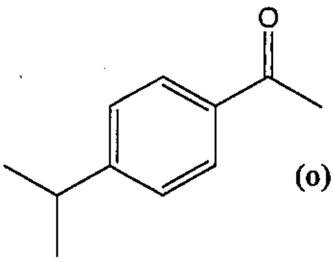
(k)



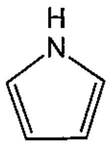
(m) (n)

1. Assign *R* or *S* configuration to the chiral centers in compounds **(k)** and **(m)**.
2. Draw the structural formula of compound **(l)** by showing the steric configuration. In addition, explain the reason for the formation of compound **(l)** as a major product by showing the reaction mechanism.
3. Explain the reason for the formation of compound **(n)** as a major product by showing the reaction mechanism.

III. Answer the following questions on aromatic compounds.



(o)



(p)

1. Show the synthetic route to compound **(o)** using benzene as a starting material. In addition, show all required reagents.
2. When the nitration of compound **(p)** is carried out, compound **(q)** is obtained as a major product. Draw the structural formula of compound **(q)**. In addition, explain the reason for the formation of compound **(q)** as a major product by showing the reaction mechanism.