2020
The Graduate School Entrance Examination
Chemistry
(Applicants for the Department of Applied Chemistry)
9:00 am－11:00 am

GENERAL INSTRUCTIONS

Answers should be written in English or Japanese.

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. Master's course applicants must answer five out of seven problems in the problem booklet. Doctoral course applicants must answer four out of seven problems in the problem booklet.

4. Master's course applicants are given five answer sheets. Doctoral course applicants are given four answer sheets. Use one answer sheet for each problem. You may use the reverse side if necessary.

5. Fill in 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 each answer sheet represent the problem number that you answer (P 1, P 2, …, P 7) and also the class of the course (master M, doctor D) that you are applying. At the end of the examination, follow your proctor's instructions and cut out carefully the two corresponding wedge marks per sheet.

6. You may use the blank sheets of the problem booklets for rough papers without detaching them.

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

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

Examinee Number	No.

Write your examinee number in the space provided above.

Problem 1 Basic Physical Chemistry

I. Consider the following two chemical reactions. Here, assume that Reaction (1) proceeds as a second-order reaction between Compounds A and B to form Compound C, and Reaction (2) proceeds as a first-order reaction to form Compound D from Compound A. Note that [A], [B], [C], and [D] denote the concentrations of Compounds A, B, C, and D, respectively.

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C} \qquad (1)$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{D} \qquad (2)$$

k_1, k_2: the rate constants for the respective reactions

1. Consider only Reaction (1). Express the production rate of Compound C, $d[\mathrm{C}]/dt$. Here, you may use the reaction time, t, the concentration of Compound A at $t = 0$, $[\mathrm{A}]_0$, the concentration of Compound B at $t = 0$, $[\mathrm{B}]_0$.
2. Consider only Reaction (1). Sketch the time dependence of $[\mathrm{A}]/[\mathrm{A}]_0$ when $[\mathrm{A}]_0 = [\mathrm{B}]_0$. Also, calculate the half-life period of Compound A and show it in the figure.
3. Consider only Reaction (2). Sketch the time dependence of $[\mathrm{A}]/[\mathrm{A}]_0$. Also, calculate the half-life period of Compound A, and show it in the figure.
4. Consider the situation where Reactions (1) and (2) occur simultaneously. Answer whether the reaction yield of Compound C increases or decreases when $[\mathrm{A}]_0$ increases. Also, explain the reason briefly, assuming that $[\mathrm{A}]_0 = [\mathrm{B}]_0$.

II. Answer the following questions on the phase diagram of the water–phenol binary system at a constant pressure shown in Figure 1.1. The phase diagram has Regions X and Y. In Region X, water and phenol are not completely soluble and separated into two phases, Phases α and β. Here, Phase α has a low mass fraction of phenol compared to Phase β.

1. Calculate the number of the degrees of freedom f of the system in Region X. Here, f is expressed as follows:

$$f = c - p + 2, \qquad (3)$$

where c is the number of components existing in the system, and p is the number of phases coexisting in the system.

2. Briefly explain the change that occurs when the system at a mass fraction of phenol of 0.5 and at a temperature of 40°C is heated to 70°C.
3. Consider the system at a mass fraction of phenol of 0.5 and at a temperature of 40°C. Estimate the mass fractions of phenol of Phases α and β. Also, estimate the mass ratio of Phase α to Phase β (mass of Phase α : mass of Phase β).

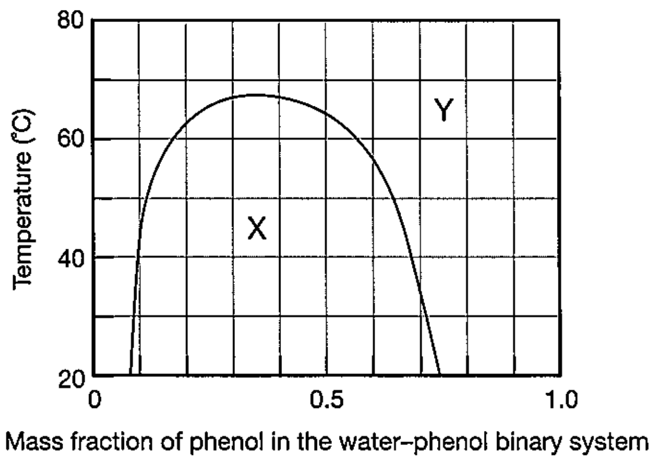


Figure 1.1

Problem 2 Basic Inorganic Chemistry

Answer the following questions on elements, ionization energies, and chemical bonds. You may use the periodic table of elements shown in Figure 2.1.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ln*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

(* lanthanoid)

Figure 2.1

I. Answer the following questions on elements.

1. Give all the elements whose simple substances are liquid at room temperature and under ordinary pressure.
2. Give the transition metal element whose simple substance has the highest melting point.
3. Give the metal element that has the highest electric conductivity at room temperature and under ordinary pressure.
4. Give two examples of allotrope.
5. Choose all the compounds that do not meet the octet rule from the followings.

   NF_3, CF_4, SF_4, SiF_4, XeF_4
6. Write the electronic configuration in the ground state of each of the following atoms according to the example.

   Example C: $1s^2 2s^2 2p^2$

   (a) Cl (b) Zn (c) Sr
7. The electronic configuration of Cr is not $[Ar]3d^4 4s^2$ but $[Ar]3d^5 4s^1$. Explain the reason briefly. Note that the electronic configuration of Ar is abbreviated to [Ar] here.
8. The lanthanoid contraction is the steady decrease in the size of lanthanoid ions with increasing atomic number. Explain the reason briefly.

II. Answer the following questions on ionization energies.

1. Choose an appropriate word or phrase from the list (i) – (iii) for each blank below.

   (i) increase (ii) decrease (iii) be constant

   For the atoms of atomic number 1 – 20, the first ionization energy tends to [(a)] with increasing atomic number in the same group of the elements, and that tends to [(b)] with increasing atomic number in the same period of the elements.

   For the atoms of transition elements, the first ionization energy tends to [(c)] with increasing atomic number in the same period of the elements.

2. Arrange Ca, Mn, and Zn in descending order of the first ionization energy. Also, explain the reason briefly.

III. The structure of diborane is shown in Figure 2.2. Provide the answer, which is longer, the bridging B–H bond (a) or the terminal B–H bond (b). Also, briefly explain the reason in terms of bond order.

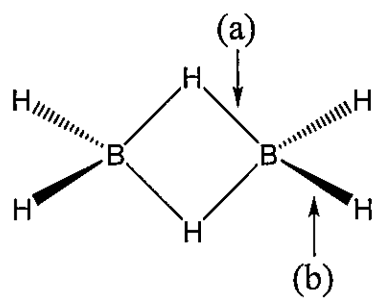


Figure 2.2

Problem 3 Basic Organic Chemistry

Answer the following questions.

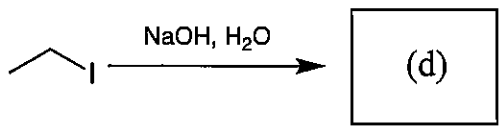
I. Draw the structural formulas of Compounds (a) – (c) below.

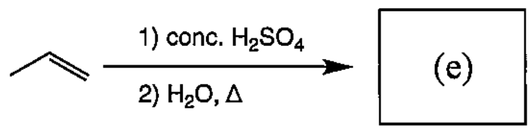
(a) 2-ethyl-1,4-pentadiene

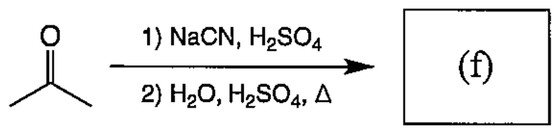
(b) 4,4-dimethylcyclohexanol

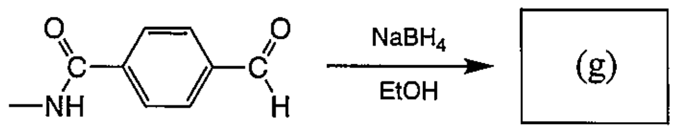
(c) 7-ethyl-1-methylnaphthalene

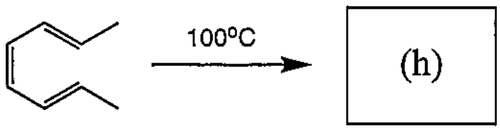
II. Draw the structural formulas of the major products (d) – (o) in the following reactions. Also, show the stereochemical configurations for Compounds (h) and (i).

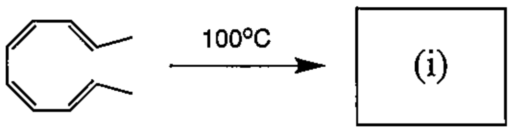


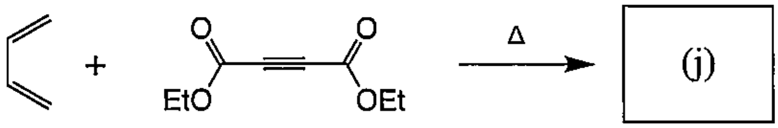


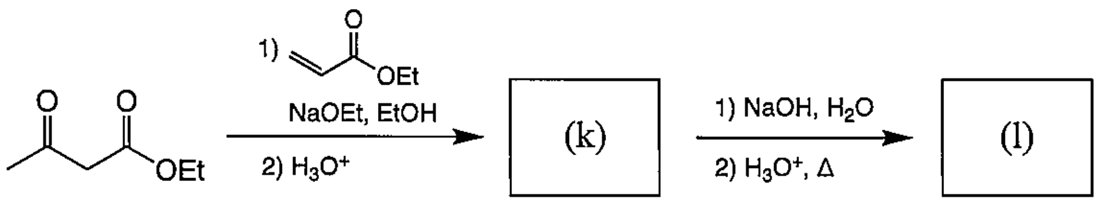


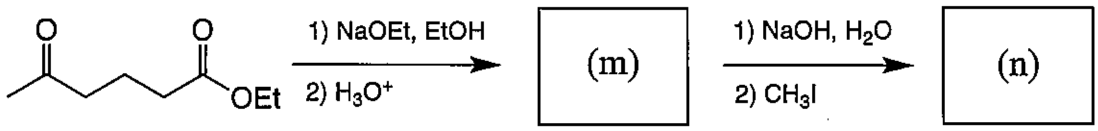


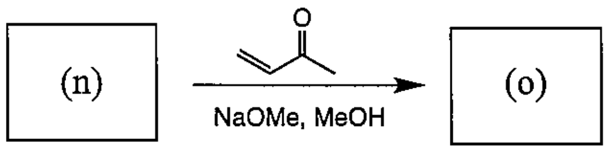












III. *p*-Nitrophenol can be obtained through the reaction of *p*-chloronitrobenzene with hydroxide ion. Answer the following questions.

1. Draw the reaction mechanism, indicating the intermediates and electron movements of *p*-chloronitrobenzene with hydroxide ion.
2. The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol. Explain the reason briefly.
3. Compared with *p*-chloronitrobenzene, *m*-chloronitrobenzene is less reactive to hydroxide ion. Explain the reason briefly.

Problem 4 Physical Chemistry

Consider a diatomic molecule, which is composed of two atoms, A and B, and one electron. The energy eigenvalues are evaluated, using the Hückel method. The molecular orbitals, $\Psi(r)$, of the molecule are expressed in the following equation:

$$\Psi(r) = c_\mathrm{A}\ \chi_\mathrm{A}(r) + c_\mathrm{B}\ \chi_\mathrm{B}(r), \tag{1}$$

where r is the electron position, $\chi_\mathrm{A}(r)$ and $\chi_\mathrm{B}(r)$ are the atomic orbitals of Atoms A and B, respectively, and c_A and c_B are the molecular orbital coefficients. $\Psi_+(r)$ and $\Psi_-(r)$ are the occupied and unoccupied orbitals, and the corresponding energy eigenvalues are ε_+ and ε_- ($\varepsilon_+ < \varepsilon_-$), respectively. $\chi_\mathrm{A}(r)$ and $\chi_\mathrm{B}(r)$ are normalized and the overlap integral is zero as follows:

$$\int_{-\infty}^{\infty} \chi_\mathrm{A}^*(r)\ \chi_\mathrm{A}(r)dr = 1, \tag{2}$$

$$\int_{-\infty}^{\infty} \chi_\mathrm{B}^*(r)\ \chi_\mathrm{B}(r)dr = 1, \tag{3}$$

$$\int_{-\infty}^{\infty} \chi_\mathrm{A}^*(r)\ \chi_\mathrm{B}(r)dr = 0, \tag{4}$$

where $\chi^*(r)$ is the complex conjugate of $\chi(r)$.

The (a) integrals α_A and α_B and the (b) integral β are expressed as follows:

$$\alpha_\mathrm{A} = \int_{-\infty}^{\infty} \chi_\mathrm{A}^*(r)\ \boldsymbol{H}\ \chi_\mathrm{A}(r)dr, \tag{5}$$

$$\alpha_\mathrm{B} = \int_{-\infty}^{\infty} \chi_\mathrm{B}^*(r)\ \boldsymbol{H}\ \chi_\mathrm{B}(r)dr, \tag{6}$$

$$\beta = \int_{-\infty}^{\infty} \chi_\mathrm{A}^*(r)\ \boldsymbol{H}\ \chi_\mathrm{B}(r)dr, \tag{7}$$

where $\boldsymbol{H}$ is the one-electron Hamiltonian, $\alpha_\mathrm{A} < \alpha_\mathrm{B}$, and $\beta \leq 0$. c_A and c_B in Equation (1) satisfy the following equation:

$$\begin{pmatrix} \alpha_\mathrm{A} & \beta \\ \beta & \alpha_\mathrm{B} \end{pmatrix} \begin{pmatrix} c_\mathrm{A} \\ c_\mathrm{B} \end{pmatrix} = \varepsilon \begin{pmatrix} c_\mathrm{A} \\ c_\mathrm{B} \end{pmatrix}. \tag{8}$$

I. Fill in the blanks (a) and (b) with appropriate terms.

II. Express ε_+ and ε_-, using α_A, α_B, and β.

III. Draw a schematic energy diagram for a heteronuclear diatomic molecule ($\alpha_A < \alpha_B$) following the example of a homonuclear diatomic molecule ($\alpha_A = \alpha_B$) shown in Figure 4.1. In addition, express the energy gap between ε_+ and ε_-, E_g, using α_A, α_B, and β.

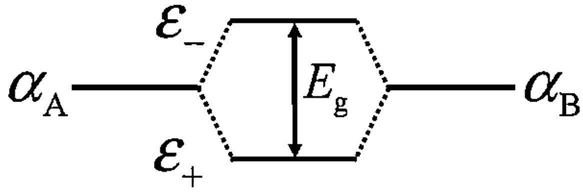


Figure 4.1

IV. Considering a diatomic molecule that has one electron with the energy eigenvalue of ε_+, briefly describe how the inter-atomic bond strength changes, as the absolute value of β increases.

V. $\Psi(r)$ in Equation (1) satisfies the normalization condition as follows:

$$\int_{-\infty}^{\infty} \Psi^*(r)\ \Psi(r)dr = 1, \tag{9}$$

where $\Psi^*(r)$ is the complex conjugate of $\Psi(r)$. Express the condition that c_A and c_B must satisfy.

VI. $\Psi_+(r)$ and $\Psi_-(r)$ are expressed, using the mixing angle of atomic orbitals, θ, as follows:

$$\Psi_+(r) = \cos\theta \ \chi_A(r) + \sin\theta \ \chi_B(r), \tag{10}$$

$$\Psi_-(r) = -\sin\theta \ \chi_A(r) + \cos\theta \ \chi_B(r), \tag{11}$$

$$\theta = \frac{1}{2}\tan^{-1}\left(\frac{2\beta}{\alpha_A - \alpha_B}\right). \tag{12}$$

1. ρ_A and ρ_B are electron densities on Atoms A and B, respectively. Express ρ_A and ρ_B, using θ.
2. Briefly explain how ρ_A and ρ_B change with respect to θ, as the bond between Atoms A and B stretches. See Figure 4.2 for $y = \tan^{-1}(x)$ if necessary.

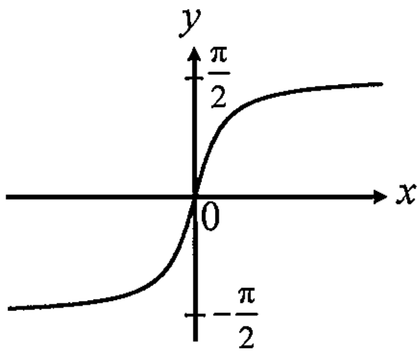


Figure 4.2

Problem 5 Inorganic Chemistry

Answer the following questions on crystal structures.

I. Fill in the blanks (i) – (xviii), using an appropriate term, symbol, or number.

The lengths (a, b, c) and angles (α, β, γ) used to define the size and shape of a unit cell in a crystal are called (i). Let $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ be the basis vectors to define the unit cell. The angle between $\boldsymbol{a}$ and $\boldsymbol{b}$ is denoted as (ii), that between $\boldsymbol{b}$ and $\boldsymbol{c}$ is (iii), and that between $\boldsymbol{c}$ and $\boldsymbol{a}$ is (iv). The unit cell is generally chosen to have the highest (v) and the smallest lattice (vi).

A (vii) lattice has only one lattice point in the unit cell. For more complex lattice types, a (viii) cubic lattice has a lattice point at the center of the unit cell as well, and a (ix) cubic lattice has lattice points at the center of the lattice planes of the unit cell as well. The unit cell of the (viii) cubic lattice involves a total of (x) lattice points, while that of the (ix) cubic lattice includes a total of (xi) lattice points.

Based on the (v) of the structure, the crystal structures in three dimensions are classified into the seven crystal systems. Table 5.1 lists the relationship between the (i) and the essential (v) in each of the crystal systems.

Table 5.1

Crystal system	Relationships between (i)	Essential (v)
(xii)	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$	None
Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$	One (xvii) rotation axis
(xiii)	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$	Three perpendicular twofold axes
(xiv)	$a = b = c$, $\alpha = \beta = \gamma \neq 90°$	One threefold rotation axis
(xv)	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$	One fourfold rotation axis
(xvi)	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$	One sixfold rotation axis
Cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$	Four (xviii) rotation axes

II. Answer the following questions on the Si crystal shown in Figure 5.1 (dashed lines indicate the unit cell). Here, the electronic configuration of Si is $1s^2 2s^2 2p^6 3s^2 3p^2$.

1. Give the name of the crystal structure.
2. Draw a schematic diagram of the electronic band structure (the energy band structure), by specifying the conduction band, the valence band, and the band gap.
3. Briefly explain the chemical bond between the Si atoms in terms of electronic orbital.
4. Write one dopant to make the crystal n-type. Also, briefly explain why the addition of the dopant makes the crystal n-type in terms of electronic configuration.
5. The electrical conductivity of an n-type crystal increases with increasing temperature. Explain the reason briefly.

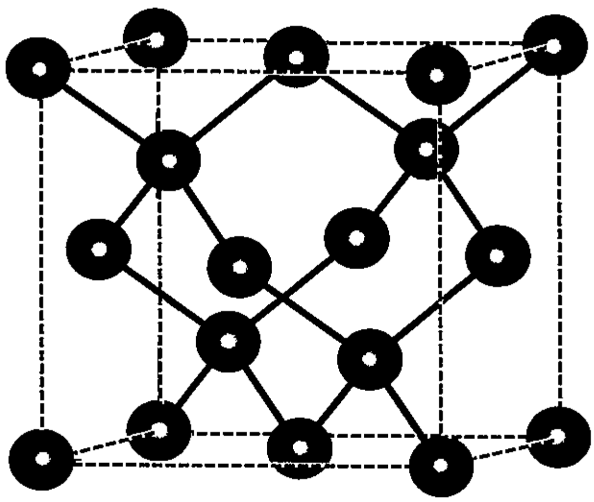


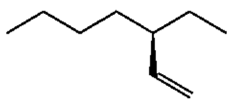
Figure 5.1

Problem 6 Organic Chemistry

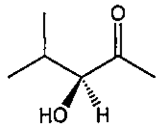
Answer the following questions.

I. Give the nomenclatures of Compounds (a), (b), and (c) according to the International Union of Pure and Applied Chemistry (IUPAC) definition.

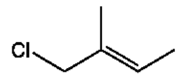
(a)



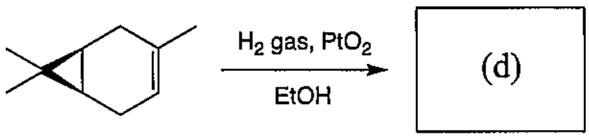
(b)

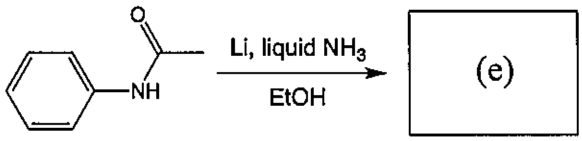


(c)



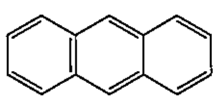
II. Draw the structural formulas of the major products (d) and (e) in the following reactions. Also, show the stereochemical configuration for Compound (d).



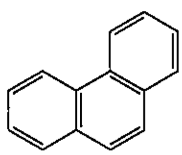


III. Answer the following questions on the properties of compounds.

1. Anthracene and phenanthrene are structural isomers. Provide the answer, which compound is more thermodynamically stable. Also, briefly explain the reason in terms of conjugation.

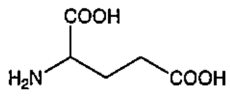


anthracene



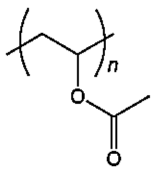
phenanthrene

2. Glutamic acid has one amino group and two carboxyl groups. The acid dissociation constants of the two carboxyl groups are different in an aqueous solution. Provide the answer, which carboxyl group has a lower acid dissociation constant. Also, explain the reason briefly.



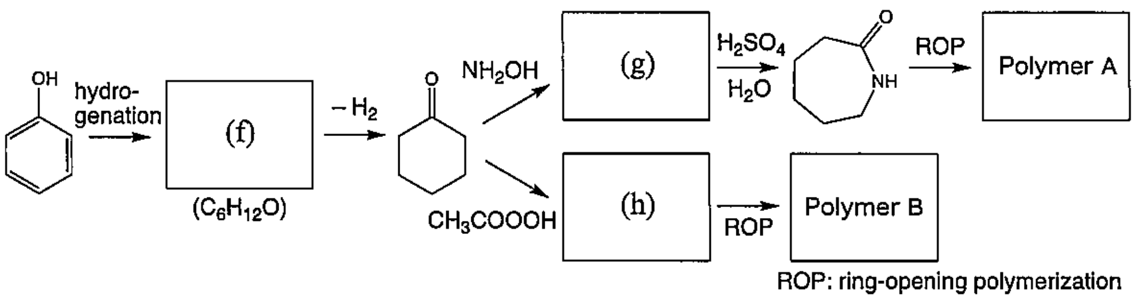
glutamic acid

3. The alkaline hydrolysis of poly(vinyl acetate) is accelerated as the reaction proceeds. Explain the reason briefly.



poly(vinyl acetate)

IV. Answer the following questions.



1. Draw the structural formulas of Compounds (f), (g), and (h).
2. The reaction to obtain Compound (h) is called the Baeyer–Villiger oxidation. Answer the main product name in the Baeyer–Villiger oxidation of 2-butanone.
3. The glass transition temperatures of Polymers A and B are approximately 50°C and −60°C, respectively. Briefly explain the reason why the glass transition temperatures are different in terms of chemical structure of the polymer chains.

Problem 7 Analytical Chemistry

Answer the following questions. If necessary, the following values can be used.
$\log_{10}2 = 0.30$, $\log_{10}3 = 0.48$, $\log_{10}5 = 0.70$, $\log_{10}7 = 0.85$

I. Answer the following questions on spectroscopies.

1. Write photon energy, E (J), using Planck's constant, h (J s), wavelength, λ (m), and the velocity of light in vacuum, c ($m\ s^{-1}$).
2. When light of a wavelength of 500 nm entered a cell with a solution, the light was absorbed by 20%. Calculate the absorbance.
3. Infrared light is often used to obtain vibrational information of molecules. Briefly explain the reason why infrared light is used.
4. Answer the number of peaks of the methyl group in ethanol in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum.
5. Explain the principle of substance identification, using X-ray fluorescence spectroscopy in approximately 50 words. Use all of the keywords below.
   Keywords: X-ray, inner-shell electron, excite, relax, energy

II. Answer the following questions on acids and bases. If necessary, the following value can be used.

$\log_{10}K_a = -4.76$
(K_a: the acid dissociation constant of acetic acid in an aqueous solution)

1. Calculate the pH of an acetic acid aqueous solution with a concentration of 1.0×10^{-2} mol L^{-1}. Assume that the degree of electrolytic dissociation is sufficiently smaller than one.
2. A sodium hydroxide aqueous solution with a concentration of 1.0×10^{-2} mol L^{-1} and a volume of 4 mL is added to an acetic acid aqueous solution with a concentration of 1.0×10^{-2} mol L^{-1} and a volume of 10 mL. Calculate the pH of the solution.
3. There are three pH regions for phosphates as a buffer solution. Briefly explain the reason why three pH regions exist.
4. Isoelectric focusing electrophoresis is used for protein analysis. Briefly explain what the isoelectric point is.

問 題 訂 正

科目名：化学（応用化学専攻）、（バイオエンジニアリング専攻）

第３問　基礎有機化学　II.　（6 ページ）

（誤）　(m)　(o)

（正）　(m) ($C_6H_8O_2$)　(o) ($C_{11}H_{14}O_2$)

Problem 3　Basic Organic Chemistry　II.　(Page 6)

(incorrect)　(m)　(o)

(correct)　(m) ($C_6H_8O_2$)　(o) ($C_{11}H_{14}O_2$)

2019 年 8 月 27 日
工学系研究科
大学院入試委員会本部