2018
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 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. 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 booklet 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 booklet 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

Answer the following questions on atoms and molecules. If necessary, use the following values in Table 1.1.

Table 1.1 Energies of atomic orbitals (eV)

Atom	1s orbital	2s orbital	2p orbital	Atom	1s orbital	2s orbital	2p orbital
H	−13.6	—	—	C	−308.2	−19.2	−11.8
He	−25.0	—	—	N	−425.3	−25.7	−15.4
Li	−67.4	−5.3	—	O	−562.4	−33.9	−17.2
Be	−128.8	−8.4	—	F	−717.9	−42.8	−19.9
B	−209.4	−13.5	−8.4	Ne	−891.8	−52.5	−23.1

I. From Table 1.1, choose all atoms that tend to become monovalent cations. In addition, answer the ionization energies (eV) of the chosen atoms.

II. Consider a cation possessing a nuclear charge of $+Ze$ and one electron by using the Bohr model. In the Bohr model, the electron undergoes uniform circular motion as shown in Figure 1.1, and the centrifugal force and the Coulomb force between the electron and the nucleus counterbalance each other. In addition, the uniform circular motion needs to meet the condition in Equation (1) (the Bohr quantum condition). Derive Equation (2) by taking the counterbalance between the centrifugal force and the Coulomb force, and the Bohr quantum condition into consideration. Here, Z: number of protons, e: elementary charge, m: mass of electron, v: velocity of electron, r: distance between the electron and the nucleus, h: Planck's constant, n: quantum number, E_n: energy level at a quantum number n, and ε_0: permittivity of vacuum.

$$mvr = \frac{hn}{2\pi} \tag{1}$$

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{Z^2}{n^2} \tag{2}$$

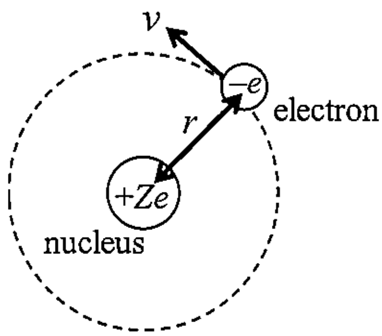


Figure 1.1

III. Answer each energy (eV) required for reactions (3), (4), and (5). In addition, answer the electron repulsion energy (eV) in a helium atom.

$$He \longrightarrow He^{+} + e^{-} \quad (3)$$

$$He^{+} \longrightarrow He^{2+} + e^{-} \quad (4)$$

$$He \longrightarrow He^{2+} + 2e^{-} \quad (5)$$

IV. From B_2, C_2, N_2, O_2, and F_2, choose all molecules that are paramagnetic. Also, explain the reason for choosing them.

V. Which molecule possesses a longer bond length between oxygen atoms, dioxygen (O_2) or hydrogen peroxide (H_2O_2)? Provide the answer with the reason by showing the electron configurations of O_2 and O_2^{2-}. Draw the electron configurations according to the example shown in Figure 1.2.

<u>Electron configuration of dihydrogen (H_2)</u>

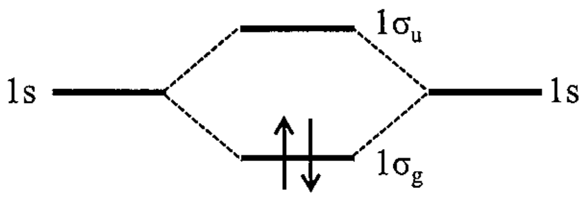


Figure 1.2

VI. Consider single molecules of lithium hydride (LiH) and hydrogen fluoride (HF). Discuss the difference between the characters of hydrogen in LiH and that in HF by showing the electron configurations of LiH and HF. Draw the electron configurations according to the example shown in Figure 1.2.

Problem 2 Basic Inorganic Chemistry

Answer the following questions.

I. H_3PO_4 is dissociated in aqueous solutions according to the following reactions.

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \quad (1)$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \quad (2)$$

The pK_a values for H_3PO_4 and $H_2PO_4^-$ at a certain temperature are 2.0 and 7.0, respectively. At this temperature, answer the concentration ratio $[H_3PO_4] : [H_2PO_4^-] : [HPO_4^{2-}]$ in the aqueous solution with pH = 5.0 in the form of $1 : x : y$.

II. Figure 2.1 shows a unit cell of TiO_2 with the rutile structure in the tetragonal system. Ti^{4+} ions occupy the octahedral holes surrounded by six O^{2-} ions. Answer the following questions.

1. Consider the case that a cation (ionic radius: r_c) is ideally 6-coordinated with surrounding anions (ionic radius: r_a). Show that the ionic radius ratio r_c/r_a is $\sqrt{2}-1$.
2. The molar masses of the Ti atom and the O atom are m_{Ti} and m_O (g mol^{-1}), respectively, and the lattice constants are a and c (cm). The Avogadro constant is N_A (mol^{-1}). Express the density d (g cm^{-3}) of TiO_2 by using m_{Ti}, m_O, a, c, and N_A.

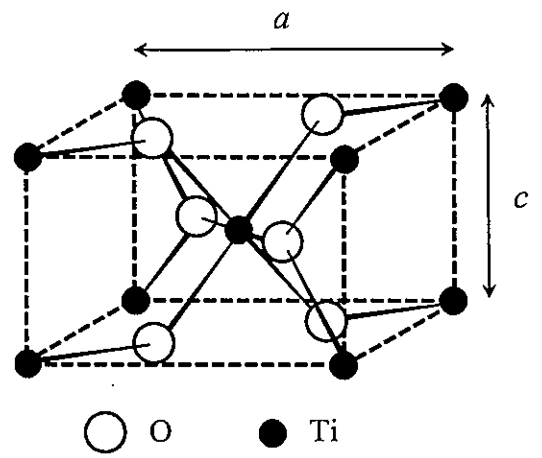


Figure 2.1

III. Consider the following reactions at 298 K. Answer the following questions using the reduction reactions (3)–(5) and the standard potentials E°. All substrates are at 1 bar and have unit activity under standard conditions.

$$Cu^+(aq) + e^- \longrightarrow Cu(s) \qquad E^\circ = +0.52\ V \qquad (3)$$

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq) \qquad E^\circ = +0.16\ V \qquad (4)$$

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad E^\circ = +1.23\ V \qquad (5)$$

1. Calculate the standard potential E° for reaction (6), and answer with the reason whether the reaction proceeds spontaneously under standard conditions.

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s) \qquad (6)$$

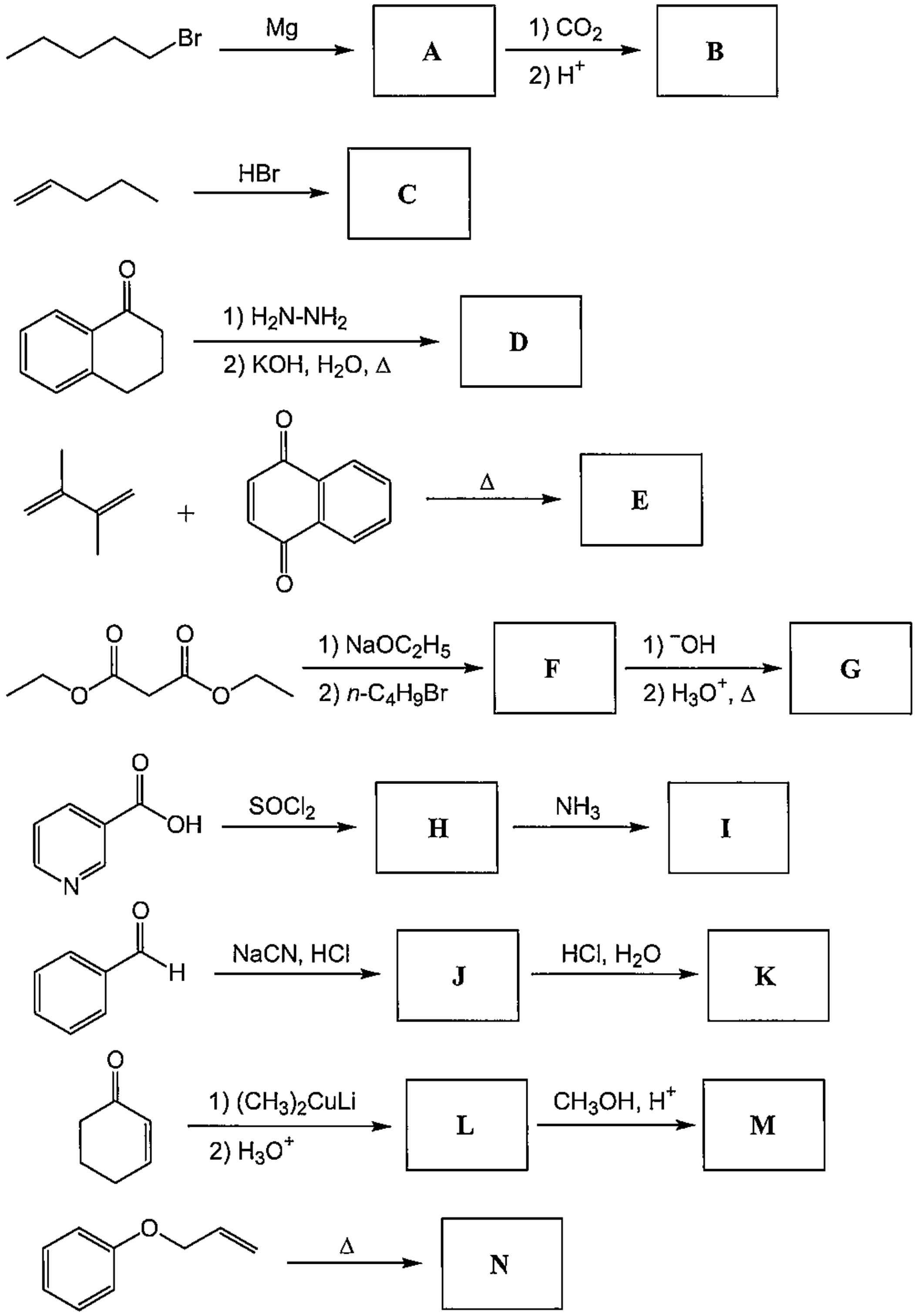
2. Assume reaction (5) in an aqueous solution with pH = x under O_2 partial pressure of 1 bar. Present the equation expressing the pH dependence of the potential of reaction (5). Use the Faraday constant F, the gas constant R, and ln 10 in the equation, if necessary.
3. Calculate the standard potential E° for reaction (7), and answer with the reason whether the reaction proceeds spontaneously under standard conditions.

$$2Cu(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Cu^{2+}(aq) + 2H_2O(l) \qquad (7)$$

Problem 3 Basic Organic Chemistry

Answer the following questions.

I. Draw the structural formulas of the major products **A–N** in the following reactions.



II. 2,3,4-Trihydroxypentane has multiple diastereomers. Among them, draw all the structural formulas of *meso* isomers.

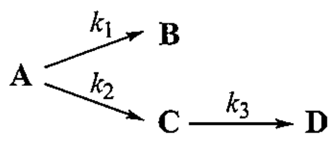
III. In the ^{1}H NMR spectrum of *N*,*N*-dimethylformamide, two signals due to the methyl groups are observed at room temperature. Explain the reason.

IV. Explain the reasons for the following phenomena by showing reaction mechanisms.

1. When heating (*S*)-2-phenyl-2-pentanol in formic acid, the corresponding formate was formed, and the optical rotation of the solution became 0 degree.
2. When adding sodium bromide to an acetone solution of (*R*)-2-bromopentane, the optical rotation of the solution gradually became 0 degree.

Problem 4 Physical Chemistry

Consider the following decomposition reactions of compound **A** in aqueous solutions. The reactions are carried out at a constant temperature, and the pH values of the reaction solutions remain unchanged during the reactions. The ionic product of water is 1.0×10^{-14} mol^2 L^{-2}.



k_1, k_2, k_3: the rate constants for each reaction (s^{-1})

The temporal changes in concentrations of compounds **A**–**D** can be expressed by the following equations.

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] = -(\alpha[OH^-] + \beta[H^+])[A]$$

$$\frac{d[B]}{dt} = k_1[A] = \alpha[OH^-][A]$$

$$\frac{d[C]}{dt} = k_2[A] - k_3[C] = \beta[H^+][A] - \gamma[H^+][C]$$

$$\frac{d[D]}{dt} = k_3[C] = \gamma[H^+][C]$$

Here, [A], [B], [C], [D]: the concentrations of each compound (mol L^{-1}) at time t (s), α, β, γ: constants (mol^{-1} L s^{-1}), [H$^+$]: the concentration of hydrogen ion (mol L^{-1}), and [OH$^-$]: the concentration of hydroxide ion (mol L^{-1}). The initial concentration of compound **A** (mol L^{-1}) is represented as $[A]_0$. The initial concentrations of compounds **B**, **C**, and **D** are 0.

When the reactions were performed at different pH and $[A]_0$, the data shown in Table 4.1 were obtained. Here, $t_{1/2}$ (s) represents the half-life of compound **A**.

Table 4.1

	pH	$[A]_0$ (mol L^{-1})	$t_{1/2}$ (s)
Condition 1	1.0	1.0	10
Condition 2	13	2.0	20

Answer the following questions. If necessary, use the following values.

$\log_{10}2 = 0.30$, $\log_{10}3 = 0.48$, $\log_{10}5 = 0.70$

I. Under acidic conditions ($k_1 << k_2$), the reaction **A**→**B** can be ignored. Express [A] under acidic conditions by using $[A]_0$, k_2, and t.

II. Draw a graph which shows the relationship between $t_{1/2}$ and pH in the range of pH = 1.0–3.0 at $[A]_0$ = 1.0 mol L^{-1}. In addition, draw a graph which shows the relationship between $t_{1/2}$ and $[A]_0$ in the range of $[A]_0$ = 1.0–3.0 mol L^{-1} at pH = 1.0. Present the graphs according to the example shown in Figure 4.1.

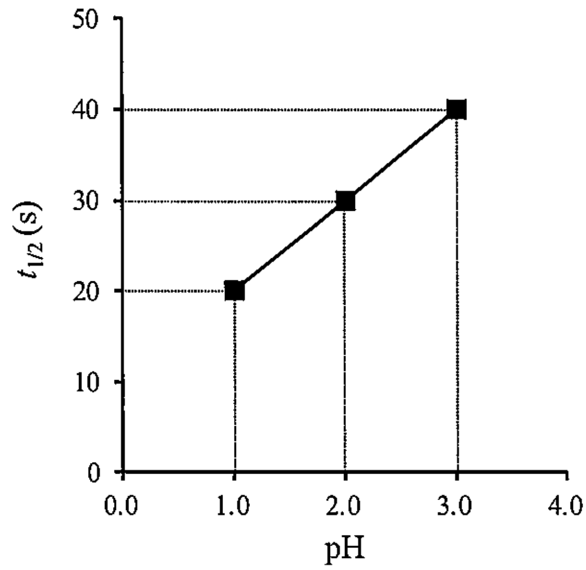


Figure 4.1

III. Under acidic conditions, [C] can be expressed by the following equation.

$$[C] = \frac{k_2[A]_0}{k_3 - k_2}\{\exp(-k_2 t) - \exp(-k_3 t)\}$$

Consider the case of $2k_2 = k_3$. For the reaction at pH = x and $[A]_0$ = 1.0 mol L^{-1}. Express the time when [C] reaches the maximum (t_{max} (s)) by using x.

IV. Consider the case of $k_2 << k_3$ under acidic conditions. Express [D] in this case by using $[A]_0$, k_2, and t.

V. Under basic conditions ($k_1 >> k_2$), the reactions **A**→**C** and **C**→**D** can be ignored. The heat of reaction for **A**→**B** is 50 kJ mol^{-1} at pH = 13. Answer the heat of reaction (kJ mol^{-1}) at pH = 12.

VI. Answer the pH where the decomposition rate of compound **A** becomes minimum.

Problem 5 Inorganic Chemistry

Answer the following questions on the metal complexes. The atomic numbers of each metal are as follows.

Cr: 24, Mn: 25, Fe: 26, Co: 27, Ni: 28, Cu: 29, Zn: 30, Ru: 44, Rh: 45

I. The reaction mechanism for the hydrogenation of ethylene by Wilkinson's catalyst is shown in Figure 5.1. Answer the following questions.

1. Give the number of total valence electrons for complex **A**.
2. Draw the molecular structures of complexes **B** and **C**, respectively.
3. Answer the name of the reaction that produces complex **A** and ethane from complex **D**.

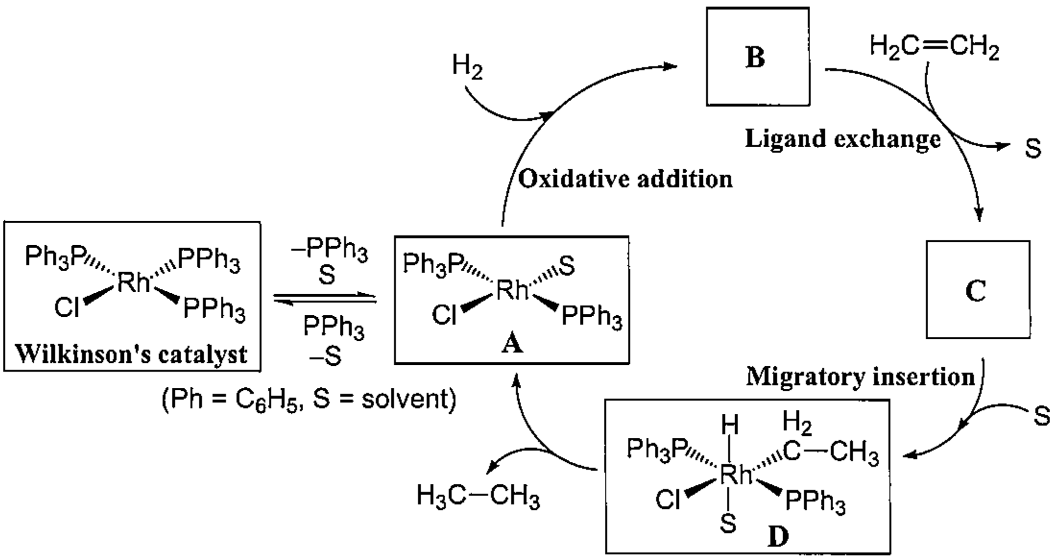


Figure 5.1

II. Answer the following questions.

1. Both hemoglobin and vitamin B_{12} consist of one metal center and one macrocyclic ligand. The combination of the central metal and the macrocyclic ligand is summarized in Table 5.1. From the following metals and ligands, choose an appropriate one for each of the blanks (i)–(iv) in Table 5.1.

   Cr, Mn, Fe, Co, Ni, Cu, Zn, porphyrin, phthalocyanine, corrin, triethylenetetramine, cyclam

Table 5.1

	Central metal	Macrocyclic ligand
Hemoglobin	(i)	(iii)
Vitamin B_{12}	(ii)	(iv)

2. Carbon monoxide is a biotoxic gas because carbon monoxide inhibits the transport of oxygen by binding to the metal center of hemoglobin. Generally, carbon monoxide strongly binds to the transition metal center through σ-donating and π-backdonating interactions. The orbital interaction diagram for the σ-donation is shown in Figure 5.2. Draw the orbital interaction diagram for the π-backdonation by referring to Figure 5.2.

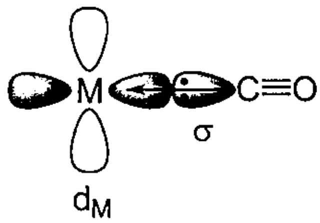
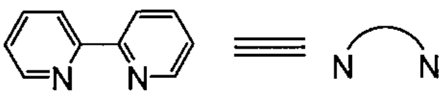


Figure 5.2

3. Metalloenzymes containing Zn^{2+} ions with a tetrahedral environment generally do not show any significant absorption in visible light region. Explain the reason.

III. Answer the following questions.

1. Draw all the possible isomers for $[Ru(bpy)_3]^{2+}$. Note that the structure of bpy is assumed to be completely planar. You may draw the structure of bpy as shown in Figure 5.3.



(bpy = 2,2'-bipyridine)

Figure 5.3

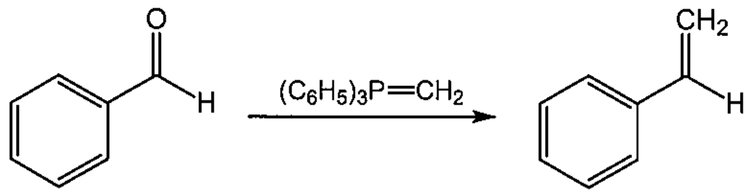
2. $[NiCl_4]^{2-}$ has tetrahedral coordination geometry, whereas $[Ni(CN)_4]^{2-}$ has square planar coordination geometry. For each complex, indicate whether the complex is paramagnetic or diamagnetic. Also, explain the reason for the answer by describing the d-orbital splitting and the electron configuration of these two complexes.

Problem 6　Organic Chemistry

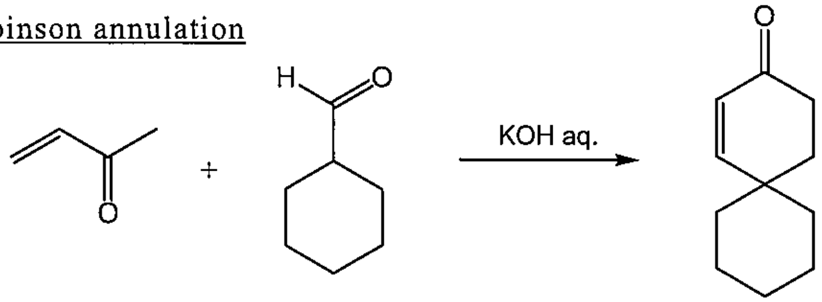
Answer the following questions.

I. Show the mechanisms of the following name reactions.

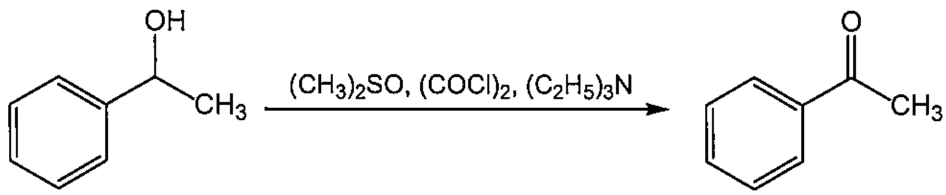
1. Wittig reaction



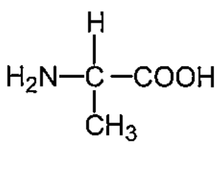
2. Robinson annulation



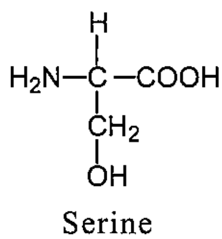
3. Swern oxidation



II. Answer the following questions on α-amino acids. The structural formulas of alanine and serine are shown below. You can ignore the absolute configurations, unless otherwise stated.

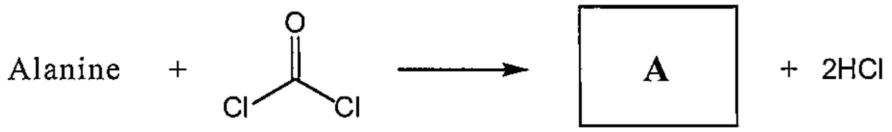


Alanine



Serine

1. Explain the meaning of α in α-amino acids.
2. Draw the structural formula of (*R*)-alanine by showing the absolute configuration.
3. The pK_a values of the carboxy, protonated amino, and hydroxy groups of serine are 2.2, 9.2, and 13, respectively. Draw the structural formula of the major ionic form of serine in an aqueous solution at pH = 7.
4. Draw the structural formula of product **A** obtained in the following reaction.



5. The ring-opening polymerization of compound **A** in Question II. 4 is initiated by the nucleophilic attack of primary amine ($R{-}NH_2$). Show the reaction mechanism of this polymerization.
6. Which peptide is more soluble in water, alanine-rich peptide or serine-rich peptide? Provide the answer with the reason.

Problem 7 Analytical Chemistry

Answer the following questions. If necessary, use the following values.
$\log_{10}2 = 0.30$, $\log_{10}3 = 0.48$, $\log_{10}5 = 0.70$

I. Answer the following questions on solvent extraction, in which ions in aqueous phase are extracted to organic phase.

1. Explain the principles of chelate extraction and ion-pair extraction, respectively.
2. Consider a repeated extraction of ions with distribution ratio of 2. The volume of the organic phase is equal to that of the aqueous phase. What percentage of the ions are extracted from the aqueous phase after the second extraction? The distribution ratio is defined below.

$$\text{Distribution ratio} = \frac{\text{Concentration of target ions in organic phase}}{\text{Concentration of target ions in aqueous phase}}$$

3. Explain the principle of impurity removal by a masking reagent.

II. Answer the following questions on spectroscopy.

1. In a cell with an optical path length of 1.0 mm, an aqueous solution of solute **A** absorbs light of a wavelength of 450 nm by 50%. In the same 1.0 mm cell, an aqueous solution of solute **B** absorbs light of a wavelength of 450 nm by 20%. Equal volumes of these two solutions are mixed, and then the absorbance at 450 nm for the resulting solution is measured in a cell with an optical path length of 2.0 mm. Calculate the absorbance.
2. Explain the selection rules of total spin angular momentum S and total orbital angular momentum L for light absorption of atoms (electric dipole transition).
3. Depict all the vibrational modes of a CO_2 molecule.
4. Depict the configuration of a Fourier-transform infrared spectrophotometer. Include the light source, the sample cell, and the interferometer in the figure. Also, explain the working principle of the interferometer.