2015
The Graduate School Entrance Examination
Chemistry
(Applicants for the Department of Applied 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. 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. 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 7) 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 per 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 Basic Physical Chemistry

Answer the following questions on quantum chemistry.

I. Answer suitable word(s) in **(a)**–**(m)** in the following sentences.

The electronic structure of a hydrogen-like atom is determined by analytical solution of the Schrödinger equation. The first step is to separate the wavefunction into the radial wavefunction and the angular wavefunction. The angular wavefunction, **(a)** quantum number, *l*, and **(b)** quantum number, *m*, are derived from the angular wave equation, where *l* and *m* are related to orbital **(c)**. Further, the radial wavefunction and **(d)** quantum number, *n*, are derived by the radial wave equation. Here, when *n* is identical, the **(e)** level of the orbitals is identical, and the **(f)** of orbitals is n^2.

In the case of the electronic structure of many-electron atoms, no more than two electrons may occupy any given orbital based on the **(g)** principle. And if two electrons do occupy one orbital, their spins must be antiparallel and paired. In addition, based on the **(h)** principle, in the case of calcium, the orbitals are normally occupied in the following order: 1s, 2s, 2p, 3s, 3p, 4s. Also, based on the **(i)** rule, an atom in its ground state adopts a configuration with the largest **(j)** quantum number, *S*.

In the case of the electronic structure of molecules, molecular orbitals can be approximated by a **(k)** combination of atomic orbitals. Based on the **(l)** principle, their coefficients are determined by solving **(m)** equations.

II. The radial wavefunction, $\psi_{3s}(r)$, of the 3s orbital in a hydrogen atom is expressed by the following equation using the Bohr radius, a_0, and the distance, r, between the atomic nucleus and the electron.

$$\psi_{3s}(r) = \frac{2}{81\sqrt{3}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(27 - \frac{18r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right)\exp\left(-\frac{r}{3a_0}\right)$$

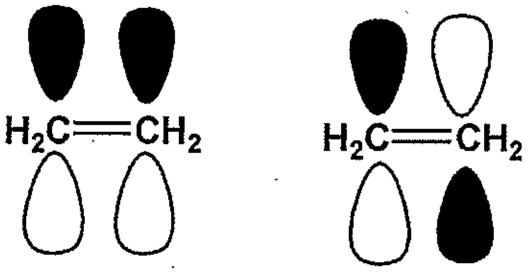
Answer the following questions. Calculate numerical value(s) in the answer sheet with two significant digits. Use the following values if necessary.

$e = 2.72,\ \pi = 3.14,\ \sqrt{2} = 1.41,\ \sqrt{3} = 1.73,\ \sqrt{5} = 2.24,\ \sqrt{7} = 2.65$

1. The positions of two nodes of $\psi_{3s}(r)$ are indicated by the distance, r_{node}. Calculate r_{node} / a_0.
2. The two positions at which $\psi_{3s}(r)$ reaches extreme values are indicated by r_{ext}. Calculate r_{ext} / a_0.
3. Using r / a_0 as a horizontal axis, draw $\psi_{3s}(r)$ with clearly indicating r_{node} / a_0 and r_{ext} / a_0.
4. The radial distribution function of the 3s orbital is defined as the function of r, $P(r)$. Express $P(3a_0)$ using a_0.

III. Answer the following questions on molecular orbital method.

1. The equilibrium bond length of H_2 shows a different value from that of H_2^+. Answer which is longer, the equilibrium bond length of H_2 or that of H_2^+. In addition, briefly explain the reason based on the properties of molecular orbitals.
2. The π and π* orbitals of ethylene are shown in Fig. 1.1, with black for the positive sign of the wavefunction and with white for the negative sign of the wavefunction. Draw all of the π and π* orbitals of 1,3-butadiene by the same drawing method in the order of their energy level from the highest to the lowest.



π orbital π* orbital

Fig. 1.1

Problem 2　Basic Inorganic Chemistry

Answer the following questions on aluminum (atomic weight = 26.98). When answering numerical value(s), describe the process with which you reached your answer. The Avogadro's constant N_A is $6.02 \times 10^{23}\,\mathrm{mol}^{-1}$. Use the following values if necessary.

$\pi = 3.14$, $\sqrt{2} = 1.41$, $\sqrt{3} = 1.73$, $\sqrt{5} = 2.24$, $\sqrt{7} = 2.65$

I. Na^+, Mg^{2+} and Al^{3+} have the same number of outermost electrons. Rank them in the increasing order of ionic radii, and explain the reason.

II. Show the chemical equation that describes the reaction of aluminum with hydrochloric acid. Also, describe the reaction of aluminum with sodium hydroxide solution.

III. Aluminum is soluble in dilute nitric acid, but is poorly soluble in concentrated nitric acid. Explain the reason.

IV. The crystal of aluminum has a face-centered cubic structure. The plastic deformation of metals is normally caused by the motion of dislocation (a kind of crystallographic defects) along the close-packed plane (slip plane). Draw the unit cell of the aluminum crystal, and show the slip plane.

V. Calculate the packing efficiency (atomic packing factor) of a face-centered cubic structure with two significant digits. Here, assume that atoms are rigid spheres forming a close-packed structure.

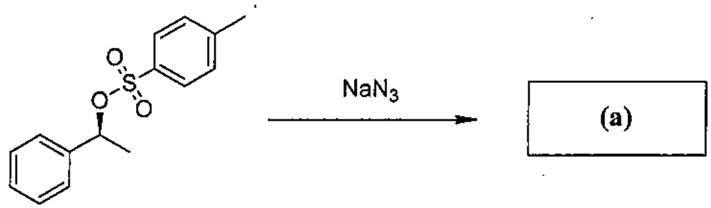
VI. Bragg's law is used for crystal structure analysis. Explain Bragg's law by drawing a figure. Also, explain briefly the principle of X-ray diffraction.

VII. By X-ray diffraction, the length of an edge of the unit cell of the aluminum crystal was determined to be 0.405 nm at 25 °C. Calculate the density (g/cm^3) of the aluminum crystal at 25 °C with two significant digits.

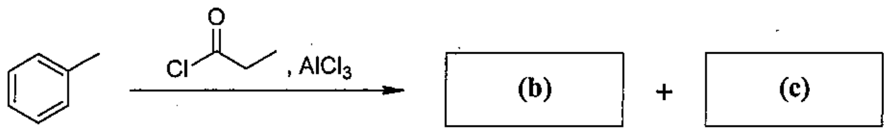
Problem 3 Basic Organic Chemistry

I. Draw the structural formulas of the main products, **(a)**–**(l)**, for the following reactions. Steric structures (stereochemical structures) should be clearly shown for **(a)** and **(d)**. Note that the yield of compound **(b)** is larger than that of **(c)**.

(1)

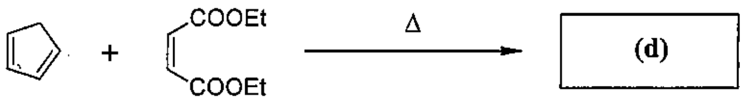


(2)



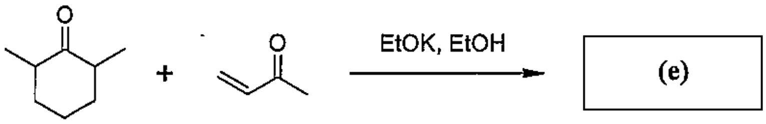
O
Cl
, AlCl3
(b)
+
(c)

(3)



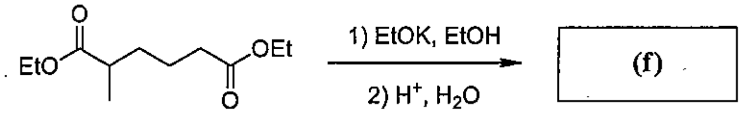
+
COOEt
COOEt
Δ
(d)

(4)



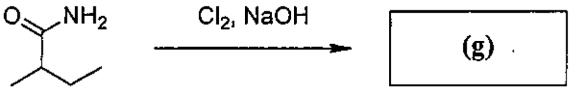
O
+
O
EtOK, EtOH
(e)

(5)



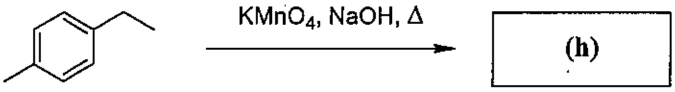
O
EtO
OEt
O
1) EtOK, EtOH
2) H+, H2O
(f)

(6)

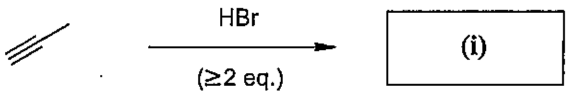


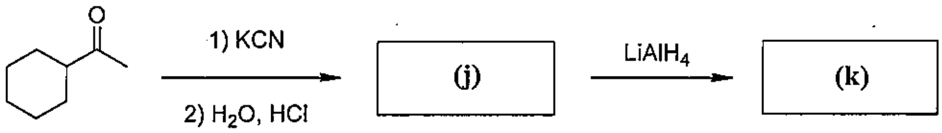
O
NH2
Cl2, NaOH
(g)

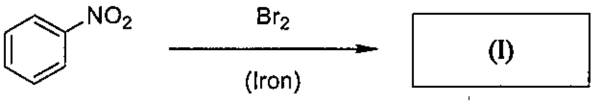
(7)



KMnO4, NaOH, Δ
(h)

(8) 

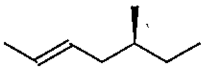
(9) 

(10) 

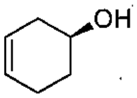
II. The reactions (2), (3), and (4) of question I are the name reactions. Give the name of each reaction.

III. Give chemical nomenclatures of the compounds **(m)** and **(n)** by following the IUPAC rules.

(m)



(n)



IV. Answer the following questions on the compounds with a chemical formula of $C_4H_{10}O$.

1. Draw the structural formulas of all constitutional isomers.
2. Show all stereoisomers. Steric structures (stereochemical structures) should be clearly shown.
3. Draw structural formulas of all compounds that are not oxidized into aldehydes or ketones in aqueous $K_2Cr_2O_7$ solutions.

Problem 4 Physical Chemistry

I. Answer the following questions on gas species N_2 and H_2. The gas constant R is 8.31 J K^{-1} mol^{-1}. Use the following values if necessary.

$\ln 2 = 0.693$, $\ln 3 = 1.10$, $\ln 5 = 1.61$, $\ln 10 = 2.30$

1. A heat insulated container is divided into two compartments by an inner wall. In the container, one compartment contains 2 mol of N_2 at 1.0 atm and 298 K, and the other compartment contains 1 mol of H_2 at 4.0 atm and 298 K. To mix the two gas species, the inner wall is removed. Assume that the reaction does not proceed when the two ideal gas species are mixed. Calculate the Gibbs energy change of mixing, $\Delta_{mix}G$, and the enthalpy change of mixing, $\Delta_{mix}H$.
2. The standard enthalpy of the reaction, $\Delta_f H^\circ$, for N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) is -46.1 kJ mol^{-1}. The equilibrium constant of the reaction at T (K) is $K_p(T)$. Calculate $\ln K_p(500)$, using $K_p(298) = 6.0 \times 10^5$. Answer the sign of the standard reaction entropy, $\Delta_f S^\circ$, of the reaction, and explain the reason, comparing the values of $K_p(298)$ and $K_p(500)$.

II. Compound A yields compound D according to the following reactions:

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B, \qquad B + C \xrightarrow{k_2} D$$

where k_1, k_{-1}, and k_2 are the rate constants for the elementary reactions. Answer the following questions. In the following, $[i]$ is the concentration of compound i, t is the reaction time, T is the temperature, and R is the gas constant.

1. Express $\frac{d[D]}{dt}$, using the rate constant(s) of the elementary reaction(s) and the concentration of the compound(s).
2. When approximating that time-dependence of [B] is constant (i.e., steady-state approximation), express $\frac{d[D]}{dt}$.
3. When approximating that time-dependence of [B] is constant and $k_{-1} \ll k_2[C]$, express $\frac{d[D]}{dt}$. The concentration of A, [A], measured experimentally

was found to satisfy the following equation: [A] = $a \exp(-bt)$. Express [D] at time t, using the rate constant(s) of the elementary reaction(s) and the constants a and b. Note that initially [D] = 0.

4. k_{obs} is the apparent rate constant for a reaction. When plotting $\ln k_{obs}$ as a function of $\frac{1}{T}$, linear relationship was observed. Express the corresponding activation energy, $E_{a(obs)}$, using $\frac{d(\ln k_{obs})}{dT}$.
5. The activation energies of $E_{a(1)}$, $E_{a(-1)}$, and $E_{a(2)}$ are associated with the rate constants, k_1, k_{-1}, and k_2, respectively. It was approximated to be $\frac{d[D]}{dt} \approx \frac{k_1 k_2}{k_{-1}} [A]^2[C]$ ($= k_{obs}[A]^2[C]$). Using $E_{a(1)}$, $E_{a(-1)}$, and $E_{a(2)}$, express $E_{a(obs)}$ which can be obtained from $\ln k_{obs}$.

Problem 5 Inorganic Chemistry

I. Answer the following questions on diatomic molecules.

1. Show the directions of electric dipole moments for heteronuclear diatomic molecules, LiH and HF.
2. In the case of homonuclear diatomic molecules, a bonding molecular orbital (MO), $2\sigma_g$, and an antibonding MO, $2\sigma_u$, are mainly comprised of two 2s atomic orbitals (AOs). A bonding MO, $3\sigma_g$, and an antibonding MO, $3\sigma_u$, are mainly comprised of two $2p_z$ AOs. Furthermore, a bonding MO, $1\pi_u$, and an antibonding MO, $1\pi_g$, are comprised of two $2p_i$ ($i = x$ or y) AOs. For N_2 and O_2 molecules, draw MO energy level diagrams, paying attention to correlations among energy levels, and describe the electronic configurations.
3. The internuclear distance of an N_2 molecule (0.110 nm) is shorter than that of an O_2 molecule (0.121 nm). Briefly explain the reason for the difference of the internuclear distance by considering the electronic configurations of N_2 and O_2 molecules.

II. Answer the following questions on transition metal complexes.

1. Let us consider the six-coordinate octahedral iron complex, $[Fe(CN)_6]^{4-}$. The coordination of CN^- to an iron ion results in a large energy of the ligand-field splitting, 10 Dq. For $[Fe(CN)_6]^{4-}$ in the ground state, answer the electronic configuration of d electrons and the spin-multiplicity. In addition, explain the reason for the large energy of the ligand-field splitting caused by the CN^- ligands.
2. Let us consider the six-coordinate octahedral complexes, $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$. Calculate the ligand-field stabilization energies of these complexes using the energy of the ligand-field splitting, 10 Dq.
3. A metal complex, $[ML_6]^{2+}$, is formed by the ligand exchange reactions between $[M(H_2O)_6]^{2+}$ and L ligands, as follows.

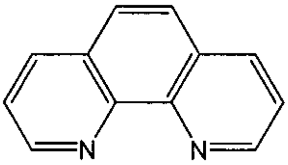
$$[M(H_2O)_6]^{2+} + 6L \rightleftharpoons [ML_6]^{2+} + 6H_2O$$

When the energy of the ligand-field splitting caused by the L ligands is larger than that by the H_2O ligand, the formation constants for $[ML_6]^{2+}$, $K(M^{2+})$, exhibit the following relationships with regard to various transition metal ions.

$$K(Mn^{2+}) < K(Fe^{2+}) < K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+}),$$
$$K(Cu^{2+}) > K(Zn^{2+})$$

Explain the reason why the formation constants indicate such magnitude correlations. Here, Mn, Fe, and Co complexes are six-coordinate octahedral complexes with high spin states.

4. Let us consider six-coordinate iron(II) complexes. When two 1,10-phenanthroline ligands (Fig. 5.1) and two chloride ion ligands are coordinating to one Fe^{2+}, two geometric isomers (*cis-trans* isomers) exist. Further, a pair of enantiomer exists for one of the geometrical isomers. Draw the structural formulas of these three isomers.



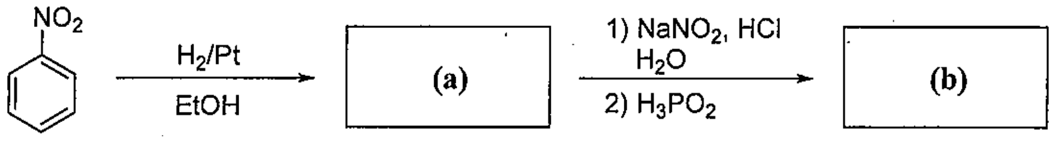
1,10-phenanthroline

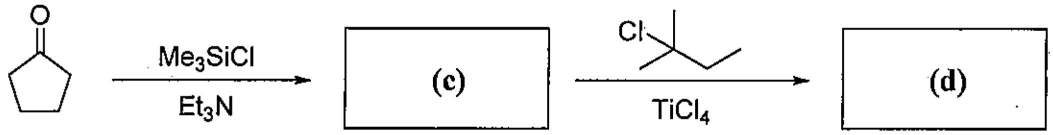
Fig. 5.1

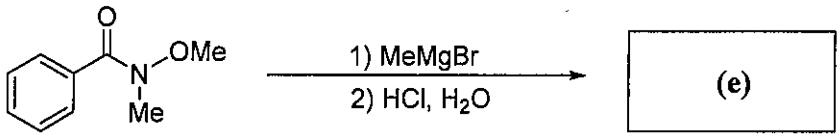
5. A heme of myoglobin is a transition metal complex. Answer the chemical symbol for the metal of this complex. In addition, answer briefly the role of this metalloprotein *in vivo*.

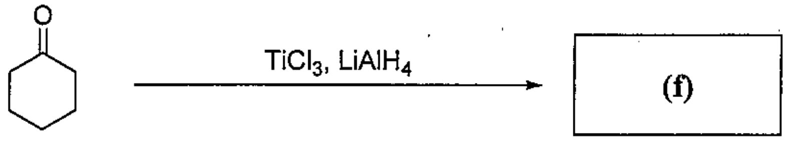
Problem 6 Organic Chemistry

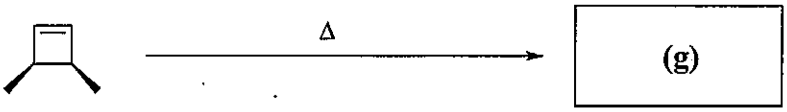
I. Draw the structural formulas of the main products **(a)**–**(h)** for the following reactions. Steric structures (stereochemical structures) should be clearly shown for the compounds **(g)** and **(h)**. In addition, answer the name of the catalyst **(i)** that produces the compound **(h)**.

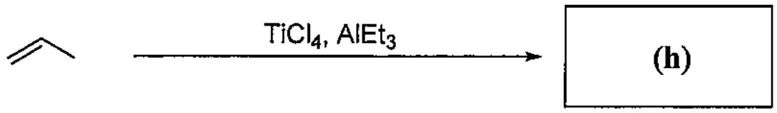

NO₂
H₂/Pt
EtOH
(a)
1) NaNO₂, HCl
H₂O
2) H₃PO₂
(b)


O
Me₃SiCl
Et₃N
(c)
Cl
TiCl₄
(d)


O
OMe
N
Me
1) MeMgBr
2) HCl, H₂O
(e)

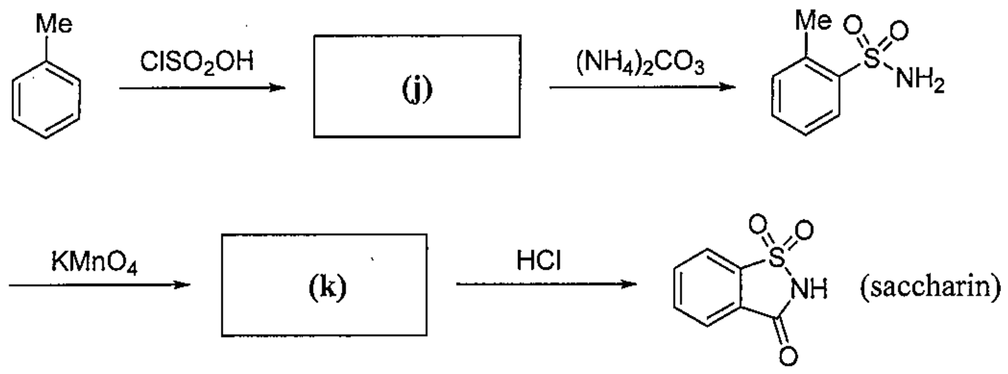

O
TiCl₃, LiAlH₄
(f)




TiCl₄, AlEt₃
(h)

name of the catalyst **(i)**

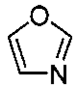
II. Answer the following questions on the synthesis of saccharin.

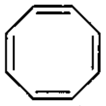
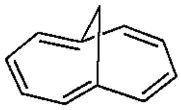
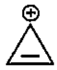


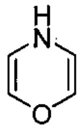
1. Draw the structural formulas of the major products **(j)** and **(k)**. Note that the compound **(k)** is not isolated in the practical synthesis.
2. Draw the structural formula of the electrophile generated from chlorosulfuric acid in the first step of the synthesis.
3. Give a main use of saccharin.

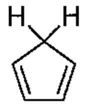
III. Answer the following questions on aromatic compounds.

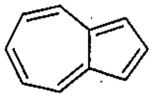
1. According to Hückel's rule, choose all the compound(s) that show aromatic character from the following compounds.



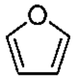




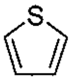


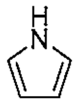


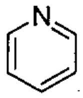


2. From the aromatic heterocyclic compounds shown below, choose all the compound(s) that can undergo [4+2] cycloaddition reaction with maleic anhydride without using acids or high pressure conditions. In addition, describe the reason for the choice(s).









Problem 7 Analytical Chemistry

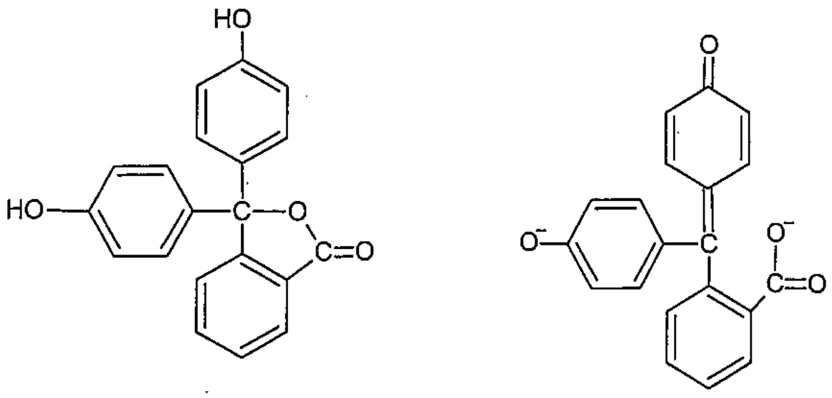
Answer the following questions on light absorption and the analytical methods utilizing the light absorption. The unit M represents molar concentration (mol L^{-1}). The Avogadro's constant N_A is 6.02×10^{23} mol^{-1}. Use the following values if necessary.

$\log_{10}2 = 0.30$

I. Calculate the frequency of light with wavelength of 500 nm. The light velocity is 3.0×10^8 m s^{-1}.

II. Depict the energy level diagrams for $(1s)^1$ and $(2p)^1$ states of an H atom by considering the electron spin angular momentum and the orbital angular momentum. Describe the process with which you reached your answer.

III. Phenolphthalein, which is used as an indicator of neutralization titration, is less colored under acidic condition (pH = 3.0) and is red-colored under alkalic condition (pH = 11). The color change can be explained by the change of the molecular structures under the acidic and alkalic conditions (Fig. 7.1). Explain briefly the reason why the phenolphthalein is colored under the alkalic conditions from the viewpoint of the molecular orbitals.



Acidic condition (pH = 3.0)

Alkalic condition (pH = 11)

Fig. 7.1

IV. The 20 % of incident light (wavelength of 500 nm) was absorbed by a solute in an absorption cell having an optical path length of 1.0 cm. Calculate the concentration of the solute, with two significant digits. Here, the molar absorptivity (extinction coefficient) is 1.0×10^3 M^{-1} cm^{-1} at the wavelength of 500 nm.

V. Calculate an absorption cross-section of a solute with the molar absorptivity of 1.0×10^3 M^{-1} cm^{-1}, with two significant digits.

VI. A prism is utilized as an optical element in a dispersive spectrometer. Explain briefly what kind of physical property, which depends on the wavelength, is utilized for optical dispersion.

VII. Fourier-transform spectroscopy is used for analysis in an infrared region. Answer the two advantages of the Fourier-transform spectroscopy compared with the dispersive spectroscopy. The reasons should also be briefly explained.

VIII. For the analysis of heavy metal ions in river water, solvent extraction procedures are sometimes used prior to light absorption measurements. Briefly explain the role of the solvent extraction.

IX. Briefly explain the principle of the absorption spectrophotometry by which enantiomers can be distinguished.

2015
The Graduate School Entrance Examination
Chemistry
(Applicants for the Department of Bio engineering)
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 four out of seven problems in the problem booklet.

4. You are given four 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 7) 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 per 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 Basic Physical Chemistry

Answer the following questions on quantum chemistry.

I. Answer suitable word(s) in **(a)**–**(m)** in the following sentences.

The electronic structure of a hydrogen-like atom is determined by analytical solution of the Schrödinger equation. The first step is to separate the wavefunction into the radial wavefunction and the angular wavefunction. The angular wavefunction, **(a)** quantum number, l, and **(b)** quantum number, m, are derived from the angular wave equation, where l and m are related to orbital **(c)**. Further, the radial wavefunction and **(d)** quantum number, n, are derived by the radial wave equation. Here, when n is identical, the **(e)** level of the orbitals is identical, and the **(f)** of orbitals is n^2.

In the case of the electronic structure of many-electron atoms, no more than two electrons may occupy any given orbital based on the **(g)** principle. And if two electrons do occupy one orbital, their spins must be antiparallel and paired. In addition, based on the **(h)** principle, in the case of calcium, the orbitals are normally occupied in the following order: 1s, 2s, 2p, 3s, 3p, 4s. Also, based on the **(i)** rule, an atom in its ground state adopts a configuration with the largest **(j)** quantum number, S.

In the case of the electronic structure of molecules, molecular orbitals can be approximated by a **(k)** combination of atomic orbitals. Based on the **(l)** principle, their coefficients are determined by solving **(m)** equations.

II. The radial wavefunction, $\psi_{3s}(r)$, of the 3s orbital in a hydrogen atom is expressed by the following equation using the Bohr radius, a_0, and the distance, r, between the atomic nucleus and the electron.

$$\psi_{3s}(r)=\frac{2}{81\sqrt{3}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(27-\frac{18r}{a_0}+2\left(\frac{r}{a_0}\right)^2\right)\exp\left(-\frac{r}{3a_0}\right)$$

Answer the following questions. Calculate numerical value(s) in the answer sheet with two significant digits. Use the following values if necessary.

$e=2.72,\ \pi=3.14,\ \sqrt{2}=1.41,\ \sqrt{3}=1.73,\ \sqrt{5}=2.24,\ \sqrt{7}=2.65$

1. The positions of two nodes of $\psi_{3s}(r)$ are indicated by the distance, r_{node}. Calculate r_{node}/a_0.
2. The two positions at which $\psi_{3s}(r)$ reaches extreme values are indicated by r_{ext}. Calculate r_{ext}/a_0.
3. Using r/a_0 as a horizontal axis, draw $\psi_{3s}(r)$ with clearly indicating r_{node}/a_0 and r_{ext}/a_0.
4. The radial distribution function of the 3s orbital is defined as the function of r, $P(r)$. Express $P(3a_0)$ using a_0.

III. Answer the following questions on molecular orbital method.

1. The equilibrium bond length of H_2 shows a different value from that of H_2^+. Answer which is longer, the equilibrium bond length of H_2 or that of H_2^+. In addition, briefly explain the reason based on the properties of molecular orbitals.
2. The π and π* orbitals of ethylene are shown in Fig. 1.1, with black for the positive sign of the wavefunction and with white for the negative sign of the wavefunction. Draw all of the π and π* orbitals of 1,3-butadiene by the same drawing method in the order of their energy level from the highest to the lowest.

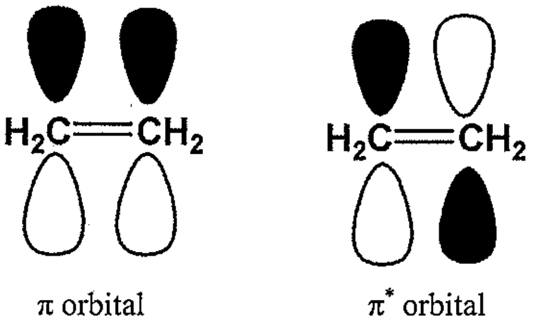


Fig. 1.1

Problem 2 Basic Inorganic Chemistry

Answer the following questions on aluminum (atomic weight = 26.98). When answering numerical value(s), describe the process with which you reached your answer. The Avogadro's constant N_A is $6.02 \times 10^{23}\ \mathrm{mol}^{-1}$. Use the following values if necessary.

$\pi = 3.14$, $\sqrt{2} = 1.41$, $\sqrt{3} = 1.73$, $\sqrt{5} = 2.24$, $\sqrt{7} = 2.65$

I. Na^+, Mg^{2+} and Al^{3+} have the same number of outermost electrons. Rank them in the increasing order of ionic radii, and explain the reason.

II. Show the chemical equation that describes the reaction of aluminum with hydrochloric acid. Also, describe the reaction of aluminum with sodium hydroxide solution.

III. Aluminum is soluble in dilute nitric acid, but is poorly soluble in concentrated nitric acid. Explain the reason.

IV. The crystal of aluminum has a face-centered cubic structure. The plastic deformation of metals is normally caused by the motion of dislocation (a kind of crystallographic defects) along the close-packed plane (slip plane). Draw the unit cell of the aluminum crystal, and show the slip plane.

V. Calculate the packing efficiency (atomic packing factor) of a face-centered cubic structure with two significant digits. Here, assume that atoms are rigid spheres forming a close-packed structure.

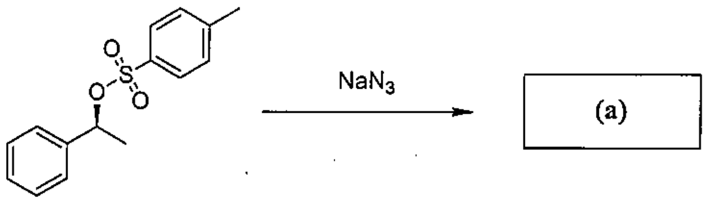
VI. Bragg's law is used for crystal structure analysis. Explain Bragg's law by drawing a figure. Also, explain briefly the principle of X-ray diffraction.

VII. By X-ray diffraction, the length of an edge of the unit cell of the aluminum crystal was determined to be 0.405 nm at 25 °C. Calculate the density (g/cm^3) of the aluminum crystal at 25 °C with two significant digits.

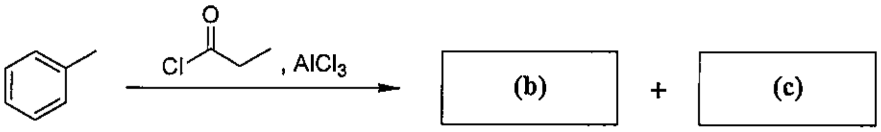
Problem 3 Basic Organic Chemistry

I. Draw the structural formulas of the main products, **(a)**–**(l)**, for the following reactions. Steric structures (stereochemical structures) should be clearly shown for **(a)** and **(d)**. Note that the yield of compound **(b)** is larger than that of **(c)**.

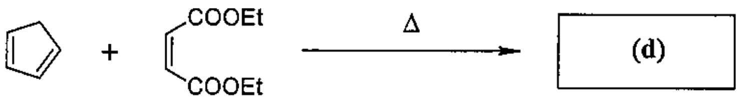
(1)



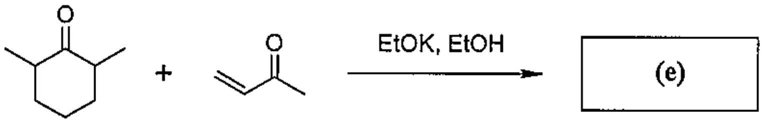
(2)


O
Cl
, AlCl3
(b)
+
(c)

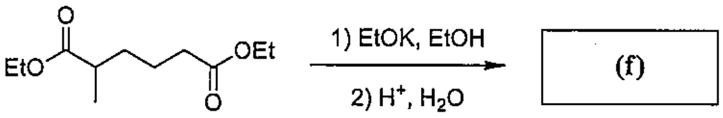
(3)


+
COOEt
COOEt
Δ
(d)

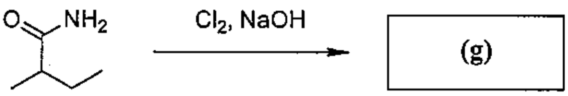
(4)


O
+
O
EtOK, EtOH
(e)

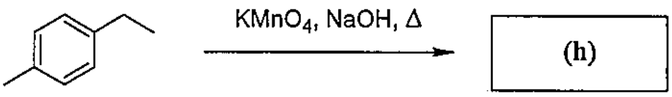
(5)


O
EtO
OEt
O
1) EtOK, EtOH
2) H+, H2O
(f)

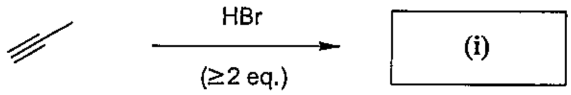
(6)


O
NH2
Cl2, NaOH
(g)

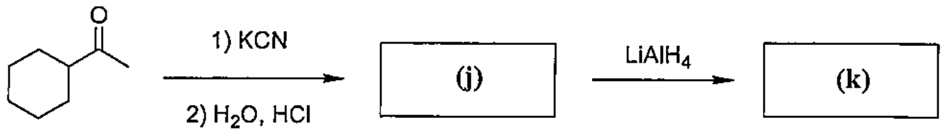
(7)


KMnO4, NaOH, Δ
(h)

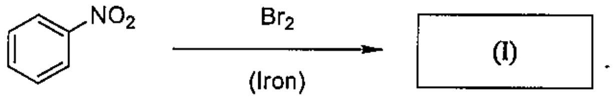
(8)



(9)



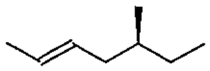
(10)



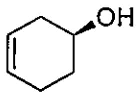
II. The reactions (2), (3), and (4) of question I are the name reactions. Give the name of each reaction.

III. Give chemical nomenclatures of the compounds **(m)** and **(n)** by following the IUPAC rules.

(m)



(n)



IV. Answer the following questions on the compounds with a chemical formula of $C_4H_{10}O$.

1. Draw the structural formulas of all constitutional isomers.
2. Show all stereoisomers. Steric structures (stereochemical structures) should be clearly shown.
3. Draw structural formulas of all compounds that are not oxidized into aldehydes or ketones in aqueous $K_2Cr_2O_7$ solutions.

Problem 4 Physical Chemistry

I. Answer the following questions on gas species N_2 and H_2. The gas constant R is 8.31 J K^{-1} mol^{-1}. Use the following values if necessary.

$\ln 2 = 0.693$, $\ln 3 = 1.10$, $\ln 5 = 1.61$, $\ln 10 = 2.30$

1. A heat insulated container is divided into two compartments by an inner wall. In the container, one compartment contains 2 mol of N_2 at 1.0 atm and 298 K, and the other compartment contains 1 mol of H_2 at 4.0 atm and 298 K. To mix the two gas species, the inner wall is removed. Assume that the reaction does not proceed when the two ideal gas species are mixed. Calculate the Gibbs energy change of mixing, $\Delta_{mix}G$, and the enthalpy change of mixing, $\Delta_{mix}H$.
2. The standard enthalpy of the reaction, $\Delta_f H^{\ominus}$, for N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) is -46.1 kJ mol^{-1}. The equilibrium constant of the reaction at T (K) is $K_p(T)$. Calculate $\ln K_p(500)$, using $K_p(298) = 6.0 \times 10^5$. Answer the sign of the standard reaction entropy, $\Delta_f S^{\ominus}$, of the reaction, and explain the reason, comparing the values of $K_p(298)$ and $K_p(500)$.

II. Compound A yields compound D according to the following reactions:

$$2\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}, \qquad \mathrm{B} + \mathrm{C} \xrightarrow{k_2} \mathrm{D}$$

where k_1, k_{-1}, and k_2 are the rate constants for the elementary reactions. Answer the following questions. In the following, $[i]$ is the concentration of compound i, t is the reaction time, T is the temperature, and R is the gas constant.

1. Express $\frac{d[\mathrm{D}]}{dt}$, using the rate constant(s) of the elementary reaction(s) and the concentration of the compound(s).
2. When approximating that time-dependence of [B] is constant (i.e., steady-state approximation), express $\frac{d[\mathrm{D}]}{dt}$.
3. When approximating that time-dependence of [B] is constant and $k_{-1} \ll k_2[\mathrm{C}]$, express $\frac{d[\mathrm{D}]}{dt}$. The concentration of A, [A], measured experimentally

was found to satisfy the following equation: [A] = a exp($-bt$). Express [D] at time t, using the rate constant(s) of the elementary reaction(s) and the constants a and b. Note that initially [D] = 0.

4. k_{obs} is the apparent rate constant for a reaction. When plotting ln k_{obs} as a function of $\frac{1}{T}$, linear relationship was observed. Express the corresponding activation energy, $E_{\text{a(obs)}}$, using $\frac{d(\ln k_{\text{obs}})}{dT}$.
5. The activation energies of $E_{\text{a(1)}}$, $E_{\text{a(-1)}}$, and $E_{\text{a(2)}}$ are associated with the rate constants, k_1, k_{-1}, and k_2, respectively. It was approximated to be $\frac{d[\text{D}]}{dt} \approx \frac{k_1 k_2}{k_{-1}}[\text{A}]^2[\text{C}]$ ($= k_{\text{obs}}[\text{A}]^2[\text{C}]$). Using $E_{\text{a(1)}}$, $E_{\text{a(-1)}}$, and $E_{\text{a(2)}}$, express $E_{\text{a(obs)}}$ which can be obtained from ln k_{obs}.

Problem 5 Inorganic Chemistry

I. Answer the following questions on diatomic molecules.

1. Show the directions of electric dipole moments for heteronuclear diatomic molecules, LiH and HF.
2. In the case of homonuclear diatomic molecules, a bonding molecular orbital (MO), $2\sigma_g$, and an antibonding MO, $2\sigma_u$, are mainly comprised of two 2s atomic orbitals (AOs). A bonding MO, $3\sigma_g$, and an antibonding MO, $3\sigma_u$, are mainly comprised of two $2p_z$ AOs. Furthermore, a bonding MO, $1\pi_u$, and an antibonding MO, $1\pi_g$, are comprised of two $2p_i$ ($i = x$ or y) AOs. For N_2 and O_2 molecules, draw MO energy level diagrams, paying attention to correlations among energy levels, and describe the electronic configurations.
3. The internuclear distance of an N_2 molecule (0.110 nm) is shorter than that of an O_2 molecule (0.121 nm). Briefly explain the reason for the difference of the internuclear distance by considering the electronic configurations of N_2 and O_2 molecules.

II. Answer the following questions on transition metal complexes.

1. Let us consider the six-coordinate octahedral iron complex, $[Fe(CN)_6]^{4-}$. The coordination of CN^- to an iron ion results in a large energy of the ligand-field splitting, 10 Dq. For $[Fe(CN)_6]^{4-}$ in the ground state, answer the electronic configuration of d electrons and the spin-multiplicity. In addition, explain the reason for the large energy of the ligand-field splitting caused by the CN^- ligands.
2. Let us consider the six-coordinate octahedral complexes, $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$. Calculate the ligand-field stabilization energies of these complexes using the energy of the ligand-field splitting, 10 Dq.
3. A metal complex, $[ML_6]^{2+}$, is formed by the ligand exchange reactions between $[M(H_2O)_6]^{2+}$ and L ligands, as follows.

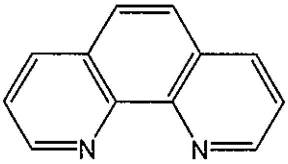
$$[M(H_2O)_6]^{2+} + 6L \rightleftharpoons [ML_6]^{2+} + 6H_2O$$

When the energy of the ligand-field splitting caused by the L ligands is larger than that by the H_2O ligand, the formation constants for $[ML_6]^{2+}$, $K(M^{2+})$, exhibit the following relationships with regard to various transition metal ions.

$$K(Mn^{2+}) < K(Fe^{2+}) < K(Co^{2+}) < K(Ni^{2+}) < K(Cu^{2+}),$$
$$K(Cu^{2+}) > K(Zn^{2+})$$

Explain the reason why the formation constants indicate such magnitude correlations. Here, Mn, Fe, and Co complexes are six-coordinate octahedral complexes with high spin states.

4. Let us consider six-coordinate iron(II) complexes. When two 1,10-phenanthroline ligands (Fig. 5.1) and two chloride ion ligands are coordinating to one Fe^{2+}, two geometric isomers (*cis-trans* isomers) exist. Further, a pair of enantiomer exists for one of the geometrical isomers. Draw the structural formulas of these three isomers.



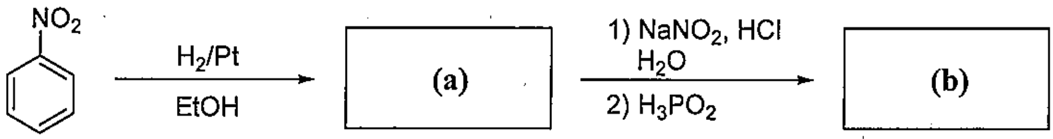
1,10-phenanthroline

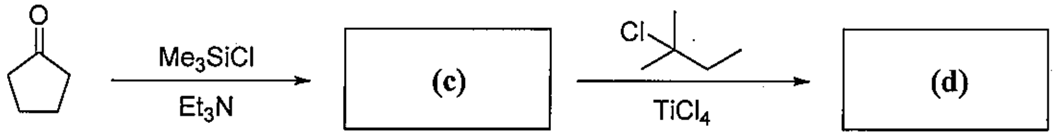
Fig. 5.1

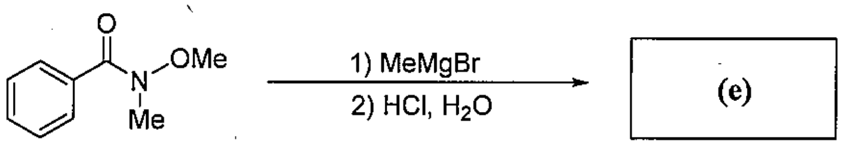
5. A heme of myoglobin is a transition metal complex. Answer the chemical symbol for the metal of this complex. In addition, answer briefly the role of this metalloprotein *in vivo*.

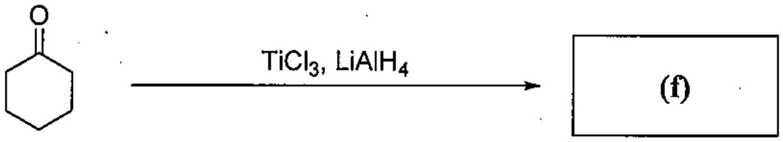
Problem 6 Organic Chemistry

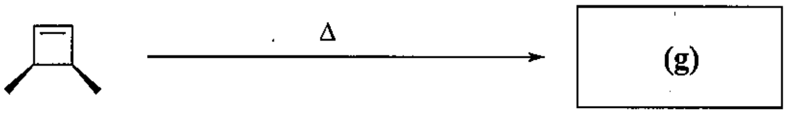
I. Draw the structural formulas of the main products **(a)**–**(h)** for the following reactions. Steric structures (stereochemical structures) should be clearly shown for the compounds **(g)** and **(h)**. In addition, answer the name of the catalyst **(i)** that produces the compound **(h)**.

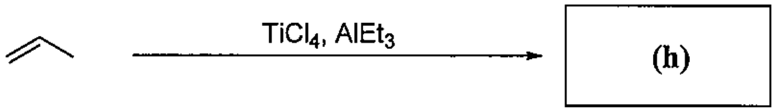

NO2
H2/Pt
EtOH
(a)
1) NaNO2, HCl
H2O
2) H3PO2
(b)


Me3SiCl
Et3N
(c)
Cl
TiCl4
(d)


OMe
N
Me
1) MeMgBr
2) HCl, H2O
(e)

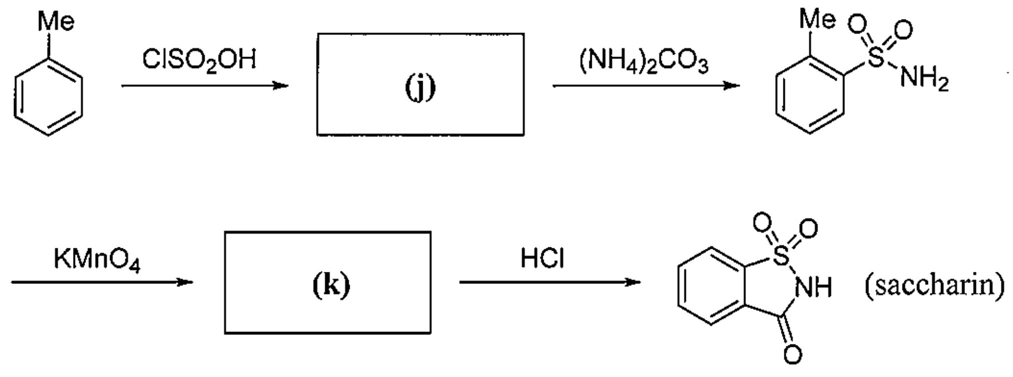

TiCl3, LiAlH4
(f)




TiCl4, AlEt3
(h)

name of the catalyst **(i)**

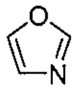
II. Answer the following questions on the synthesis of saccharin.

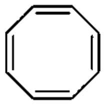
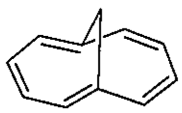
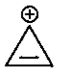


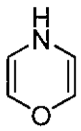
1. Draw the structural formulas of the major products **(j)** and **(k)**. Note that the compound **(k)** is not isolated in the practical synthesis.
2. Draw the structural formula of the electrophile generated from chlorosulfuric acid in the first step of the synthesis.
3. Give a main use of saccharin.

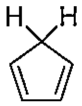
III. Answer the following questions on aromatic compounds.

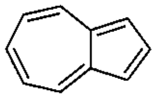
1. According to Hückel's rule, choose all the compound(s) that show aromatic character from the following compounds.



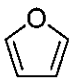




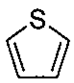


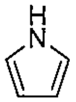


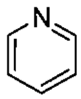


2. From the aromatic heterocyclic compounds shown below, choose all the compound(s) that can undergo [4+2] cycloaddition reaction with maleic anhydride without using acids or high pressure conditions. In addition, describe the reason for the choice(s).









Problem 7 Analytical Chemistry

Answer the following questions on light absorption and the analytical methods utilizing the light absorption. The unit M represents molar concentration (mol L^{-1}). The Avogadro's constant N_A is 6.02×10^{23} mol^{-1}. Use the following values if necessary.

$\log_{10}2 = 0.30$

I. Calculate the frequency of light with wavelength of 500 nm. The light velocity is 3.0×10^{8} m s^{-1}.

II. Depict the energy level diagrams for $(1s)^1$ and $(2p)^1$ states of an H atom by considering the electron spin angular momentum and the orbital angular momentum. Describe the process with which you reached your answer.

III. Phenolphthalein, which is used as an indicator of neutralization titration, is less colored under acidic condition (pH = 3.0) and is red-colored under alkalic condition (pH = 11). The color change can be explained by the change of the molecular structures under the acidic and alkalic conditions (Fig. 7.1). Explain briefly the reason why the phenolphthalein is colored under the alkalic conditions from the viewpoint of the molecular orbitals.

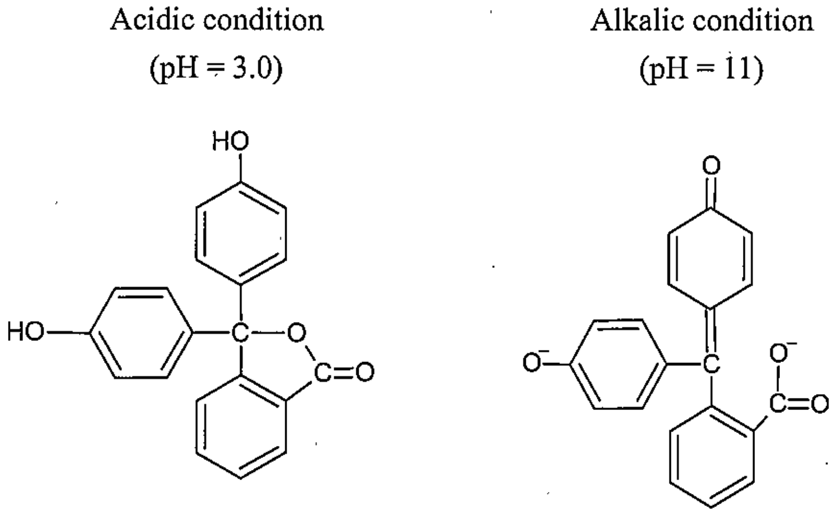


Fig. 7.1

IV. The 20 % of incident light (wavelength of 500 nm) was absorbed by a solute in an absorption cell having an optical path length of 1.0 cm. Calculate the concentration of the solute, with two significant digits. Here, the molar absorptivity (extinction coefficient) is 1.0×10^{3} M^{-1} cm^{-1} at the wavelength of 500 nm.

V. Calculate an absorption cross-section of a solute with the molar absorptivity of 1.0×10^{3} M^{-1} cm^{-1}, with two significant digits.

VI. A prism is utilized as an optical element in a dispersive spectrometer. Explain briefly what kind of physical property, which depends on the wavelength, is utilized for optical dispersion.

VII. Fourier-transform spectroscopy is used for analysis in an infrared region. Answer the two advantages of the Fourier-transform spectroscopy compared with the dispersive spectroscopy. The reasons should also be briefly explained.

VIII. For the analysis of heavy metal ions in river water, solvent extraction procedures are sometimes used prior to light absorption measurements. Briefly explain the role of the solvent extraction.

IX. Briefly explain the principle of the absorption spectrophotometry by which enantiomers can be distinguished.