2017
The Graduate School Entrance Examination
Chemistry
(Applicants for the Department of Bioengineering)
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. 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 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 scissors.
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

I. The overall reaction of a fuel cell, in which hydrogen and oxygen are used, is the oxidation reaction of hydrogen shown below.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$$

This reaction is exothermic, and its standard reaction enthalpy is −286 kJ mol^{-1} at 298.15 K. Supposing that the temperature is maintained at 298.15 K, answer the following questions. The number of significant digits is three. Use the following values if necessary.

Table 1.1 Standard molar entropies at 298.15 K

H_2 (g)	131	J K^{-1} mol^{-1}
O_2 (g)	205	J K^{-1} mol^{-1}
H_2O (g)	189	J K^{-1} mol^{-1}
H_2O (l)	69.9	J K^{-1} mol^{-1}

1. Calculate the standard entropy of the oxygen-oxidation reaction of H_2 (g).
2. Calculate the entropy change of the surroundings caused by the oxygen-oxidation reaction of H_2 (g).
3. Calculate the standard Gibbs energy of the generation of H_2O (l) by the oxygen-oxidation reaction of H_2 (g).
4. Calculate the standard electromotive force of the fuel cell which uses hydrogen fuel. The Faraday constant is 9.65×10^4 C mol^{-1}.
5. Does the voltage of the fuel cell increase or decrease with increasing the operation temperature? Provide the answer with the reason.

II. It is known that the decomposition reaction of N_2O_5 ($2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$) obeys first-order reaction experimentally, and the activation energy E_a is 103.4 kJ mol^{-1}. Also, it is considered that this reaction is caused by the combination of the chemical reactions (1) to (4) of nitrogen oxides as shown below. Answer the following questions using rate constants k_1 to k_4 for the reactions (1) to (4), respectively. The gas constant R is 8.31 J K^{-1} mol^{-1}.

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3 \quad (1)$$

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5 \quad (2)$$

$$NO_2 + NO_3 \xrightarrow{k_3} NO_2 + O_2 + NO \quad (3)$$

$$NO + N_2O_5 \xrightarrow{k_4} 3NO_2 \quad (4)$$

1. Derive the differential equation indicating the temporal change of N_2O_5 concentration with assuming steady state approximation regarding the concentrations of the reaction intermediates, NO and NO_3.
2. Using the result of Question II. 1, show the temporal change of N_2O_5 concentration when the initial concentration of N_2O_5 at $t = 0$ is $[N_2O_5]_0$.
3. At 367 K and 1.0×10^5 Pa, 1.0 mol of N_2 gas was reversibly and adiabatically compressed until the volume decreases to 80% of the original volume. Calculate the final temperature after the compression assuming that N_2 is an ideal gas. Molar heat capacity at constant volume of N_2 is 20.74 J K^{-1} mol^{-1}. The number of significant digit is two. Use the following values if necessary.

$$1.25^{2.5} = 1.75, \quad 1.25^{0.4} = 1.09, \quad 0.8^{2.5} = 0.572, \quad 0.8^{0.4} = 0.915$$

4. When N_2 containing a very small amount of N_2O_5 is compressed under the same condition as Question II. 3, how does the initial decomposition rate change before and after the compression? Provide the answer with the reason with considering the activation energy and the change of the concentration. The decomposition of N_2O_5 can be ignored during the compression.

Problem 2 Basic Inorganic Chemistry

Answer the following questions. 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. Answer the following questions on atoms and molecules.

1. Hydrogen molecules exist as homonuclear diatomic molecules (H_2 molecules). In contrast, helium molecules generally exist as monoatomic molecules (He molecules), not as homonuclear diatomic molecules (He_2 molecules). Explain the reason, based on the orbital correlation diagram.
2. Show the molecular structures of BCl_3 and NH_3 based on the valence-shell electron-pair repulsion (VSEPR) model. Also, state which molecule has a higher polarity, together with the reason.

II. Answer the following questions on ionic crystals.

1. Arrange the following substances in the descending order of their degrees of ionic bonding. Use the following values of electronegativities (χ) if necessary.

   $\chi_{H} = 2.20$, $\chi_{Na} = 1.01$, $\chi_{F} = 4.10$, $\chi_{Cl} = 2.83$

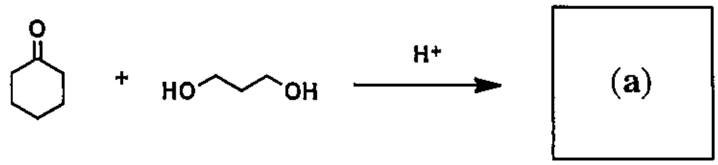
   (a) HF (b) HCl (c) NaF (d) NaCl

2. In general, crystal structures of ionic crystals are strongly influenced by the radius ratio of cationic to anionic ions. On the other hand, crystal structures of covalent crystals are hardly influenced by the radius ratio of constituent atoms. Explain the reason for this difference briefly.
3. NaCl is a typical ionic crystal, which has the coordination number of 6. Draw the positions of Cl^- and Na^+ ions in a unit cell.
4. Calculate the atomic packing factor of NaCl crystal, with the two significant digits. Here, assume that each ion can be approximated as a rigid sphere, and that the radius ratio of cationic to anionic ions is 0.52.

Problem 3 Basic Organic Chemistry

I. Draw the structural formula for the major products (**a**) to (**n**) of the following reactions.

(1)



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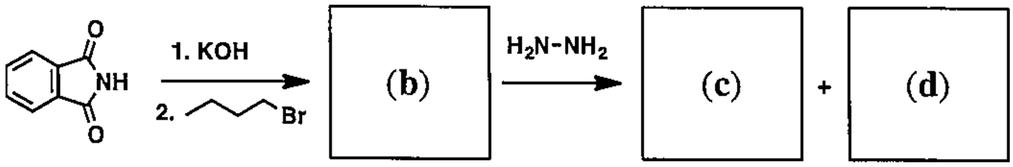

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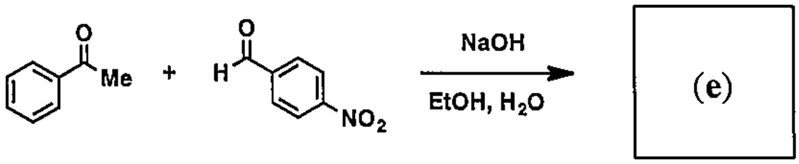

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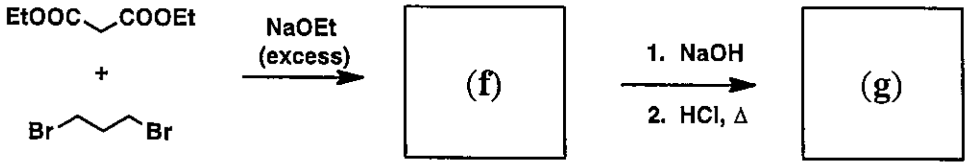

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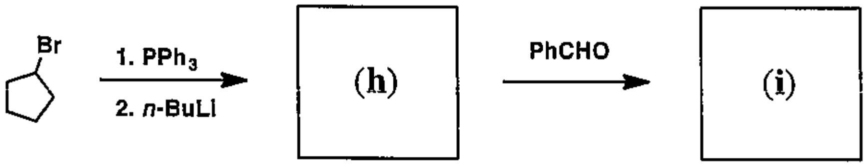

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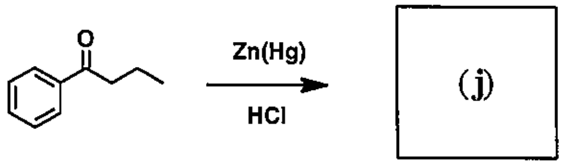

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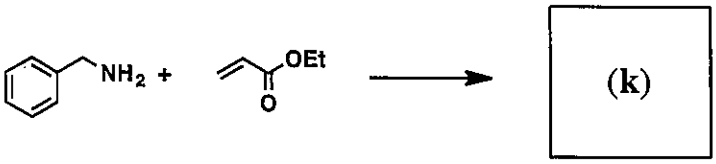

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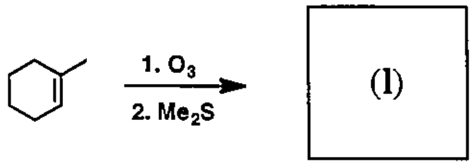

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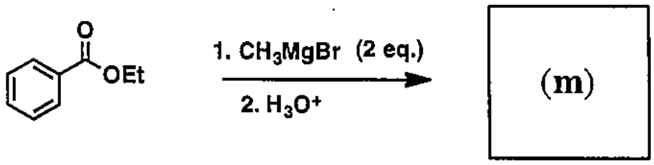

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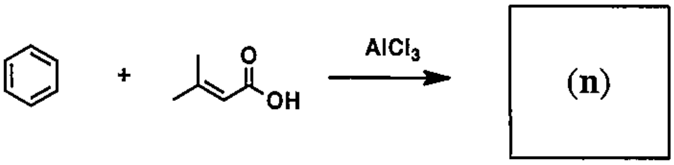
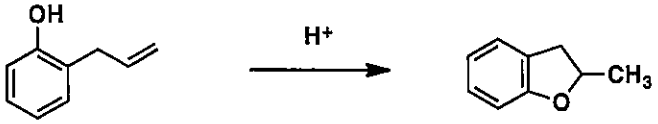


II. Show the reaction mechanisms for the following reactions.

(1)


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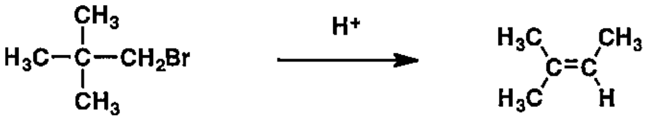
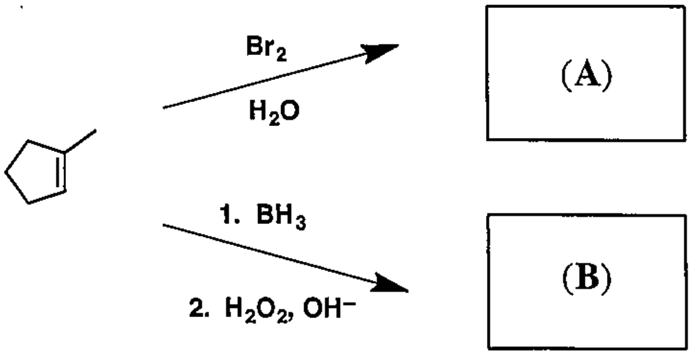


(3)


III. Draw the structural formula for the products (**A**) and (**B**) for the following reactions, paying attention to the stereochemistry.



Problem 4 Physical Chemistry

I. The wave function of an electron in a hydrogen atom is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi),$$

using the polar coordinates system (r, θ, ϕ). Here, n is the principal quantum number, l is the azimuthal quantum number, m is the magnetic quantum number, and $Y_l^m(\theta, \phi)$ is the spherical harmonics. $R_{nl}(r)$ is the radial wavefunction, given by

$$R_{nl}(r) = C_{nl} r^l \exp\left(-\frac{r}{na_0}\right) L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

Here, C_{nl} is a normalization constant, a_0 is the Bohr radius, and $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ is a function called as the associated Laguerre polynomial. Answer the following questions.

1. Answer all combinations of (n, l, m) that represent the 3s, 3p and 3d orbitals.
2. The spherical harmonics $Y_l^m(\theta, \phi)$ when $l = 1$ are given by

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta, \quad Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi}, \text{ and } Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\phi},$$

where i is the imaginary unit, and the relationship between the polar coordinates system (r, θ, ϕ) and the rectangular coordinates system (x, y, z) is given by

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad \text{and} \quad z = r\cos\theta.$$

Because $Y_1^0 \propto z$, Y_1^0 directly represents the p_z orbital (i.e., $Y_{pz} = Y_1^0$). On the other hand, the p_x orbital and the p_y orbital are obtained by taking the real linear combinations of $Y_1^{\pm 1}$. Express the spherical harmonics Y_{px} and Y_{py} of the p_x and p_y orbitals using $Y_1^{\pm 1}$. Here, the normalization is not needed.

3. Figure 4.1 shows $R_{nl}(r)$ on an arbitrary scale. Specify the corresponding orbital from 1s, 2s, 2p, 3s, 3p or 3d orbitals for each of Figures 4.1 (i) to (vi), respectively.

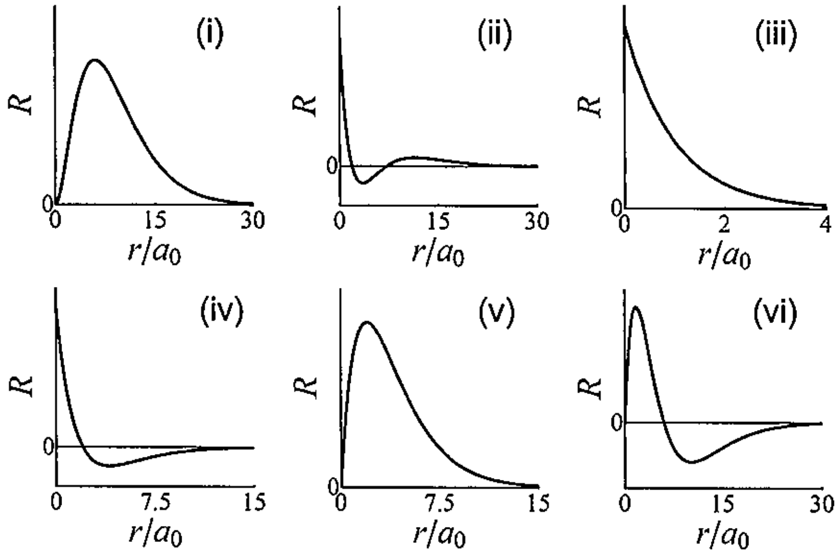


Figure 4.1

4. Figure 4.2 shows distributions of the sign of the values for some of $Y_l^m(\theta, \phi)$ being real functions, where the contrasting density represents the absolute magnitude and the dotted line represents the node, respectively. Specify the corresponding orbital from s, p or d orbitals for each of Figures 4.2 (A) to (F), respectively.

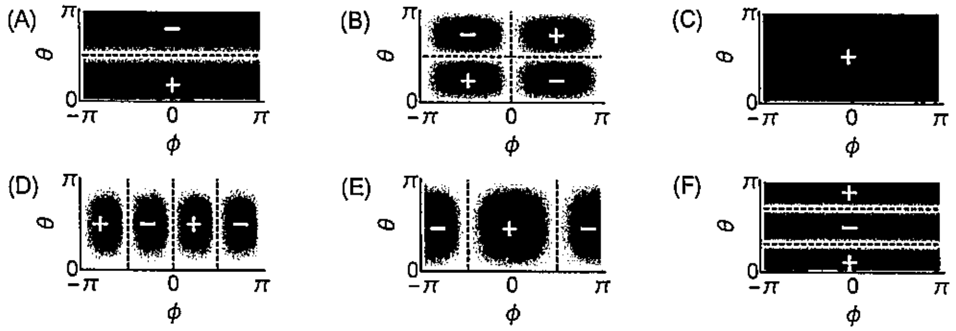


Figure 4.2

II. Answer the following questions on the electronic states of a He atom.

1. How do energies of the individual orbitals of a He^+ ion differ from those of a hydrogen atom? Provide the answer with the reason.
2. A He atom is formed by adding one electron to a He^+ ion. How do energies of the individual orbitals of the He atom differ from those of the He^+ ion? Provide the answer with the reason.
3. The following Equations (1) to (4) are wavefunctions $\psi(1,2)$, which represent some of the electronic states in the ground state or in the excited states of a He atom with the atomic orbital approximation.

$$\psi(1,2) = [\phi_{1s}(1)\phi_{2s}(2) + \phi_{2s}(1)\phi_{1s}(2)]\,[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\,/\,2 \qquad (1)$$

$$\psi(1,2) = [\phi_{1s}(1)\phi_{2s}(2) + \phi_{2s}(1)\phi_{1s}(2)]\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\,/\,2 \qquad (2)$$

$$\psi(1,2) = [\phi_{1s}(1)\phi_{2s}(2) - \phi_{2s}(1)\phi_{1s}(2)]\,[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\,/\,2 \qquad (3)$$

$$\psi(1,2) = \phi_{1s}(1)\phi_{1s}(2)\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\,/\sqrt{2} \qquad (4)$$

Here, ϕ_{1s} and ϕ_{2s} represent the 1s and 2s orbitals, respectively, and α and β represent the different electronic spin states to each other. The 1 and 2 in the wavefunctions are the indices of the electronic coordinates. Answer the following questions.

   (a) Which of Equations (1) to (4) is inappropriate as a wavefunction describing an electronic state of a He atom? Provide the answer with the reason.

   (b) Which of Equations (1) to (4) is the wavefuction describing a spin-singlet excited state?

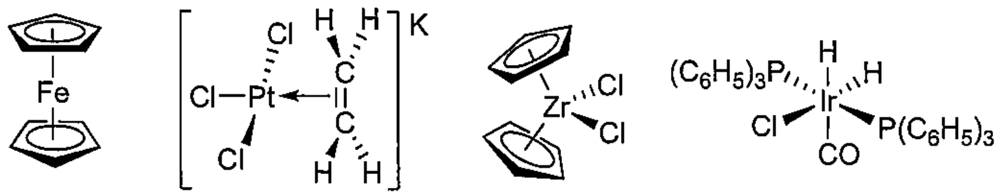
   (c) Which of Equations (1) to (4) is the wavefuction describing a spin-triplet excited state?

4. Which of the electronic states in Question II. 3 has lower energy, the spin-singlet excited state or the spin-triplet excited state? Also, explain the reason based on the properties of $\psi(1,2)$.

Problem 5 Inorganic Chemistry

Answer the following questions about the transition metal complexes. Here, the atomic numbers of Cr, Fe, Ni, Zr, Ir, and Pt are 24, 26, 28, 40, 77, and 78, respectively.

I. Give the numbers of valence electrons for the complexes (**A**) to (**D**) shown in Figure 5.1.



(A) **(B)** **(C)** **(D)**

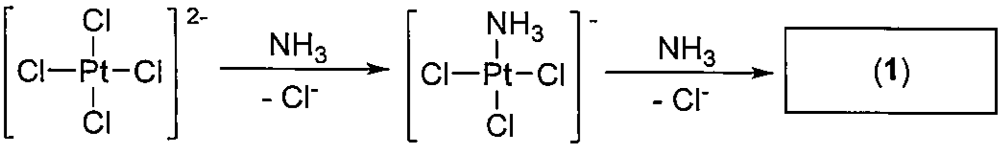
Figure 5.1

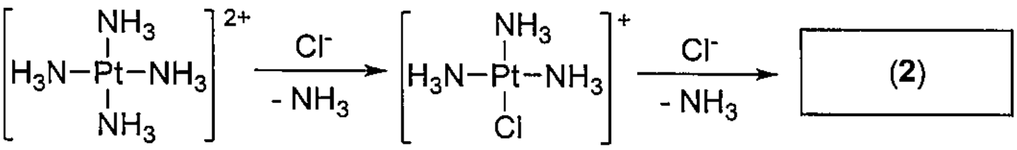
II. Fill in the blanks $\boxed{\text{(i)}}$ to $\boxed{\text{(viii)}}$ with appropriate terms, symbols, and numerals. For the blanks $\boxed{\text{(i)}}$ and $\boxed{\text{(ii)}}$, choose all appropriate terms from the following: d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}. Fill in the blanks $\boxed{\text{(v)}}$ and $\boxed{\text{(vi)}}$ with appropriate numerals. Also, choose either "longer" or "shorter" to fill in the blank $\boxed{\text{(vii)}}$.

In a transition metal complex having an octahedral structure, the five d orbitals split into two subsets. Among the five d orbitals, the $\boxed{\text{(i)}}$ orbitals lie lower in energy than the $\boxed{\text{(ii)}}$ orbitals. Based on the character table in group theory, the former orbitals are defined to have $\boxed{\text{(iii)}}$ symmetry, whereas the latter orbitals are defined to have $\boxed{\text{(iv)}}$ symmetry. In considering the electronic configuration of the complex $[Cr(OH_2)_6]^{2+}$, the number of electrons in the orbitals having $\boxed{\text{(iii)}}$ symmetry is $\boxed{\text{(v)}}$, whereas that of electrons in the orbitals having $\boxed{\text{(iv)}}$ symmetry is $\boxed{\text{(vi)}}$. The bond distance of Cr-(OH_2) (axial) is $\boxed{\text{(vii)}}$ than that of Cr-(OH_2) (equatorial). This type of geometrical distortion is called as $\boxed{\text{(viii)}}$ distortion.

III. The color of the aqueous solution of the complex $[Ni(OH_2)_6]Cl_2$ is green, whereas that of the complex $[Ni(NH_3)_6]Cl_2$ is blue-purple. Explain the reason why these complexes show different colors depending on the ligands on the metal.

IV. The following two synthetic routes give geometrical isomers of $[PtCl_2(NH_3)_2]$, either of which is an anticancer agent cisplatin, [*cis*-$PtCl_2(NH_3)_2$]. Draw the molecular structure of the products (1) and (2) with indicating the geometrical structure. Also, explain the reason why two geometrical isomers are formed in these synthetic routes.

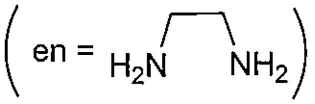




V. Fill in the blanks $\boxed{\text{(a)}}$ and $\boxed{\text{(b)}}$ in the following sentences with appropriate terms.

In general, a complex containing multidentate ligands is thermodynamically more stable than a complex containing similar monodentate ligands with the same coordination number. For instance, the formation of the complex $[Ni(en)_3]^{2+}$ is preferred in the following reaction. This is because of the $\boxed{\text{(a)}}$ effect and the effect is mainly attributed to an increase of $\boxed{\text{(b)}}$.

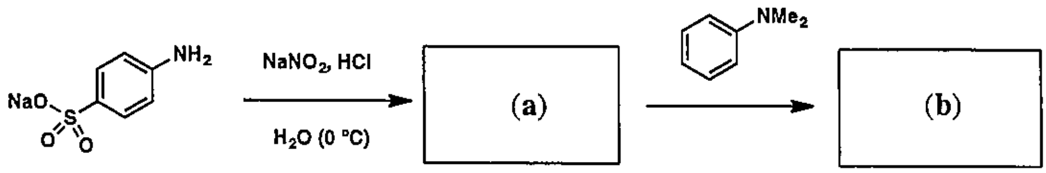
$$[Ni(NH_3)_6]^{2+}\,(aq) + 3\ en\,(aq) \rightleftharpoons [Ni(en)_3]^{2+}\,(aq) + 6\ NH_3\,(aq)$$



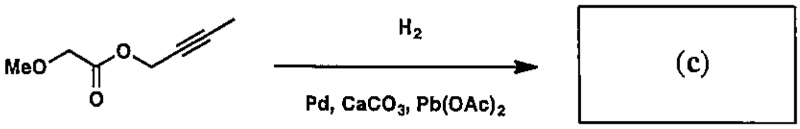
Problem 6 Organic Chemistry

I. Draw the structural formula for the major products (**a**) to (**i**) of the following reactions. Show clearly the stereochemical structure for compound (**f**).

(1)



(2)



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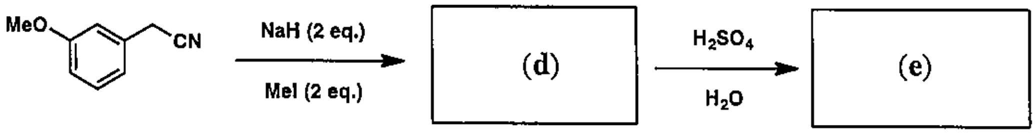
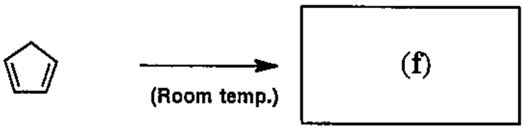


(4)



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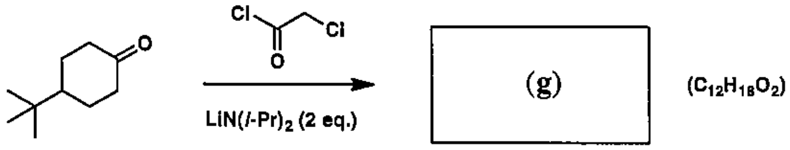

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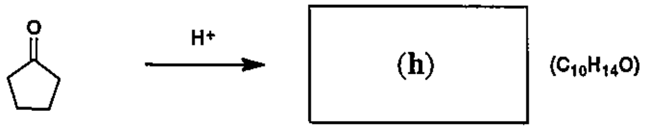

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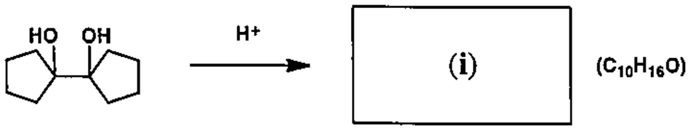
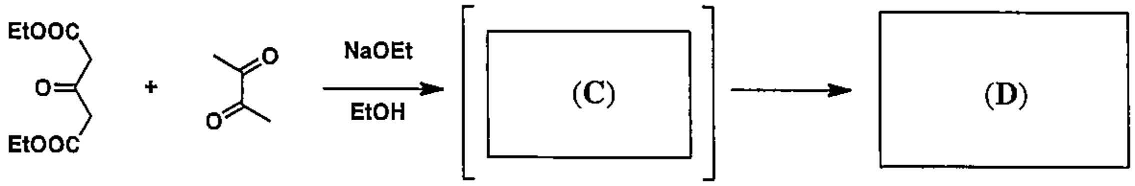
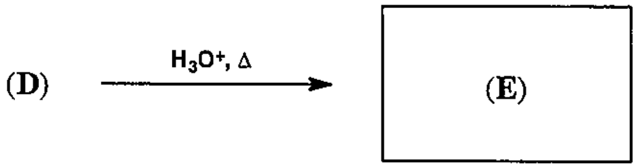


II. Answer the following questions for the reactions below.

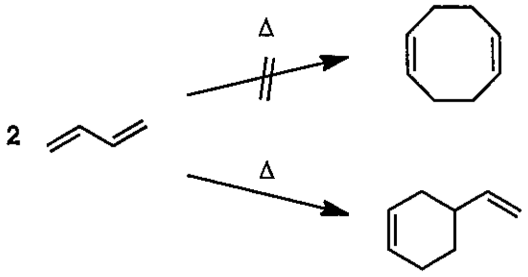


(A) (B) ($C_{22}H_{30}O_{10}$)

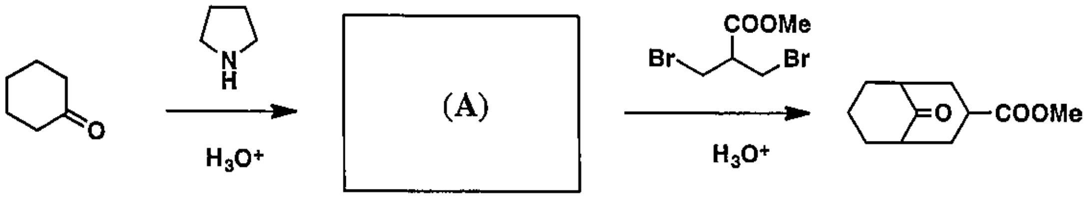


1. Compound (**A**) reacts with compound (**B**) to produce compound (**D**). The product (**D**) is produced by the conjugate addition of compound (**A**) to the intermediate (**C**). Draw the structural formula of the intermediate (**C**) and the product (**D**).
2. Compound (**E**) is produced by acid hydrolysis and decarboxylation of compound (**D**). Draw the structural formula of the product (**E**).

III. The thermal [4+2] cyclization reaction is allowed, but the thermal [4+4] cyclization reaction is forbidden for butadiene. Explain this reason using the molecular orbital.



IV. Draw the structure of compound (**A**), and show the reaction mechanism from (**A**) to (**B**).



(**B**)

Problem 7 Analytical Chemistry

Answer the following questions on the biochemical analyses in blood test.

I. Concentration of potassium ion (K^+) is measured using the potassium ion sensor based on the ion-selective electrode (ISE) method.

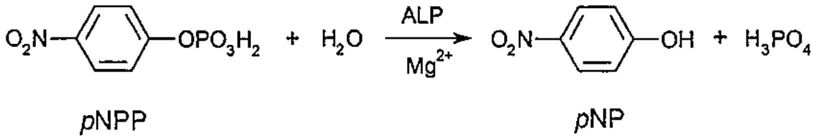
1. Explain the principle of the quantitative analysis using the ISE method.
2. Express the electric potential at the potassium ion sensor, E, using the Nernst equation. Here, the standard electrode potential, the gas constant, the absolute temperature, the Faraday constant, and the concentration of potassium ion are given as E_0, R, T, F, and $[K^+]$, respectively.
3. When the potassium ion sensor was exposed to the solution containing 1.0×10^{-3} mol L^{-1} of K^+, it exhibited the electric potential of +100 mV. This sensor exhibited +141.3 mV when exposed to a blood sample. Answer the concentration of K^+ in the blood sample with one significant digit. Here, the measurement was conducted at 25°C. Use the following values if necessary.

Gas constant R: 8.31 J K^{-1} mol^{-1}, Faraday constant F: 9.65×10^4 C mol^{-1}
$\log_{10}2 = 0.30$, $\log_{10}3 = 0.48$, $\log_{10}7 = 0.85$, $\log_e 10 = 2.3$

II. In the analysis of urea concentration, other components in the blood sample should be removed by using the high performance liquid chromatography (HPLC).

1. The chromatography with octadecyl-silica (ODS) columns is used for the urea analysis. To which method is this chromatography categorized? Choose one from the following.
   a) Normal-phase chromatography
   b) Reversed-phase chromatography
   c) Size-exclusion chromatography
   d) Ion-exchange chromatography
2. Explain the principle of the separation method using the chromatography with ODS columns.

III. Alkaline phosphatase (ALP) is an enzyme which hydrolyses organic phosphate esters in alkaline conditions. *p*-Nitrophenylphosphate (*p*NPP) is used for the concentration analysis of ALP, where *p*NPP is hydrolyzed into *p*-nitrophenol (*p*NP) and inorganic phosphate as follows.



1. *p*NP shows yellow color in alkaline conditions, while *p*NP is almost colorless in acidic conditions. Explain the reason why *p*NP shows yellow color in alkaline conditions.
2. The concentration of *p*NP is measured using the absorption spectrometry. Explain the principle of this quantitative analysis.
3. ALP was added to the cuvette (optical path-length: 1.0 cm) filled with 1.0 mL of the alkaline buffer containing 5.0×10^{-6} mol of *p*NPP in order to make the final concentration of ALP 1.0×10^{-7} mol L^{-1}. After 100 seconds, the absorbance at 405 nm was 0.18. Answer the concentration of the produced *p*NP with two significant digits. Here, the molar absorptivity of *p*NP at 405 nm is 1.8×10^{4} L mol^{-1} cm^{-1}, and the change in the volume of the alkaline buffer after the addition of ALP is assumed to be negligible.
4. When 1.0×10^{-5} L of the blood sample was added to the cuvette (optical path-length: 1.0 cm) filled with 1.0 mL of the alkaline buffer containing 5.0×10^{-6} mol of *p*NPP, the absorbance after 100 seconds was 9.0×10^{-3}. Answer the concentration of ALP in the blood sample with two significant digits, assuming that the concentration of *p*NP in the cuvette is proportional to that of ALP.