

**2019**  
**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.
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Write your examinee number in the space provided above.

## Problem 1 Basic Physical Chemistry

- I. A piston-cylinder device is filled with 1 mol of an ideal gas as shown in Figure 1.1. This device is a closed system and changes reversibly. Answer the following questions. Here for the gas,  $p$  is pressure,  $V$  is volume, and  $T$  is temperature. The gas constant  $R$  is  $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ . Use the following values if necessary.  $\ln 2 = 0.693$ ,  $\ln 3 = 1.10$ ,  $\ln 5 = 1.61$ ,  $\ln 10 = 2.30$

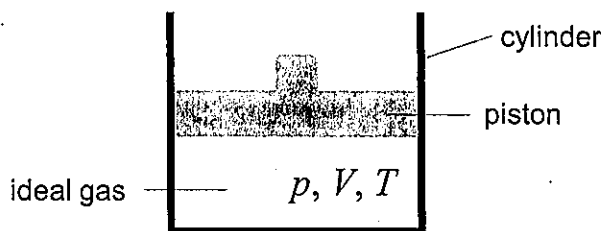


Figure 1.1

1. Show the ideal gas equation. Also, when  $V = 100 \text{ L}$  and  $T = 300 \text{ K}$ , calculate the pressure  $p$  (kPa). Here,  $1 \text{ kPa} = 1 \text{ J L}^{-1}$ .
  2. When the pressure  $p$  increases from  $200 \text{ kPa}$  to  $400 \text{ kPa}$  at  $T = 300 \text{ K}$ , calculate the change in work  $\Delta W$  (kJ) done on the ideal gas and the change in entropy  $\Delta S$  ( $\text{J K}^{-1} \text{ mol}^{-1}$ ).
  3. The heat capacity at constant pressure is  $C_p$  and the heat capacity at constant volume is  $C_v$ . Derive the relation between  $C_p$  and  $C_v$ .
  4. When the temperature increases from  $T_i$  to  $T_f$ , the changes in entropy at constant pressure and at constant volume are  $\Delta S_p$  and  $\Delta S_v$ , respectively. Express  $\Delta S_p / \Delta S_v$  using  $C_p$  and  $C_v$ . Also, show the steps leading to the answer.
- II. A particle is confined to a one-dimensional infinite potential well with a length of  $L$  as shown in Figure 1.2. Answer the following questions. Here,  $U$  is potential energy,  $\psi(x)$  is the wavefunction,  $h$  is Planck's constant, and  $\hbar = h / 2\pi$ .

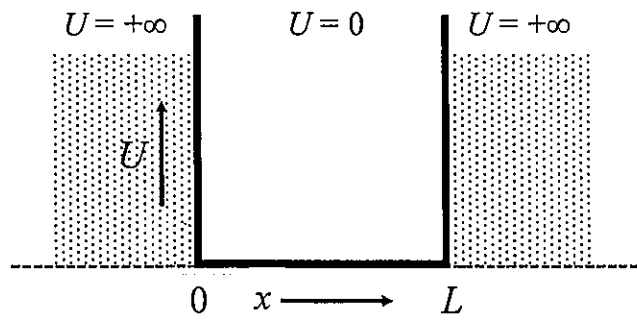


Figure 1.2

1. Express the total energy  $E$  of the particle, using the mass of the particle  $m$  and the momentum of the particle  $p$ .
2. Express the Schrödinger equation  $\hat{H}\psi(x) = E\psi(x)$  using  $m$ ,  $\hbar$ ,  $x$ , and  $\psi(x)$ . Here,  $\hat{H}$  is the Hamiltonian operator, and  $\hat{p} = -i\hbar \frac{d}{dx}$  is the momentum operator.
3. The eigenfunction  $\psi_n(x) = C \sin \frac{n\pi x}{L}$  is obtained by solving the Schrödinger equation. Here,  $n$  is the quantum number ( $n = 1, 2, 3, \dots$ ), and  $C$  is a constant. Sketch the graph of the eigenfunction  $\psi_1(x)$  when the quantum number  $n = 1$ . Also, when the potential energy barrier is finite, sketch its eigenfunction  $\psi_1(x)$  and explain how the eigenfunction  $\psi_1(x)$  differs from that of the infinite potential well.

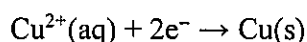
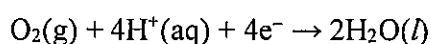
## Problem 2 Basic Inorganic Chemistry

I. Give the oxidation number of the atoms in the underlined part of the following substances.



II. When hydrogen peroxide is reacted with potassium permanganate under neutral conditions, write the equations for the half-reactions and the overall reaction.

III. Answer the following questions on an oxidation reaction of copper based on the following half-reactions.



1. Write the equation for the overall reaction.
2. Briefly explain the relationship between the oxidation reaction of copper and pH.
3. Briefly explain the reason why the described reaction does not actually occur for a roof made of copper.

IV. Answer the following questions on nitrogen oxides.

1. Draw the energy levels of the molecular orbitals in NO along with the electron configuration.
2. Give the bond orders of NO and NO<sup>+</sup>.
3. Briefly explain the magnetic properties of NO and NO<sup>+</sup>.

V. Answer the following questions on halides.

1. Arrange HF, HCl, HBr, and HI in descending order of boiling point, and briefly explain the reason.
2. Arrange HF, HCl, HBr, and HI in ascending order of pH in the aqueous solution at the same concentration, and briefly explain the reason.

VI. Answer the following questions on substituted oxoacids.

1. Briefly explain the reason why the acidity of fluorosulfuric acid O<sub>2</sub>SF(OH) is stronger than that of sulfuric acid O<sub>2</sub>S(OH)<sub>2</sub>.

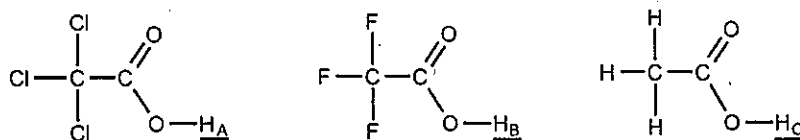
2. Briefly explain the reason why the acidity of sulfamic acid  $\text{O}_2\text{S}(\text{NH}_2)(\text{OH})$  is weaker than that of sulfuric acid  $\text{O}_2\text{S}(\text{OH})_2$ .

### Problem 3 Basic Organic Chemistry

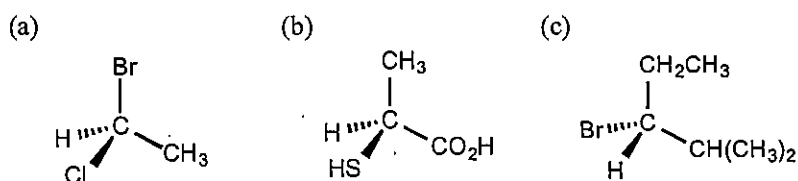
I. Draw the structural formulas of the following common organic solvents.

- (a) acetone      (b) diethyl ether      (c) tetrahydrofuran  
(d) dimethyl sulfoxide      (e) *N,N*-dimethylformamide

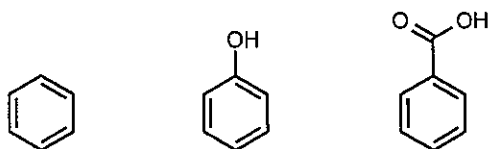
II. Arrange the underlined three hydrogen atoms ( $H_A$ ,  $H_B$ ,  $H_C$ ) in order of decreasing  $pK_a$ . Also, explain the reason.



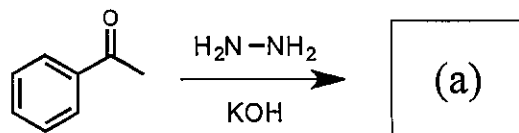
III. Assign *R/S* configurations to the chiral centers of the following three molecules.

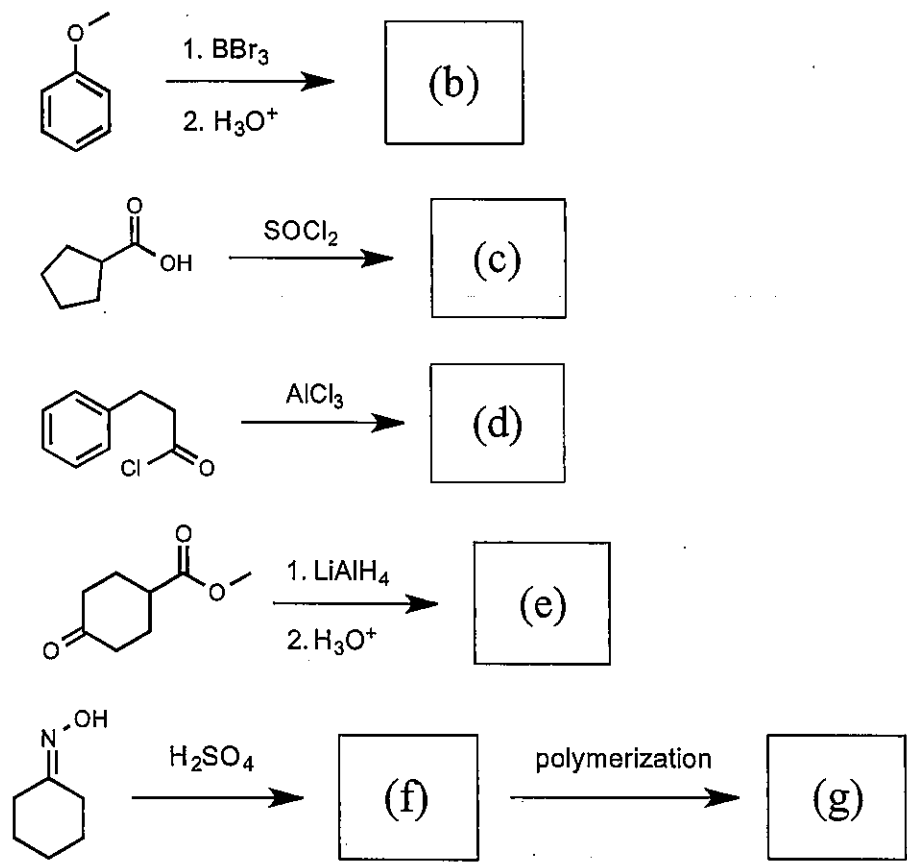


IV. Arrange the following three molecules in order of decreasing reactivity toward electrophilic aromatic substitution. Also, explain the reason.

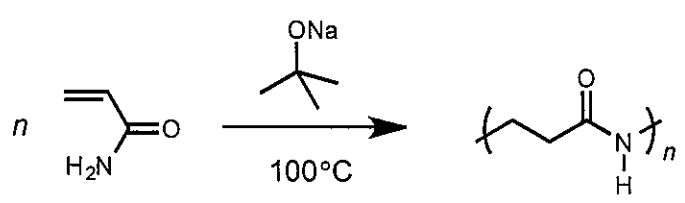


V. Draw the structural formulas of the major products (a)–(g) in the following reactions.





VI. Polymerization of acrylamide in the presence of sodium *tert*-butoxide at 100 °C gave poly( $\beta$ -alanine). Show the reaction mechanism.



## Problem 4 Physical Chemistry

Consider the following reactions of an enzyme in an aqueous solution.



$k_1, k_{-1}, k_{11}$ : the rate constants for the respective reactions

Here, EH is the protonated enzyme, S is the substrate, and P is the product. Assume that the enzyme-substrate complex ESH is immediately protonated or deprotonated so that it is in an equilibrium state according to the following equations.



$K_{a1}, K_{a2}$ : the equilibrium constants

Answer the following questions.

- I. Express the equilibrium constants  $K_{a1}$  and  $K_{a2}$  by using  $[\text{H}^+]$ ,  $[\text{ES}^-]$ ,  $[\text{ESH}]$ , and  $[\text{ESH}_2^+]$  ( $\text{mol L}^{-1}$ ). Here, the activity coefficients are assumed to be unity.
- II. Express the production rate  $\frac{d[\text{ESH}]}{dt}$  of ESH by using  $[\text{EH}]$ ,  $[\text{S}]$ ,  $[\text{ESH}]$ ,  $k_1$ ,  $k_{-1}$ , and  $k_{11}$ .
- III. The total enzyme concentration  $[\text{E}]_T$  ( $\text{mol L}^{-1}$ ) is given by  $[\text{E}]_T = [\text{EH}] + [\text{ESH}_2^+] + [\text{ESH}] + [\text{ES}^-]$ . Provided  $f = \left( \frac{[\text{H}^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[\text{H}^+]} \right)$ , show  $[\text{E}]_T = [\text{EH}] + f[\text{ESH}]$ .
- IV. The time dependence of the concentration  $[\text{P}]$  shown in Figure 4.1 was observed after the substrate S was added at time  $t = 0$  to an aqueous solution of the enzyme. Sketch the graph of the time dependence of the concentration  $[\text{ESH}]$  in the same time window as that in Figure 4.1.



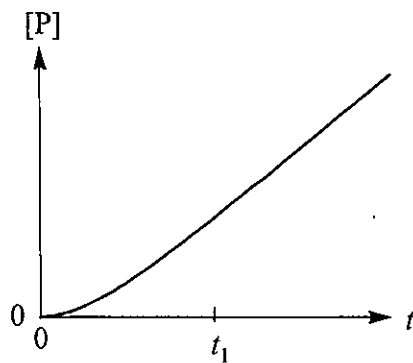


Figure 4.1

V. Let us define  $v$  as the production rate  $\frac{d[P]}{dt}$  of the product P at  $t > t_1$  in Figure 4.1.

Provided  $K_M = \frac{k_{-1} + k_{II}}{k_1}$ , show  $v = \frac{k_{II}[E]_T[S]}{K_M + [S]f}$ .

VI. Choose the correct curve from (a)-(f) in Figure 4.2 showing the dependence of the rate  $v$  on the concentration [S]. Also express the maximum value of  $v$  ( $V_{max}$ ) by using  $[E]_T$ ,  $k_{II}$ , and  $f$ .

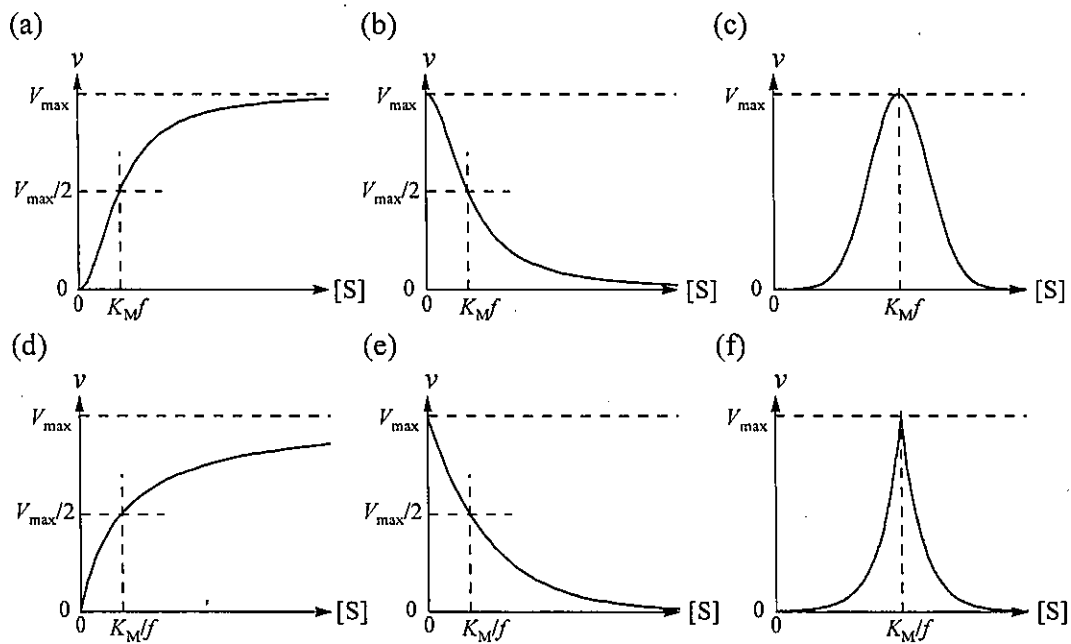


Figure 4.2

VII. Answer the following questions on the pH dependence of  $V_{\max}$ .

1. When  $\text{pH} = x$ , express  $V_{\max}$  as a function of  $x$  by using  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$ .
2. Consider the case of  $\text{p}K_{\text{a}1} = 3.0$  and  $\text{p}K_{\text{a}2} = 9.0$ . When  $V_{\max} = 5.0 \mu\text{mol L}^{-1} \text{s}^{-1}$  at  $\text{pH} = 3.0$ , sketch the graph of  $V_{\max}$  as a function of  $\text{pH}$ .

VIII. In many cases, an enzyme is active only in a specific pH range. Discuss the reason.

## Problem 5 Inorganic Chemistry

Answer the following questions regarding the inorganic compounds with the rock-salt structure (MX, Figure 5.1), where M is a metallic element, X is either a chalcogen or halogen element, and  $a$  is the lattice parameter. In reaction formulas, mark a solid with (s), a liquid with (l), a gas with (g), and an aqueous solution with (aq). If necessary, use the following atomic numbers: Ca, 20; Ti, 22; Mn, 25; Ni, 28.

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

(i) enthalpy,  $\Delta_L H^\circ$ , is the standard molar enthalpy change accompanying the formation of a gas of ions from the solid. Because this formation is an (ii) reaction,  $\Delta_L H^\circ$  is always positive. The most stable structure of the compounds under the prevailing conditions is the structure with the greatest  $\Delta_L H^\circ$  if the (iii) term is neglected. If the value of  $\Delta_L H^\circ$  calculated on the assumption that the lattice of MX is formed by the Coulomb interaction between the ions of M and X is in good agreement with the measured value, then it is considered that the MX is a type of (iv) compound. A discrepancy indicates a degree of the contribution of (v) bonding.

As a general trend, a smaller ionic radius of M results in a higher  $\Delta_L H^\circ$ . In the metal monoxide of MO (X = O), although  $\text{Ti}^{2+}$  has a large ionic radius compared with  $\text{Mn}^{2+}$ , the  $\Delta_L H^\circ$  of TiO is higher than that of MnO. Given that the ligand-field splitting parameter in an octahedral crystal field is  $\Delta_o$ , the ligand-field stabilization energy is estimated to be (vi) for TiO and (vii) for MnO. It follows that the greater  $\Delta_L H^\circ$  of TiO arises from (viii).

The Born-Mayer equation is used to estimate  $\Delta_L H^\circ$  for an ionic solid. For NaCl and MgO with almost the same  $a$ , the  $\Delta_L H^\circ$  of MgO is almost (ix) times that of NaCl. With increasing atomic number of X from F, Cl, Br, to I, a discrepancy between the experimental  $\Delta_L H^\circ$  and the value calculated from the Born-Mayer equation is (x). This discrepancy stems from a high (xi) of X.

In general, the alkali metal halides are soluble in water while LiF has a low (xii) in water. This can be traced to the fact that the high  $\Delta_L H^\circ$  due to the small ionic radius of  $\text{Li}^+$  is not offset by the enthalpy of (xiii).

II. Give the reaction formula of sodium hydride NaH(s) with water  $\text{H}_2\text{O}(l)$ . If NaH(s) reacts with water and burns, such fires are difficult to extinguish. Give a practical and effective method for extinguishing a fire caused by NaH(s), and briefly explain the reason.

III. Answer the following questions regarding metal monoxides (X = O).

1. In a simple ionic model, CaO can be regarded as being composed of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ . Give the electron configurations of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ .
2. In the electronic band structure of insulating CaO (Figure 5.2), write the predominant element and orbitals forming the electronic states near the valence band maximum and those forming the electronic states near the conduction band minimum.
3. Give the electron configuration of  $\text{Ti}^{2+}$  in TiO. In addition, briefly explain the reason why TiO shows metallic conduction.
4. The stoichiometric NiO is an insulator. Write the predominant element and orbitals forming the electronic states near the valence band maximum and those forming the electronic states near the conduction band minimum.
5. In general, NiO is a nonstoichiometric compound and its composition is expressed as  $\text{Ni}_{1-x}\text{O}$ . In the compound with  $\text{Ni}_{1-x}\text{O}$ , briefly explain the influences of ① Ni vacancies on the electronic band structure and of ② Ni vacancies on the electrical conductivity.

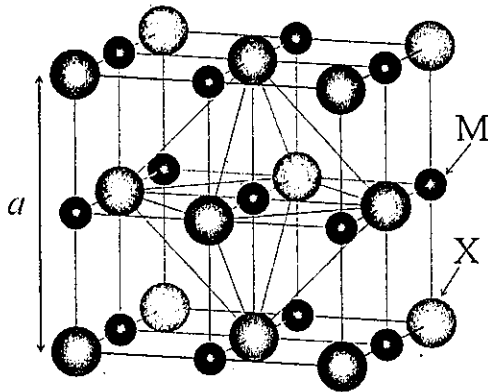


Figure 5.1

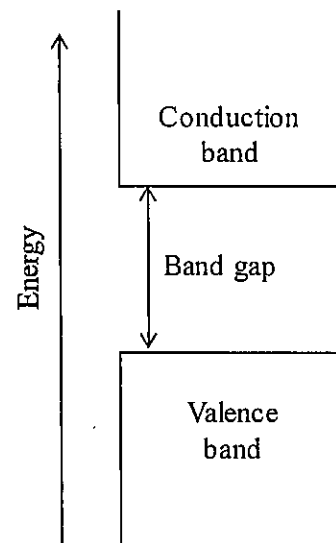
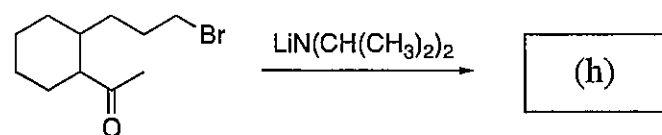
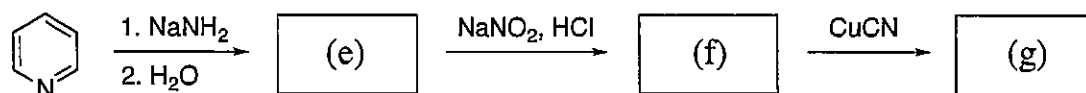
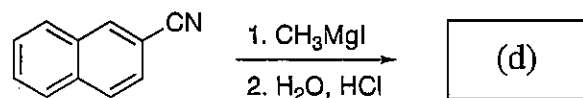
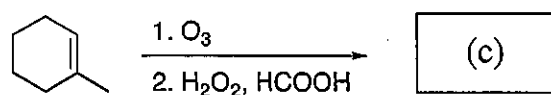
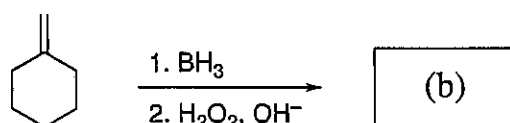
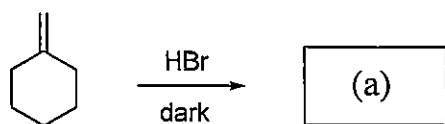


Figure 5.2

## Problem 6 Organic Chemistry

I. Draw the structural formulas of the major products (a)–(h) in the following reactions.

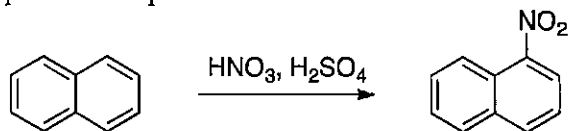


II. Answer the following questions on acidity and basicity.

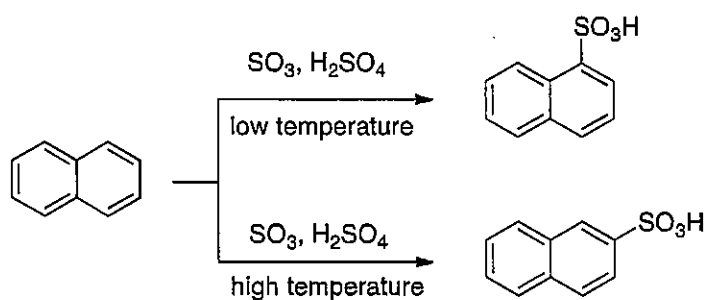
1. Arrange phenol, *p*-nitrophenol, and *m*-nitrophenol in descending order of acidity. Also, explain the reason.
2. Which is more basic, pyridine or pyrrole? Provide the answer with the reason.
3. Which is more basic, 1,8-bis(dimethylamino)naphthalene or *N,N*-dimethylaniline? Provide the answer with the reason.

III. Answer the following questions on substitution reactions of naphthalene.

1. By nitration of naphthalene, 1-nitronaphthalene is obtained as the major product. Explain the reason.

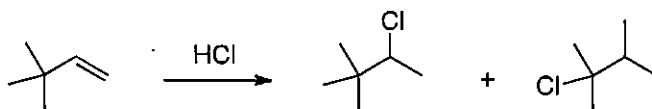


2. By sulfonation of naphthalene, 1-naphthalene sulfonic acid is obtained as the major product at low temperature, and 2-naphthalene sulfonic acid is obtained as the major product at high temperature. Explain the reason.

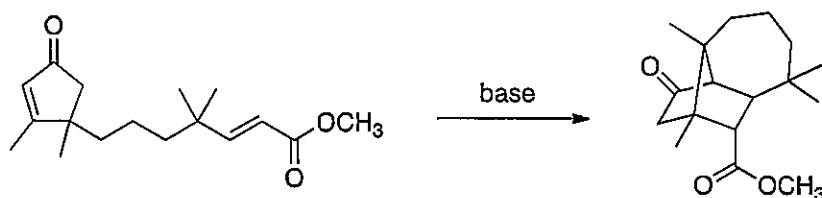


IV. Show the mechanisms of the following reactions.

1.



2.



## Problem 7 Analytical Chemistry

Answer the following questions. Here, the temperature  $T$  is 298 K. Use the following values if necessary:

gas constant  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ , Faraday constant  $F = 9.65 \times 10^4 \text{ C mol}^{-1}$ , and  $\ln 10 = 2.30$ .

I. It was attempted to titrate a solution of Fe(II) salt with a solution of Ce(IV) salt. In this experiment, the state of titration was monitored by a potentiometer without using an indicator. Two beakers were prepared, and the apparatus as shown in Figure 7.1 was assembled. However, the potential could not be measured correctly in the apparatus. When a device was added to the apparatus, measurement became possible. Answer the following questions. Here, it is not necessary to consider reactions except for the following half-reactions.

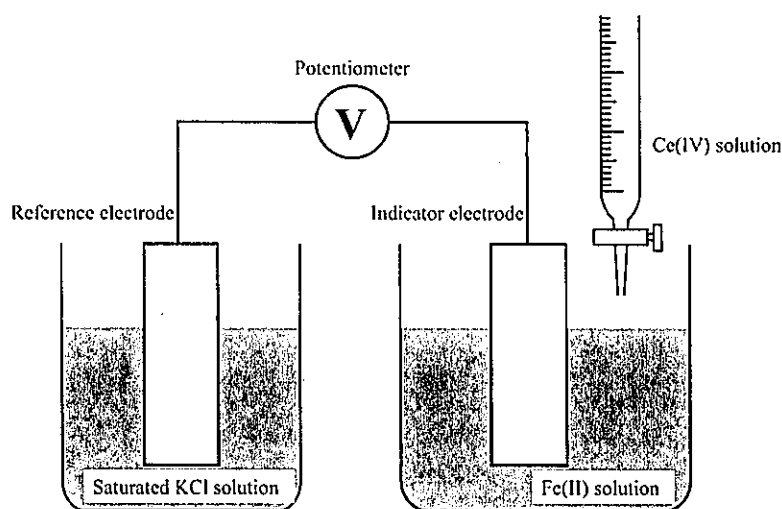
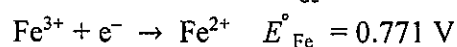
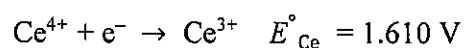


Figure 7.1

1. Give the name of the device added to the apparatus. Also briefly explain why it is needed.
2. What is the name of this type of titration?
3. Describe the equation for the reaction that proceeds in the titration.

4. The equilibrium constant of the above reaction is  $K$ . Give the value of  $\log_{10}K$ . Also show the steps leading to the answer.
5. Calculate the potential at the equivalent point of the above titration. Also show the steps leading to the answer.

II. Sodium dodecyl sulfate (SDS) polyacrylamide gel electrophoresis of immunoglobulin (IgG) was performed. Answer the following questions.

1. It was expected that bands would appear at positions of  $50 \text{ kg mol}^{-1}$  and  $25 \text{ kg mol}^{-1}$ . As a result of the experiment, however, only a single band was observed at a position greater than  $50 \text{ kg mol}^{-1}$ . Describe the reason. Also give the method for obtaining the expected result, together with the name of the reagent commonly used for the method.
2. The following four kinds of oligopeptides were separated by electrophoresis using a polyacrylamide gel without SDS having a pH gradient in which the starting point was alkaline and the end point was acidic. Arrange the oligopeptides ①–④ in descending order of the electrophoresis distance. Also explain the reason why the electrophoresis distance is different using the words of  $pK_a$  and pH. The molecular weight of the oligopeptide is taken not to affect the electrophoresis distance.

- ① Arg-Glu-Lys-Ala-Asp-Gly
- ② Ala-Lys-His-Gly-Ser-Lys
- ③ Arg-Lys-Ala-Arg-Gly-Arg
- ④ Glu-Gly-Ala-Asp-Glu-Asp

III. Answer the following questions.

1. A solid surface having microscopic pores with a diameter of 10 nm and a depth of 20 nm was observed with an atomic force microscope (AFM). The diameter and the depth of the pores were evaluated from the obtained data. However, the values were smaller than the actual values. Explain the reason. Also give a way to obtain more accurate values.
2. A fine powder with a uniform particle size was analyzed by X-ray diffraction. Compared to a single-crystal substrate of the same material, the peak was broad. Explain the reason.