2012
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. Answer all three problems in the problem booklet.

4. You are given three 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 3) 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

I. Answer the following questions on the Daniell cell:

$Zn \mid Zn^{2+}$ (1.00 mol L^{-1}) $\|$ Cu^{2+} (0.100 mol L^{-1}) $\mid Cu$.

Take the activity coefficient = 1, the change in the standard Gibbs energy according to the cell reaction = 200 kJ mol^{-1}, the Faraday constant = 9.65×10^4 C mol^{-1}, and the gas constant = 8.31 J K^{-1} mol^{-1}. Standard conditions are 25°C, 1 bar.

1. Write the reactions in each electrode of the cell.
2. Which electrode, Cu or Zn, is the anode in the cell? Explain the reason briefly.
3. Calculate the electromotive force of the cell at 25°C. Use the following values if necessary.

   ln 2 = 0.693, ln 3 = 1.10, ln 5 = 1.61

II. A buffer solution of pH = 4.7 is prepared by mixing acetic acid and sodium acetate. Answer the following questions.

1. The concentration of hydrogen ion in a 1.0×10^{-2} mol L^{-1} acetic acid aqueous solution was 7.2×10^{-4} mol L^{-1}. Calculate the acid dissociation constant K_a for this case.
2. Calculate the concentration of hydroxide ion in a 5.0×10^{-2} mol L^{-1} sodium acetate aqueous solution, by using the value of K_a calculated above. Assume that sodium acetate is completely ionized.
3. Calculate the volume mixing ratio of the two aqueous solutions prepared above, needed to make a buffer solution of pH = 4.7. Use $10^{-4.7} = 2.0 \times 10^{-5}$.

III. Various analyses were performed on a sample composed of a pure metal element. Answer the following questions.

1. Figure 1.1 shows an X-ray diffraction pattern obtained for the sample. The wavelength of the X-ray was 0.154 nm. Explain in about 50 words the reason for the appearance of diffraction peaks in the X-ray diffraction analysis. In addition, calculate the lattice spacing d which corresponds to the peak Q with $2\theta = 78.2°$. Here, $\sin 39.1° = 0.631$.

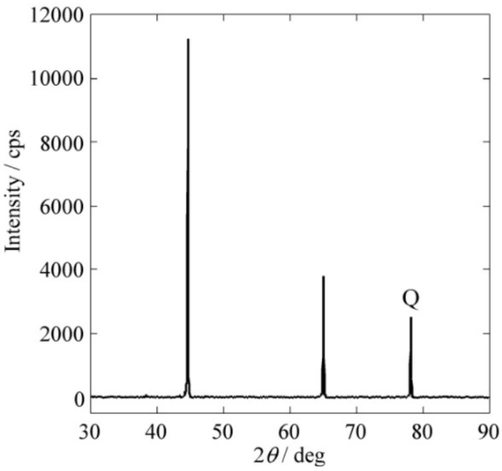


Fig. 1.1

2. Analysis of the results shown in Fig. 1.1 revealed that the sample has a face-centered cubic lattice. Draw an image of the unit cell of the face-centered cubic lattice. Moreover, indicate the number of atoms included in the unit cell.
3. The density of the sample was determined to be 2.70×10^{3} kg m^{-3}. Furthermore, the lattice constant of the sample was determined to be 0.405 nm through analysis of the results shown in Fig. 1.1. Calculate the molar mass [g mol^{-1}] of the element of the sample. Avogadro's number is 6.02×10^{23} mol^{-1}.
4. X-ray fluorescence analysis is one of the nondestructive analysis methods that can identify the constituent element of the sample. Describe in about 50 words the principle of the method.
5. A small piece cut from the sample was slowly heated in vacuum up to 700°C in a differential thermal analyzer. In this measurement, an endothermic peak was observed at ~660°C. After cooling, the sample was confirmed melted during heating. Explain in about 30 words the reason why an endothermic process occurs when the solid-state crystal melts.
6. The powder ground down from the sample burned intensely during heating in air and resulted in a white oxide. The density of the oxide was 3.97×10^{3} kg m^{-3}. Explain the reason why the density increased after oxidation.

Problem 2

I. Answer the following questions on the heat capacities of gases. Here, C_P is the heat capacity at constant pressure, C_V heat capacity at constant volume, P pressure, T temperature, V volume, U internal energy, S entropy, H enthalpy, A Helmholtz energy, G Gibbs energy, a, b constants and R gas constant. If needed, use the relations in Table 2.1.

1. Show that $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ using

$$C_P - C_V = \left\{P + \left(\frac{\partial U}{\partial V}\right)_T\right\}\left(\frac{\partial V}{\partial T}\right)_P$$ and $A = U - TS$.

2. One mole of a nonideal gas obeys the van der Waals equation, $\left(P + \frac{\mathrm{a}}{V^2}\right)(V - \mathrm{b}) = \mathrm{R}T$.

   Derive an equation for $C_P - C_V$ in terms of a, b, R, V, T, and show that $C_P - C_V = \mathrm{R}$ in the ideal gas limit.

Table 2.1

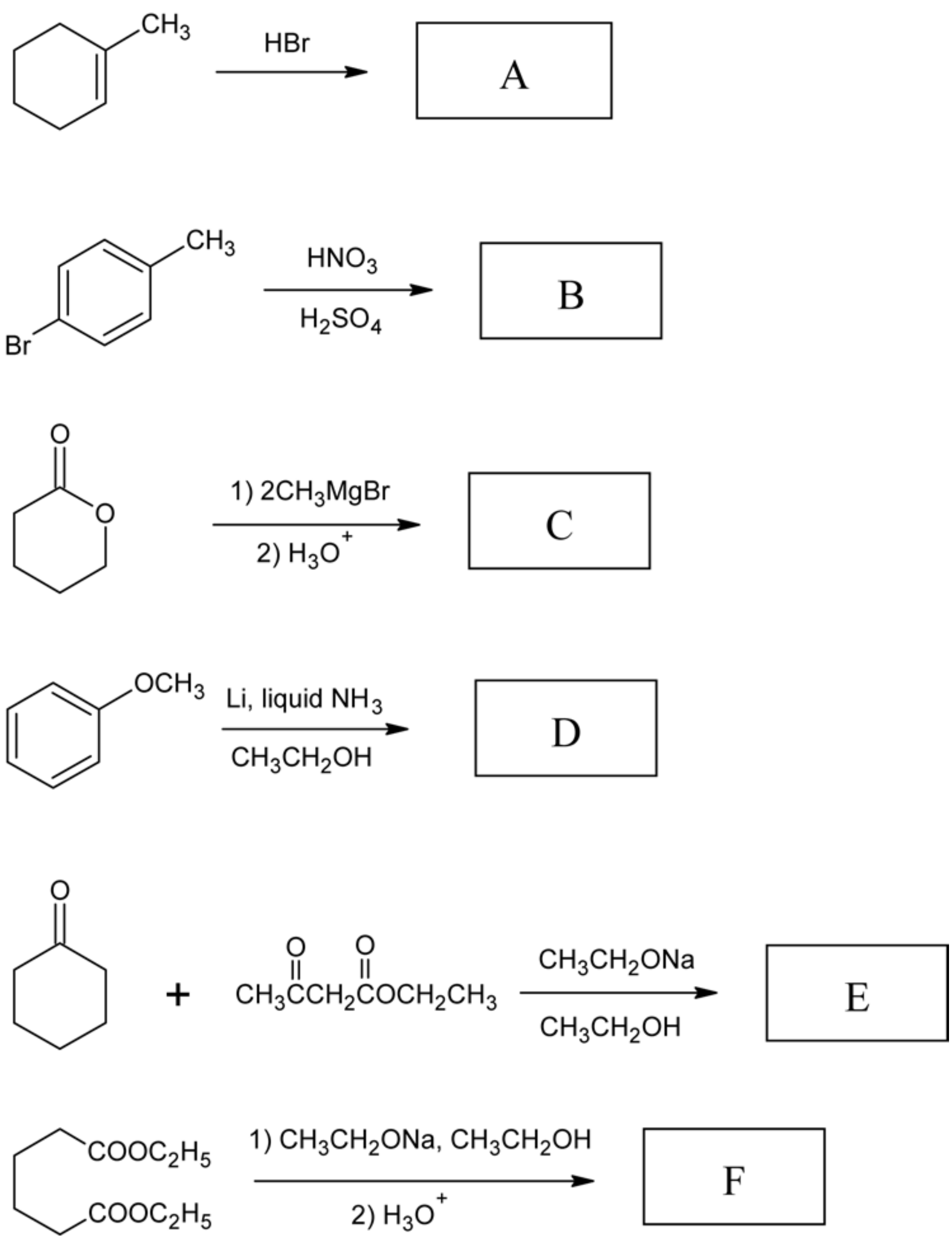
$dU = -PdV + TdS$	$dH = VdP + TdS$
$dA = -PdV - SdT$	$dG = VdP - SdT$
$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

II. Answer the following questions concerning chemical reactions.

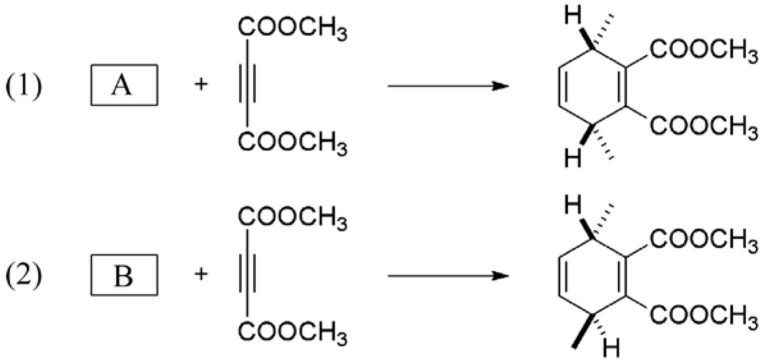
1. The reaction A→ P proceeds as a second -order reaction. Write the expression for the concentration of A, [A], at reaction time, t. The rate constant is k, and the concentration of A at t=0 is $[A]_0$. In addition, give an expression for the half-life, $t_{1/2}$, the time needed for [A] to reach one-half $[A]_0$.
2. The isomerization of cyclopropane to propene in the gas phase proceeds as a first-order reaction. Such a reaction is called a unimolecular reaction. Using the reaction A → P, explain the reaction mechanism and conditions for a unimolecular reaction. Define any needed parameters or variables.
3. Consider the ethene hydrogenation reaction to ethane on a Ni metal catalyst. If the reaction is carried out with deuterium, i.e. $C_2H_4 + D_2$, the product will consist of a mixture of $C_2H_{6-x}D_x$(x=0~6) with all x values. It is known that the reaction proceeds with adsorption of both ethene and hydrogen on the Ni surface. Suggest a plausible reaction mechanism to explain the reason that the product is not only $C_2H_4D_2$, but a mixture of $C_2H_{6-x}D_x$(x=0~6).

Problem 3

I. For the following reactions, draw the chemical structures of the main products A~F.



II. In reactions (1) and (2), stereoisomers A and B, respectively, react as starting materials and produce the shown cyclic products. Answer the following questions about the reactions.



1. The cyclization reaction is a famous named reaction. Write the name of the reaction.
2. Draw the structures of the starting materials A and B so that the three-dimensional structure can be understood.
3. Draw the transition state of reaction (1) using the frontier molecular orbitals of the two starting materials, so that the three-dimensional structure can be understood.

III. The following three reactions involve carbocation intermediates. Draw the reaction mechanisms including the intermediates and electron movements as shown in the example below.