# 2010
# The Graduate School Entrance Examination
# Chemistry
# 1:00－3:00 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 if you find any page missing, out of order or unclear.

3. Answer all three problems of 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 on that sheet and also the class of 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.

## Problem 1

I. Answer the following questions on molecular structures.

1. Consider molecular structures with the valence bond theory.
   (a) Indicate the order of bond angles, $\angle H-C-H$, $\angle H-N-H$, and $\angle H-O-H$ of $CH_4$, $NH_3$, and $H_2O$, respectively. Explain the reason for the order.
   (b) Depict the structures of $ClF_3$ and $SF_4$, and explain the reason why such structures are formed.
2. Consider the structure of $H_2O$ with the molecular orbital theory.
   (a) The occupied molecular orbitals of $H_2O$ are $1a_1$, $2a_1$, $1b_2$, $3a_1$, and $1b_1$. Indicate which orbitals in the O atom and the $H_2$ molecule combine to form each molecular orbital of $H_2O$. The coordinate of $H_2O$ is shown in Figure 1.1.
   (b) Consider a case where the $H_2O$ molecule forms a linear configuration virtually. Copy the Walsh diagram in Figure 1.2 to the answer sheet, and indicate the change of energy of each molecular orbital in the diagram between the bent case and the linear case. Explain the reasons for the changes.

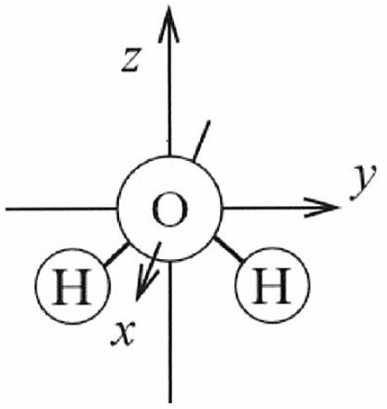


Figure 1.1

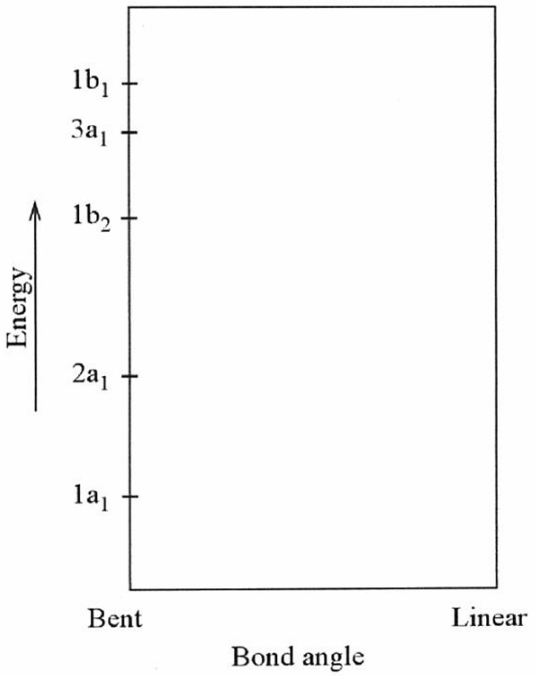


Figure 1.2

II. Answer the following questions.

1. Calculate the standard enthalpy $\Delta H°(1)$ of the reaction $KCl(s) \rightarrow K^+(g) + Cl^-(g)$, using the following thermochemical values.

Table 1.1

| | |
|---|---|
| $K(s) + 1/2\ Cl_2(g) \rightarrow KCl(s)$ | $\Delta H° = -438\ kJ\ mol^{-1}$ |
| $K(s) \rightarrow K(g)$ | $\Delta H° = 89\ kJ\ mol^{-1}$ |
| $K(g) \rightarrow K^+(g) + e^-$ | $\Delta H° = 425\ kJ\ mol^{-1}$ |
| $Cl_2(g) \rightarrow 2Cl(g)$ | $\Delta H° = 244\ kJ\ mol^{-1}$ |
| $Cl(g) + e^- \rightarrow Cl^-(g)$ | $\Delta H° = -355\ kJ\ mol^{-1}$ |

2. When a pair of A ion with a charge of $Z_A e$ and B ion with a charge of $Z_B e$ exists with a separation $r$ between the centers of both ions, the electrostatic energy $E_C$ between them is given by the following equation.

$$E_C = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r} \qquad (1)$$

Here, $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity. In KCl crystal with the NaCl structure, the nearest distance between $K^+$ and $Cl^-$ is assumed to be $r_0$. Derive the number of $Cl^-$ ions at the nearest positions around one $K^+$ ion, and the electrostatic energy $E_C(1)$ by these ions. Derive also the number of $K^+$ ions at the nearest positions around one $K^+$ ion, and the electrostatic energy $E_C(2)$ by these ions.

3. The lattice enthalpy $U$ is given by summing the electrostatic energy $E_C$ and the repulsion energy $E_R$ between electron clouds of the ions, for all ions in the crystal lattice. The lattice enthalpy of KCl for 1 mol is then approximated by the next equation.

$$U = -N_A \Sigma (E_C + E_R) = \frac{N_A A e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \qquad (2)$$

Here, $N_A$ is the Avogadro constant, $A$ is the Madelung constant depending on the crystal form, and $n$ is a constant. The standard

reaction enthalpy $\Delta H°(1)$, obtained in Question 1, corresponds approximately to the lattice enthalpy of KCl. How many times larger is the standard enthalpy $\Delta H°(2)$ of the reaction $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ for NaCl than $\Delta H°(1)$ of the reaction for KCl ? Answer in two significant figures with the reason. Use the following ionic radii below.

$r_{K^+} = 0.138$ nm, $r_{Na^+} = 0.102$ nm, $r_{Cl^-} = 0.181$ nm

## Problem 2

I. Answer the following questions on the formation and hydrolysis reactions of ethyl acetate. Use the numerical values below if necessary.

$\sqrt{2}=1.41$, $\sqrt{3}=1.73$, $\log 2=0.301$, $\log 3=0.477$

1. When the reaction of 2.0 mmol of acetic acid and 3.0 mmol of ethanol was carried out with $1.0\times10^{-2}$ mmol of sulfuric acid as a catalyst, 1.5 mmol of ethyl acetate was formed, and then the reaction stopped. Answer the maximum amount of ethyl acetate obtainable at this temperature with $5.0\times10^{-3}$ mmol of sulfuric acid as the catalyst.
2. Answer the maximum amount of ethyl acetate obtainable by the reaction of 1.0 mmol of acetic acid and 1.0 mmol of ethanol at the same temperature with $1.0\times10^{-2}$ mmol of sulfuric acid as the catalyst.
3. The half-life for the hydrolysis of ethyl acetate ($4.0\times10^{-2}$ mol $L^{-1}$ aqueous solution) with a solid acid catalyst was 30 min. Calculate the pH value of this solution 60 min after the reaction started. Suppose that this hydrolysis is a pseudo-first-order reaction. The p$K_a$ value of acetic acid is 4.8. Ignore the dissociation reaction of ethanol and the pH change of the aqueous solution by the solid acid catalyst.

II. Ideal gas molecules are colliding with a solid surface. The collision frequency, $Z_W$, of the gas molecules per unit time and unit area is expressed by the following equation.

$$Z_W = \frac{pN_A}{\sqrt{2\pi MRT}} \qquad (1)$$

Here $p$ is the gas pressure, $T$ is the absolute temperature, $M$ is the molar weight of the gas, $R=8.31$ J $K^{-1}$ $mol^{-1}$ is the gas constant, and $N_A=6.02\times10^{23}$ $mol^{-1}$ is the Avogadro constant.

1. Calculate $Z_W$ for gas molecule X at $p=1.0\times10^5$ Pa and $T=274$ K. Here the molar weight of X is $2.8\times10^{-2}$ kg $mol^{-1}$.
2. A chamber of volume $V$ is filled with gas X of Question 1 and kept at a constant temperature $T$ as shown in Figure 2.1. The chamber has an orifice of area $A$ on its wall, and X is effusing from

the orifice to the vacuum outside of the chamber. The number of gas molecule X decreasing in the chamber per unit time is the same as the number of X reaching the orifice per unit time. Derive a differential equation for the time dependence of pressure $p$ of X within the chamber. Assume that $p$ within the chamber is uniform.

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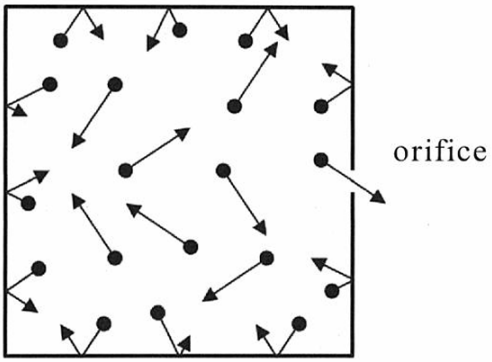


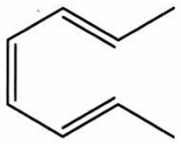

Figure 2.1

3. Express pressure $p$ of X as a function of time $t$ by solving the differential equation derived in Question 2. Here the pressure of X is $p_0$ at time $t = 0\,\mathrm{s}$.
4. The gas pressure of X decreased from $p_0 = 3.0\times10^{1}\,\mathrm{Pa}$ at $t = 0\,\mathrm{s}$ to $p = 1.0\times10^{1}\,\mathrm{Pa}$ at $t = 1.0\times10^{2}\,\mathrm{s}$. Calculate the time $t$ when $p = 1.0\times10^{0}\,\mathrm{Pa}$. Use the numerical values below if necessary.
$\ln 2 = 0.693,\ \ln 3 = 1.10,\ \ln 5 = 1.61$

## Problem 3

I. Draw the structural formulae of the main products, (A)～(E), in the following reactions.

1.

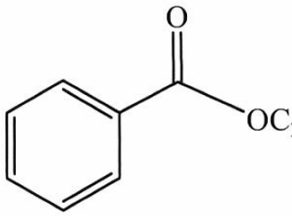


$\xrightarrow{\Delta}$ (A)

2.

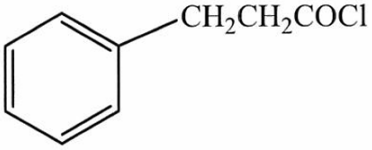
$+ Br_2 \longrightarrow$ (B)

3.



$+ CH_3CO_2C_2H_5 \xrightarrow{NaOC_2H_5}$ (C)

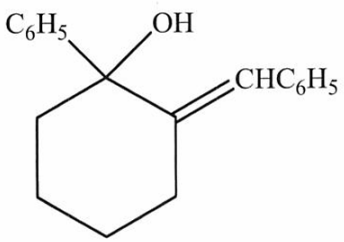
4.



$\xrightarrow[0\ ℃]{AlCl_3/C_6H_6}$ (D)

5. $H_2C{=}CHCH{=}CH_2 + HCl \xrightarrow[100\ ℃]{HOAc}$ (E)

II. Show the synthetic method of 2-benzylidenyl-1-phenylcyclohexanol from cyclohexanone.



III. Answer the following questions on the reactions related to (*R*)-2-bromobutane.

1. Draw the structural formula of (*R*)-2-bromobutane.
2. Draw the structural formulae for (F) ~ (J).