2016
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

The pressure dependence of the chemical potential, μ, of a pure substance depends on the molar volume, V_m. The response of melting temperature against pressure is rationalized by differences in the pressure dependences of μ between the solid and the liquid phases. At the constant temperature, the variation of μ with pressure is expressed by the following equation.

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m \qquad (1)$$

Here, P and T represent pressure and temperature, respectively. At a pressure P_1, the temperature dependences of μ of the substance A in the solid and the liquid phases are represented as Figure 1.1.

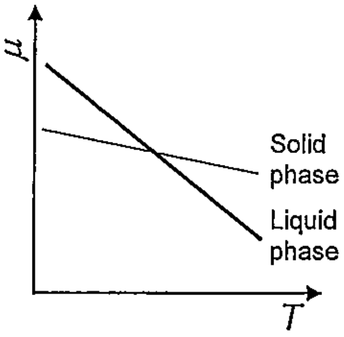


Figure 1.1

Answer the following questions. Note: 1 J = 1 N m and 1 Pa = 1 N m^{-2}.

I. Assume that the temperature dependences of μ for the solid and the liquid phases are identical between the substances A and B under the pressure P_1. From the graphs of (i) - (iv) in Figure 1.2, choose a suitable graph that represents the changes in the temperature dependences of μ for the substances A and B, respectively, when the pressure is increased from P_1 to P_2. Here, the relationship between the molar volume of the solid phase, V_m^s, and that of the liquid phase, V_m^l, for the substances A and B are expressed as follows.

Substance A: $V_m^s < V_m^l$
Substance B: $V_m^s > V_m^l$

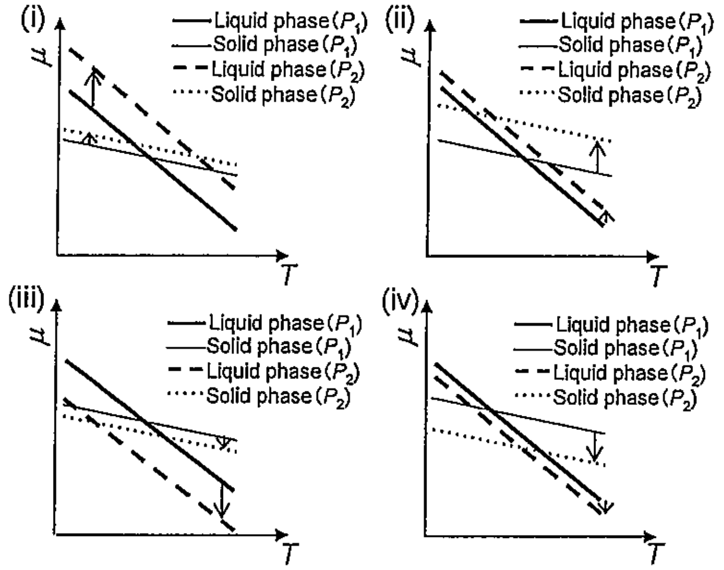


Figure 1.2

II. Answer the changes in the melting temperatures for the substances A and B, respectively, when the pressure is increased from P_1 to P_2. In addition, explain the reason for the changes using the chosen graph in Question I.

III. Let us consider water. Calculate the changes in μ at 0 °C for the liquid and the solid phases, respectively, when the pressure is increased from 1.00×10^5 Pa to 2.00×10^5 Pa. Provide the answer in the unit of J mol^{-1} with two significant digits. Here, the densities of the solid and the liquid phases are 0.917 g cm^{-3} and 0.999 g cm^{-3}, respectively, which are constant under the considered conditions. The molar mass of water is 18.0 g mol^{-1}.

IV. Assume that the equilibrated solid and liquid phases of water coexist at 1.00×10^5 Pa and 0 °C. Explain the change of the system when the pressure is increased to 2.00×10^5 Pa with keeping the temperature constant. In addition, explain the reason of the change briefly in terms of μ. Here, the densities of the solid and the liquid phases are 0.917 g cm^{-3} and 0.999 g cm^{-3}, respectively, which are constant under the considered conditions.

V. In most substances, the molar volume of the liquid phase is larger than that of the solid phase. However, this is not the case with water. Explain the reason briefly.

Problem 2 Basic Inorganic Chemistry

Answer the following questions. Use the following values if necessary.
$\sqrt{2} = 1.414$, $\sqrt{3} = 1.732$, $\sqrt{5} = 2.236$, $\sqrt{7} = 2.646$

I. Show the oxidation number of underlined atoms in the following substances.

(a) $Fe\underline{S}$ (b) $\underline{S}O_2$ (c) $Fe\underline{S}O_4$ (d) $Fe(\underline{O}H)_2$ (e) $H_2\underline{O}_2$

II. Answer the following questions on iron(II) sulfate aqueous solution.

1. When aqueous solution of sodium hydroxide is added to aqueous solution of iron(II) sulfate, precipitate is formed. Show the chemical equation of this reaction.
2. When aqueous solution of potassium cyanide is added excessively to aqueous solution of iron(II) sulfate beforehand, no precipitate is formed by the addition of aqueous solution of sodium hydroxide. What is the produced ion that contains iron? Also, draw its steric structure.

III. Iron is dissolved in dilute sulfuric acid. Answer the following questions on this reaction.

1. Show the chemical equation that describes the dissolution.
2. When hydrogen peroxide is added to the solution obtained by the reaction above, the color of the solution changes. Answer the colors before and after the addition of hydrogen peroxide. Also, explain the reason.
3. Show the chemical equation of the reaction described in Question III. 2.

IV. Iron has a body-centered cubic structure at atmospheric pressure and room temperature (α iron). When heated, it transforms to a face-centered cubic structure at 912 °C (γ iron). Furthermore, it changes to a body-centered cubic structure again at 1394 °C (δ iron), and melts at 1538 °C. Answer the following questions on the crystal structure of iron.

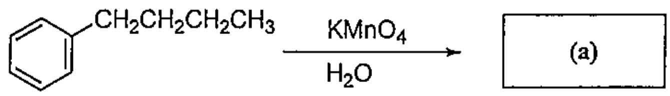
1. Which is the structure with the higher volumetric packing efficiency of atoms, the body-centered cubic structure or the face-centered cubic structure?

2. Calculate the maximum diameter of interstitial atoms that can occupy the space among iron atoms for body-centered cubic structured and face-centered cubic structured irons, with two significant digits. Here, assume that atoms are rigid spheres forming a close-packed structure, and that the lattice constants of body-centered cubic structured iron and face-centered cubic structured iron are 0.287 nm and 0.358 nm, respectively. Also, based on the calculation result, explain the reason why γ iron can contain higher concentration of carbon than α iron.

Problem 3 Basic Organic Chemistry

I. Draw the structural formulas of the main products, (a)–(j), for the following reactions.

(1)



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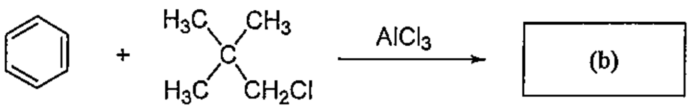

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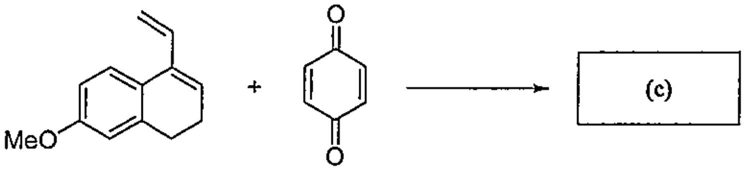

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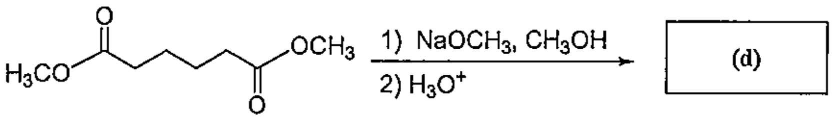

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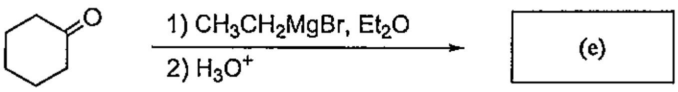

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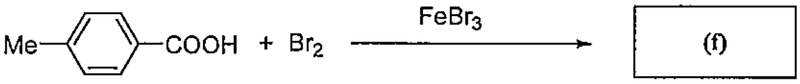
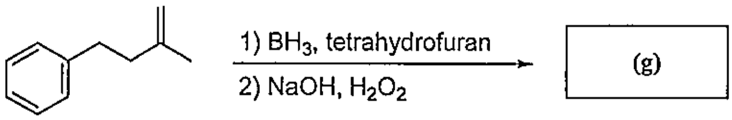
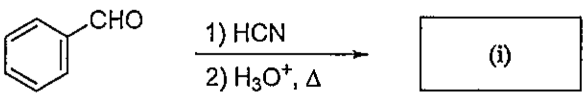


(7)



(8) $CH_3CH_2CH_2CH_2OH + HBr \xrightarrow{H_2SO_4} \boxed{(h)}$

(9)



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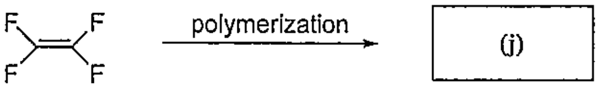
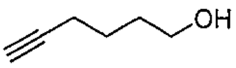


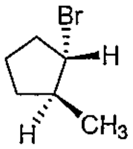
II. The reactions (2), (3), and (4) of Question I are the name reactions. Give the name of each reaction.

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

(k)



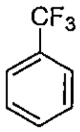
(l)



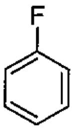
IV. Answer the following questions.

1. From the following compounds **(m)–(t)**, select all compounds which undergo selective nitration at the *meta* position upon treatment with HNO_3 in the presence of H_2SO_4.

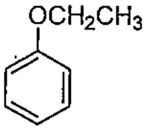
(m)



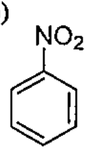
(n)



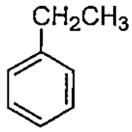
(o)



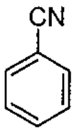
(p)



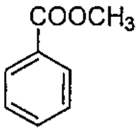
(q)



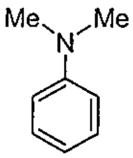
(r)



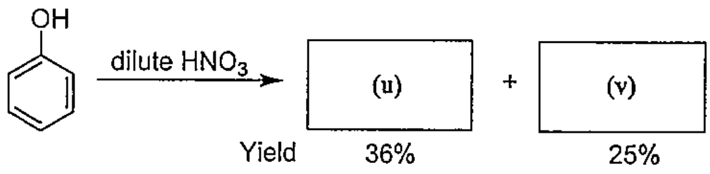
(s)



(t)



2. Compounds **(u)** and (v) are obtained from the following reaction. The boiling temperature of the compound **(u)** is lower than that of the compound (v). Draw the structural formulas of the compounds **(u)** and (v). Also, briefly explain the reason why the boiling temperatures are different.



Problem 4 Physical Chemistry

I. Let us consider a particle in a one-dimensional box, in which a particle of mass m is confined between two walls at $x = 0$ and $x = L$. Using wavefunction, $\phi_n(x)$, the Schrödinger equation of the particle is expressed as follows.

$$\frac{d^2\phi_n(x)}{dx^2}+\left(\frac{8\pi^2 m}{h^2}\right)\{E-V(x)\}\phi_n(x)=0 \tag{1}$$

h : Planck's constant, E : energy eigenvalue,
$V(x)=\infty$ for $x \le 0$ and $L \le x$, $V(x)=0$ for $0<x<L$

Answer the following questions.

1. When the boundary conditions are $\phi_n(0) = 0$ and $\phi_n(L) = 0$, the wavefunction is expressed as $\phi_n(x) = A\sin(n\pi x/L)$. Obtain the normalization constant A using L.
2. Express the energy eigenvalue E using n. Here, the lowest energy that the particle possesses is not zero. Answer the name of this lowest energy.
3. Draw the probability density function of the particle for $n = 3$. Also, indicate the maximal values and their positions in the figure.
4. Let us consider the π electrons of conjugated polyenes, $\mathrm{H{-}\!\left(CH{=}CH\right)_{\!k}\!{-}H}$, as a particle in a one-dimensional box. Using k, express the energy difference between the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO. Here, assume that the π conjugation length is obtained as the function of k by calculating the distance between the carbon atoms at both ends along the carbon-carbon bonds, and that the length of all carbon-carbon bonds is l.

II. Answer the following questions about electronic states of the hydrogen molecule.

1. The Hamiltonian for the single electron in the hydrogen atom is expressed as follows.

$$\hat{H}=-\frac{h^2}{8\pi^2 m_e}\Delta-\frac{e^2}{4\pi\varepsilon_0 r} \tag{2}$$

h : Planck's constant, m_e : electron mass, e : elementary electric charge,
ε_0 : vacuum permittivity, r : distance between the electron and the atomic nucleus

Express the Hamiltonian for the single electron in the hydrogen molecule-ion, H_2^+, using the distance of the electron from the nucleus a, r_a, that of the electron from the nucleus b, r_b, and that between the nuclei a and b, R_{ab}.

2. In the molecular orbital theory using LCAO (linear combination of atomic orbitals) approximation, the secular determinant for H_2^+ is expressed as follows.

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{3}$$

$$\alpha = \int \phi_a^* \hat{H} \phi_a d\tau = \int \phi_b^* \hat{H} \phi_b d\tau \tag{4}$$

$$\beta = \int \phi_a^* \hat{H} \phi_b d\tau = \int \phi_b^* \hat{H} \phi_a d\tau \tag{5}$$

$$S = \int \phi_a^* \phi_b d\tau = \int \phi_b^* \phi_a d\tau \tag{6}$$

Here, ϕ_i is the wavefunction of 1s orbital of the nucleus i. By solving this secular determinant, express the wavefunctions and the energy eigenvalues for the bonding orbital, ϕ_H, and the anti-bonding orbital, ϕ_L, using α, β and S.

3. Draw all electronic configurations for the hydrogen molecule, H_2, using the molecular orbital energy-level diagram based on the answer of Question II. 2. Also, answer the spin quantum numbers and the spin multiplicities for these electronic configurations.

Problem 5 Inorganic Chemistry

I. Answer the following questions on the structures of carbon and silicon compounds at ambient temperature and atmospheric pressure.

1. Carbon forms diamond by single bonds between carbon atoms. In addition, double or triple bonds can be formed between carbon atoms. On the contrary, multiple bonds between silicon atoms are not frequently found, while a single-bonded Si forms silicon crystal. Explain the reason for the difference.
2. Oxides of carbon are gaseous molecules, while oxides of silicon are typically solid which consists of SiO_2 as a chemical formula. Explain the reason for the difference.

II. The following reactions are the oxidation of graphite, iron, and aluminum. The temperature dependence of the change of standard Gibbs energy for each oxidation, ΔG° (kJ mol^{-1}), is given below. The graphical representation of these equations is given in Fig. 5.1. Consider the range of temperature T (K) from 300 to 2300 K, and ignore the influence of phase transformations for those substances. Answer the following questions.

$C + O_2 = CO_2$ $\Delta G^\circ = -390 - 2.08\times10^{-3}\,T$ (1)

$2C + O_2 = 2CO$ $\Delta G^\circ = -230 - 0.178\,T$ (2)

$\frac{3}{2}Fe + O_2 = \frac{1}{2}Fe_3O_4$ $\Delta G^\circ = -600 + 0.200\,T$ (3)

$2Fe + O_2 = 2FeO$ $\Delta G^\circ = -560 + 0.160\,T$ (4)

$\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3$ $\Delta G^\circ = -1140 + 0.222\,T$ (5)

1. The temperature dependences of ΔG° for the reactions (1), (2), and (5) are different. Explain the reason.
2. Assume that only the reactions (1)−(4) occur. Equimolar amounts of graphite, iron, and FeO were put into a robust container. The container was evacuated at room temperature, and then the substances were heated to 1500 K. Answer the main product.
3. Consider reduction of Al_2O_3 to Al. Generation of Al by the reaction (5) does not take place spontaneously. Hence, let us promote the reduction by combining one of the reactions (1)−(4) and the reaction (5). Express the

changes of standard Gibbs energy of reaction, ΔG°, for these four reduction reactions as a function of T.

4. Choose the most appropriate reaction from the four reduction reactions to obtain Al from the viewpoint of the change of standard Gibbs energy of the reactions. Also, answer the temperature range where the reactions occur spontaneously.
5. In industry, reduction of Al_2O_3 to Al is carried out by electrolytic smelting using carbon electrodes at around 1300 K. Explain the change in the electrical energy required for the reduction reaction with the reason, if inert electrodes were used instead of the carbon electrodes.

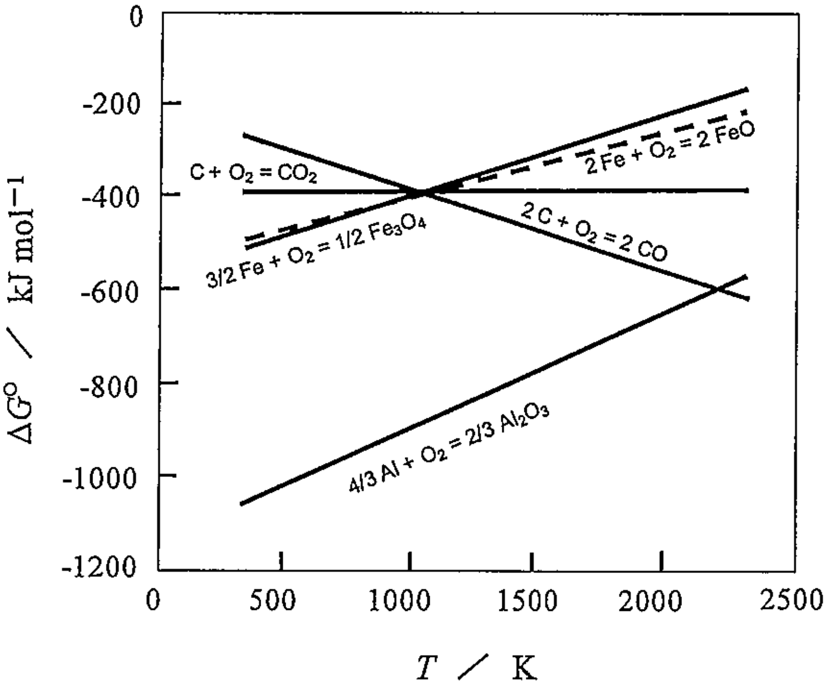
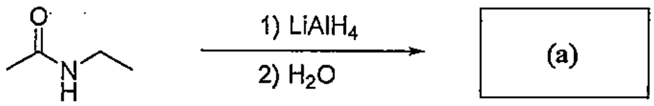
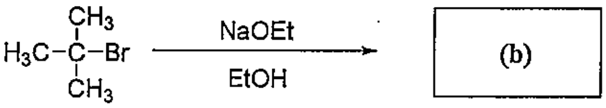


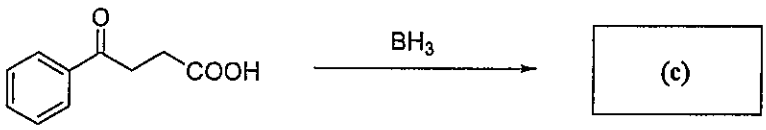
Figure 5.1

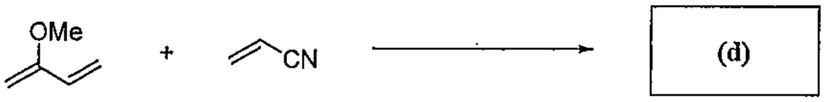
Problem 6 Organic Chemistry

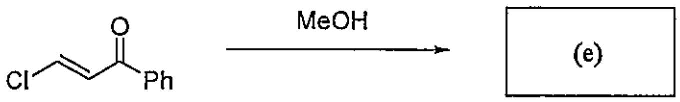
I. Draw the structural formulas of the main products, (a)–(i), for the following reactions. Steric structure (stereochemical structure) should be clearly shown for compound (f).

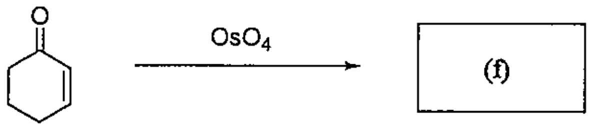


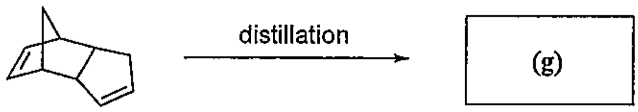


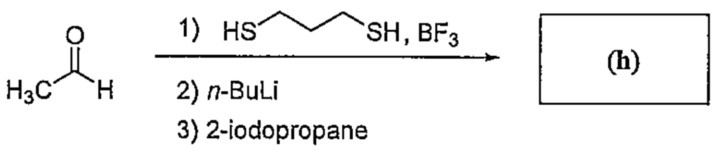


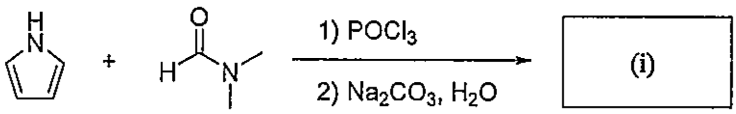












II. Explain the reasons for the following phenomena. You may use figures if necessary.

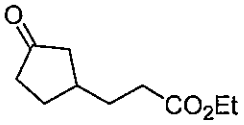
1. The reaction rate of hydrolysis of 2-chloro-2-methylpropane increases as the polarity of the solvent increases.

2. After benzene was treated with an excess amount of D_2SO_4, the signal originated from benzene disappeared in the ^{1}H-NMR spectrum.

3. Cyclopentane-1,2-dione exists almost entirely as the monoenol form in solution.

III. Answer the following questions.

1. Draw all the structural formulas of monoenolate ions that can be generated from compound (j) upon the treatment with NaOEt as a base.



(j)

2. When compound (j) was subjected to the intramolecular Claisen condensation reaction in the presence of NaOEt followed by treatment with an acid, only one dicarbonyl compound was obtained. Draw the structural formula of this product, and explain the reason why only one condensation product was obtained. You may use figures for the explanation if necessary.

Problem 7 Analytical Chemistry

"Hot Spring Law" defines a type of "hot spring (*Onsen*)" as spring water which contains any of substances listed in Table 7.1 in 1 kg of the water with more than or equal to the amount shown in the right column of the table. Also, analytical instruments for analyzing these substances are shown in Table 7.2.

Answer the following questions on the analyses of the substances listed in Table 7.1 contained in hot spring water with the instruments shown in Table 7.2.

Table 7.1

Substance	Content
CO_2	250 mg
Li^+	1 mg
Sr^{2+}	10 mg
Ba^{2+}	5 mg
$Fe^{2+} + Fe^{3+}$	10 mg
Mn^{2+}	10 mg
H^+	1 mg
Br^-	5 mg
I^-	1 mg
F^-	2 mg
$HAsO_4^{2-}$	1.3 mg
$HAsO_2$	1 mg
S [Only originated from HS^-, $S_2O_3^{2-}$ or H_2S]	1 mg
HBO_2	5 mg
H_2SiO_3	50 mg
$NaHCO_3$	340 mg
Rn	74 Bq
Ra	10^{-8} mg

Table 7.2

Analytical instruments
Atomic absorption spectrophotometer
UV-Visible absorption spectrophotometer
pH meter
Ion chromatograph
Liquid scintillation counter
Mercury atomic absorption photometer

I. The value of pH of a certain spring water is 2.3. Answer the concentration of hydrogen ion in the water, with one significant digit. Use the following values if necessary.

$$\log_{10}2 = 0.30,\quad \log_{10}3 = 0.48,\quad \log_{10}7 = 0.85$$

II. Explain the principle of the quantitative analysis and the instrumental setup of an atomic absorption spectrophotometer.

III. Answer all the substances which can be analyzed quantitatively with the atomic absorption spectrophotometer.

IV. Answer all the substances which can be separated with the ion chromatograph using resins containing quaternary ammonium group as the stationary phase.

V. Concentrations of Fe^{2+} and Fe^{3+} are selectively determined using an instrument shown in Table 7.2. Select two of applicable instruments. For each instrument, explain the principle of the analysis. In addition, for each instrument, explain the method to quantify the Fe^{2+} and the Fe^{3+} selectively.