2011
The Graduate School Entrance Examination
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 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 (P 1, P 2, P 3) 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 water and ice.

1. Water can act both as an acid and a base, depending on the counterpart of the reaction. Write the ionizing reactions of HCl and NH_3 with H_2O in aqueous solutions respectively, and explain briefly for each case the role of H_2O as a Brønsted acid or a Brønsted base.
2. The boiling point of H_2O is 100°C at 1 atm. The boiling points of H_2S and H_2Se are −60°C and −41°C, respectively at 1 atm, and much lower than that of H_2O although all three are the hydrides of the Group16 elements. Explain briefly why the boiling point of H_2O is high. The electronegativities of H, O, S, Se atoms are 2.2, 3.4, 2.6 and 2.6.

There are several polymorphs with different crystal structures for ice. The crystal structure of a cubic form, one of the polymorphs, can be considered to be similar to the diamond structure shown in Fig. 1.1. In the structure, O atoms are situated close to the C atom positions in diamond and H atoms are located on the lines connecting the nearest O atoms. Answer the following questions assuming that the O atoms of ice form an ideal diamond structure.

3. Which hybrid orbital can be expected for the O atoms of ice with this structure?
4. Derive an equation for the density d [g cm^{-3}] of an ice crystal, using the molecular weight W [g mol^{-1}] of H_2O, the lattice constant a [m] and the Avogadro constant N_A [mol^{-1}]. Calculate the density d [g cm^{-3}] of an ice crystal to two significant figures, for a case where the volume of unit cell a^3 equals 2.6×10^{-28} m^3. Use $W = 18$ g mol^{-1} and $N_A = 6.0 \times 10^{23}$ mol^{-1}.

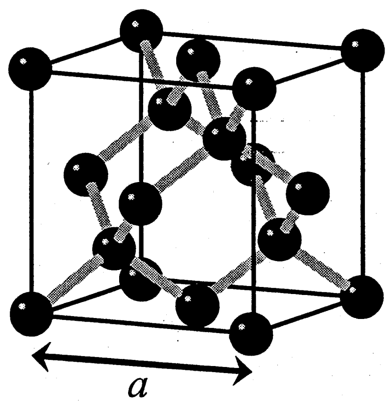


Figure 1.1 Diamond structure

II. Answer the following questions on metal complexes.

1. Illustrate the structures of all isomers of $[CoCl_2(en)_2]^+$ which is a complex with a central metal ion of Co^{3+}. The notation “en” indicates ethylenediamine.
2. Explain the formation of coordination bonds between a central metal ion and ligands as an acid-base model in about 50 words.
3. Metal complexes often form their structures using the d orbitals of central metal ions. There are five discrete orbitals in the d orbitals. One of them is illustrated in Figure 1.2 with its name. Illustrate the other four orbitals and note their names in a similar way to Figure 1.2.
4. Based on ligand field theory, the energy levels of d orbitals of a central metal ion are split by the ligand field as shown in Figure 1.3. Answer the coordination structures of ligands for cases A and B. Explain for case A in about 100 words why the energy levels are split as shown in Figure 1.3.
5. The magnetic moment of $[Fe(H_2O)_6]^{3+}$ is larger than that of $[Fe(CN)_6]^{3-}$, though both complexes consist of Fe^{3+} with d^5 configuration. $[Fe(H_2O)_6]^{3+}$: $\mu = 5.3\mu_B$, $[Fe(CN)_6]^{3-}$: $\mu = 2.3\mu_B$, where μ_B denotes the Bohr magneton. Explain the reason for the difference in about 100 words.

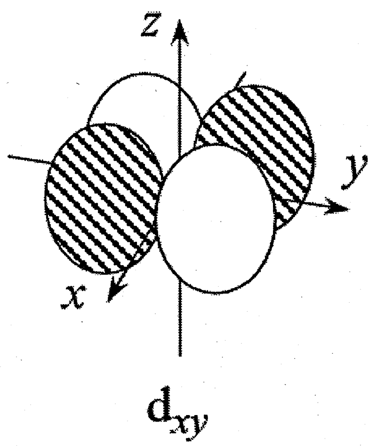


Figure 1.2

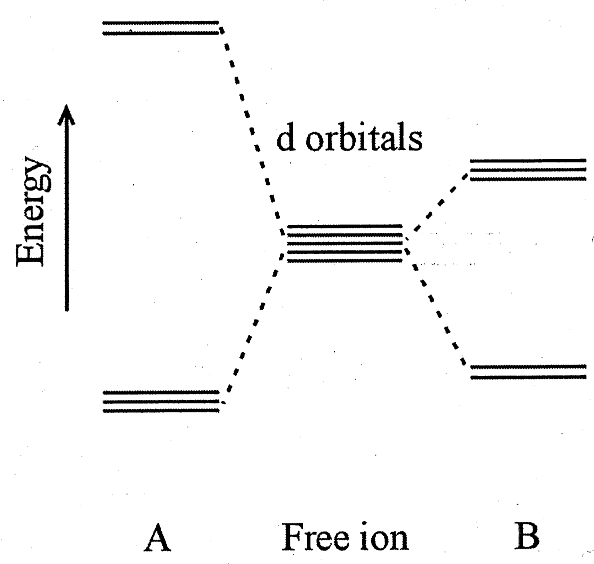


Figure 1.3

Problem 2

I. Answer the following questions on nitrogen.

1. The pressure and temperature are represented by p and T, respectively. Draw a phase diagram of nitrogen in ranges of p = 0~500 kPa and T = 50~100 K based on the following data. Regions of gas, liquid and solid phases must be indicated in the phase diagram.

melting point :	63.2 K (p = 100 kPa)
boiling point :	77.4 K (p = 100 kPa), 93.5 K (p = 500 kPa)
triple point :	63.0 K, 12 kPa
critical point :	126.2 K, 3.4 MPa

2. The slope of the vaporization curve, which lies at the boundary of gas and liquid phases, is always positive, that is, $\mathrm{d}p / \mathrm{d}T > 0$. Explain the reason.
3. The vaporization enthalpy is 5.6 kJ mol^{-1} for nitrogen at 77.4 K and 100 kPa. Show the change in entropy per 1 mol of liquid nitrogen at 77.4 K. The vaporization enthalpy of liquid nitrogen at 65.0 K is larger than that at 77.4 K. Between liquid nitrogen and nitrogen gas, explain which has a larger molar heat capacity at constant pressure at a temperature range of 65.0 K to 77.4 K.
4. 1 mol of liquid nitrogen at 77.4 K and 1 mol of liquid nitrogen at 65.0 K were mixed in an insulating container. The pressure was kept at 100 kPa. Assuming the molar heat capacity at constant pressure of liquid nitrogen to be constant, calculate the temperature of liquid nitrogen after mixing. In addition, show that the entropy change through the mixing process is positive.
5. Express the equilibrium constant K of the ammonia synthesis reaction,

$$N_2(\mathrm{gas}) + 3H_2(\mathrm{gas}) \overset{K}{\rightleftharpoons} 2NH_3(\mathrm{gas})$$

using partial pressures of gases, $p(N_2)$, $p(H_2)$ and $p(NH_3)$. These gases can be assumed as ideal gases. Describe how the mole fraction of NH_3 changes when the total gas pressure is lowered.

II. Figure 2.1 shows a schematic presentation of a binary phase diagram with one intermediate stoichiometric compound, AB, where T is the temperature and x is the mole fraction of B ($0 \leq x \leq 1$). Points in the phase diagram are denoted as (x, T). Solid states of A, B, and AB are represented by vertical solid lines in the phase diagram, indicating their stable temperature regions. Liquid phase dominates all composition of $0 \leq x \leq 1$ at high temperatures, while various regions consisting of liquid and solid phases exist at intermediate temperatures. Answer the following questions.

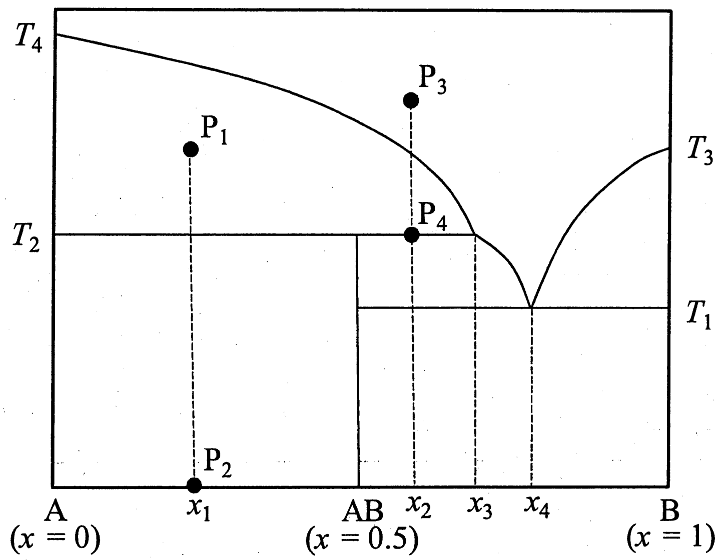


Figure 2.1

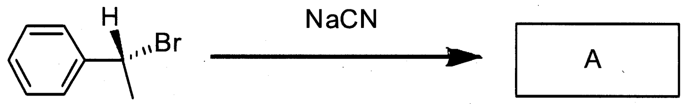
1. Answer the name of the boundary line connecting points, (0, T_4) - (x_3, T_2) - (x_4, T_1) - (1, T_3).
2. Answer the name of the boundary lines connecting points (0, T_2) - (x_3, T_2), or points (0.5, T_1) - (1, T_1).
3. Starting from point P_1, point P_2 was reached by a very slow cooling process. Answer all existing phases with their abundance ratio using x_1.
4. Answer the names of points (x_3, T_2) and (x_4, T_1). Then, answer all coexisting phases at each point together with their states and compositions.
5. When cooling from the liquid state, show the appropriate ranges of the composition and the temperature that gives only AB as the solid phase. Answer with symbols in the figure.

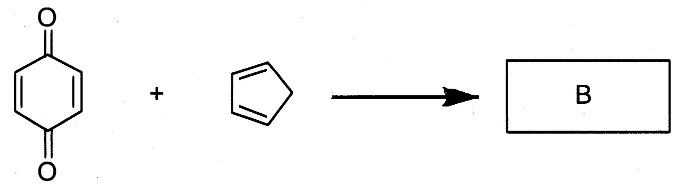
6. The following sentence describes the phenomena occurring during a slow cooling process from point P_3, when passing through point P_4. Fill in (i) ~ (iv), using symbols given in the figure.

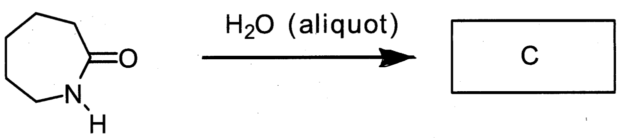
[(i)] in the solid state reacts with a liquid phase to transform into [(ii)] in the solid state, and the mole fraction of the liquid phase changes from [(iii)] to [(iv)].

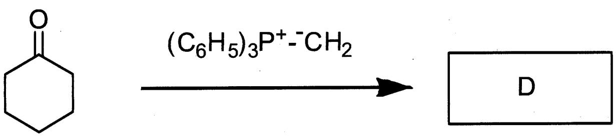
Problem 3

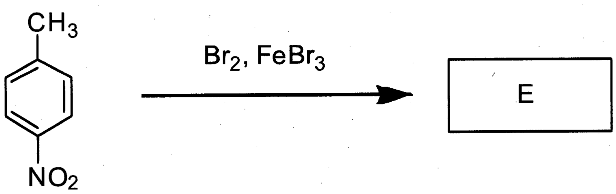
I. Draw the chemical structures of main products A~G. Specify the stereochemistry when necessary.

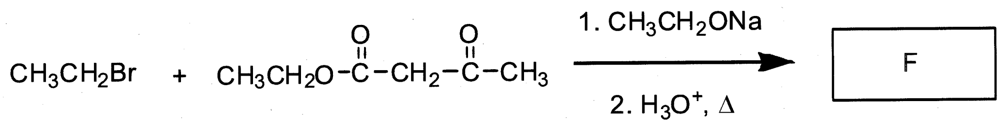
(1) 

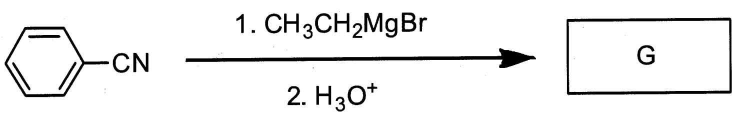
(2) 

(3) 

(4) 

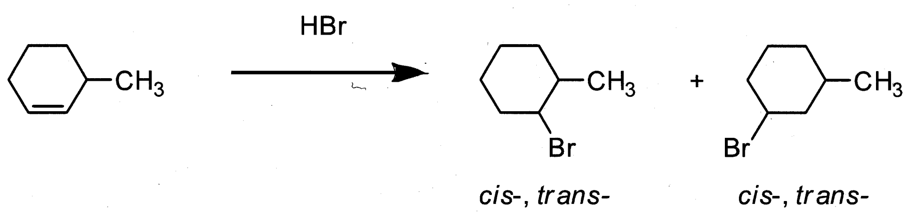
(5) 

(6) 

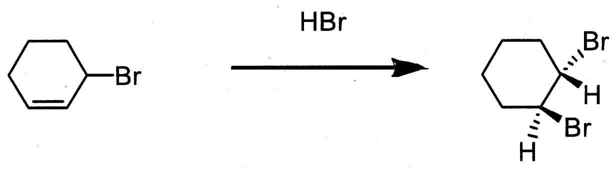
(7) 

II. Answer the following questions on reactions (1) and (2).

(1)



(2)



1. Draw all possible intermediates of reaction (1).
2. Why does reaction (2) give only one kind of product? Explain the reaction mechanism.

III. Explain briefly the following terms and clarify their differences.

1. Tautomer and Resonance Form
2. Enantiomer and Diastereomer
3. Block Copolymer and Graft Copolymer