2013
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 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 on each 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 chemical bonding.

1. The bonding and anti-bonding orbitals of the HF molecule are formed from the valence orbitals of the H and F atoms. Depict the relative order of energies of the valence orbital of the H atom, the valence orbital of the F atom, the bonding orbital of the HF molecule, and the anti-bonding orbital of the HF molecule. In addition, explain the reason why electrons filling the bonding orbital are distributed towards the side of the F atom.
2. The d-orbital of Ti^{3+} in the $[Ti(H_2O)_6]^{3+}$ complex in aqueous solution splits into t_{2g} and e_g orbitals. Explain the reason why the $[Ti(H_2O)_6]^{3+}$ aqueous solution is colored magenta by using t_{2g} and e_g orbitals.
3. The molecular orbitals of the O_2 molecule are presented in Fig. 1.1. Explain the reason why the O_2 molecule in the ground state is paramagnetic.

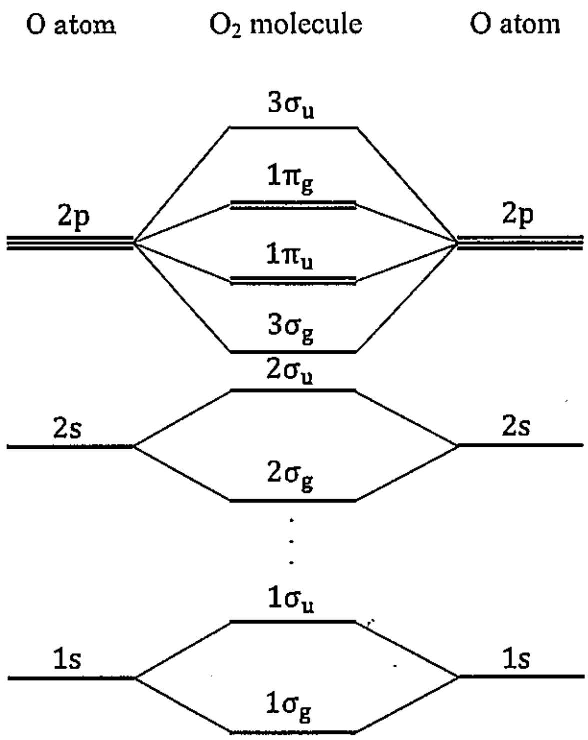


Fig. 1.1

4. Consider metals or insulators which are solids at ordinary temperature. Explain briefly the reason why there is a large difference in electrical conductivity between metals and insulators by depicting the energy bands.

II. Answer the following questions on UV-vis absorption spectroscopy.

Compound **A** in aqueous solution shows an absorption maximum at 472 nm. Compound **B** in aqueous solution shows an absorption maximum at 502 nm. The molar absorptivities of compounds **A** and **B** at 472 nm are 2.0×10^{3} M^{-1} cm^{-1} and 4.0×10^{2} M^{-1} cm^{-1}, respectively. The molar absorptivities of compounds **A** and **B** at 502 nm are 2.0×10^{2} M^{-1} cm^{-1} and 5.0×10^{3} M^{-1} cm^{-1}, respectively. The optical path length defined by the Beer-Lambert law is 1.0 cm. The symbol M represents the molar concentration [mol L^{-1}].

1. Compound **A** in aqueous solution showed transmittance of 10% at 472 nm. Calculate the absorbance of compound **A** in aqueous solution at 472 nm. Furthermore, calculate the molar concentration of compound **A** in units of M.
2. A mixed aqueous solution of compounds **A** and **B** showed absorbance of 0.44 and 0.54 at 472 nm and 502 nm, respectively. Calculate the molar concentrations of compounds **A** and **B** in units of M.

III. Answer the following questions on the electrolysis of water.

An aqueous solution of dilute sulfuric acid was put into an electrolytic cell, and water was electrolyzed by applying a current of 1.50 A for 180 min. The temperature was 27 °C, and the pressure was 1.01×10^{5} Pa. Use the following values for calculations.

Faraday constant $F = 9.65\times10^{4}$ C mol^{-1}, Gas constant $R = 8.31$ J K^{-1} mol^{-1},
1 J = 1 kg m^{2} s^{-2}, 1 Pa = 1 kg m^{-1} s^{-2}

1. Explain the reason why the electrolysis of pure water is not easy.
2. Describe the equations of the chemical reactions that occur on the anode and cathode of the electrolytic cell.
3. Calculate the electric charge [C] that flowed through the electrolytic cell.
4. Calculate the volume [m^3] of produced H_2(g) and O_2(g). Assume that both H_2(g) and O_2(g) are ideal gases.

Problem 2

I. The Schrödinger equation for a hydrogen atom is given by the following expressions using the Hamiltonian $\hat{H}$ and wavefunction Ψ.

$$\hat{H}\Psi = \left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\Psi = E\Psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad \hbar = \frac{h}{2\pi}$$

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

Here, the first and second terms in the Hamiltonian $\hat{H}$ denote the kinetic energy of the electron and the potential energy between the nucleus and the electron, respectively. Answer the following questions about the Schrödinger equation. Here, the wavefunction Ψ is normalized by the following equation.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\Psi|^2\, r^2 dr \sin\theta\, d\theta\, d\varphi = 1$$

1. By reference to the hydrogen atom, give the Hamiltonian $\hat{H}$ for a lithium ion, Li^+. Here, the effective nuclear charge of Li^+ is Z'.
2. In the case of the hydrogen atom, using the Bohr radius a_0 (= 0.529 Å), the wavefunctions Ψ of the 2s and 2p orbitals are expressed by the following equations. Prove that the $2p_x$ and $2p_z$ orbitals are orthogonal.

$$\text{2s orbital}: \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{2\sqrt{2\pi}}\left(1-\frac{r}{2a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$$

$$2p_z \text{ orbital}: \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{4\sqrt{2\pi}}\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)\cos\theta$$

$$2p_x \text{ orbital}: \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{4\sqrt{2\pi}}\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)\sin\theta\cos\varphi$$

$$2p_y \text{ orbital}: \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{4\sqrt{2\pi}}\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)\sin\theta\sin\varphi$$

3. Draw the wavefunction Ψ of the 2s orbital of the hydrogen atom using r as the horizontal axis. In addition, calculate the position of the node in the 2s orbital, and indicate it clearly.

II. A compound A B is formed from compounds A and B by the following chemical reaction.

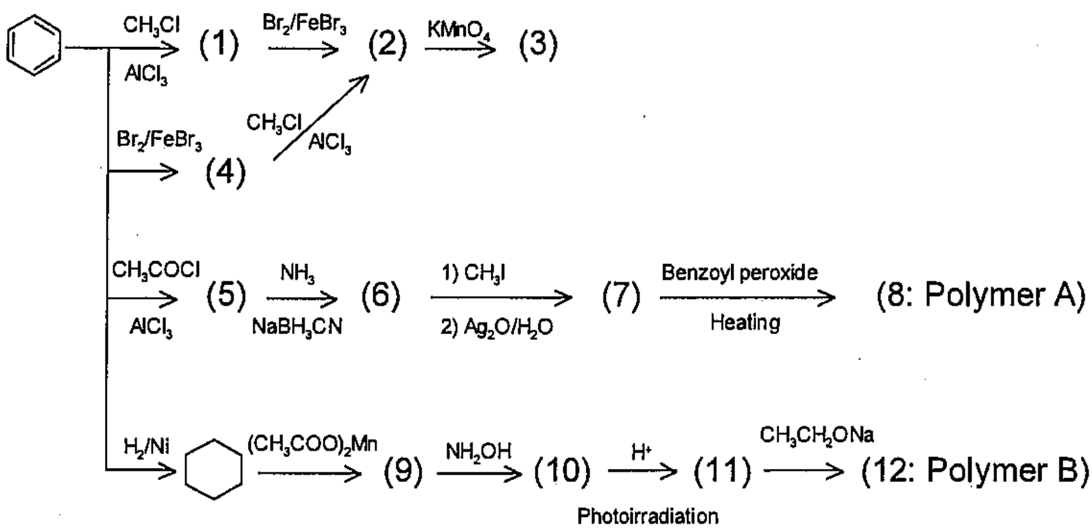
$$\text{A} + \text{B} \rightleftharpoons \text{AB}$$

Answer the following questions about this chemical equilibrium.
Here, the gas constant R is 8.31 J K^{-1} mol^{-1}, and $\log_e x = 2.30 \log_{10} x$.

1. The equilibrium constant K is 1.00×10^5 at 17 °C. Calculate the change in the Gibbs free energy, ΔG, for this reaction at 17 °C.
2. The equilibrium constant K is 1.00×10^4 at 87 °C. Calculate the change in the enthalpy, ΔH, for this reaction at 87 °C.
3. Calculate the change in the entropy term, $-T\Delta S$, for this reaction at 27 °C.

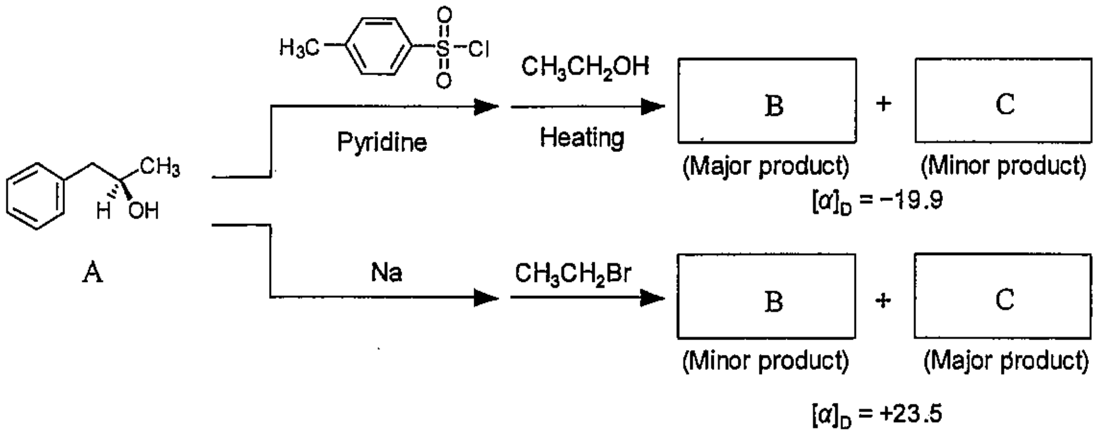
Problem 3

I. Answer the questions below about chemical reactions of benzene as a starting compound.



1. Draw the chemical structures of the compounds numbered from (1) to (12).
2. Give the names of polymer A and polymer B.
3. Explain in about 60 words representative applications of polymer A and polymer B from the standpoint of their chemical structures.
4. Describe in about 30 words an alternative route to polymer B starting from another monomer. Difference in the end group structures and the molecular weights of the polymers may be ignored.

II. As shown below, two reaction paths starting from compound A resulted in the formation of mixtures of compounds B and C that are enantiomers of each other. However, the specific rotation $[\alpha]_D$ of the mixtures were different between the reaction paths. Answer the following questions.



1. Give the name of compound A including its *R*, *S* configuration.
2. Draw the stereostructures of compounds B and C.
3. Why did the two reaction paths give mixtures with opposite signs of specific rotation? Explain the reasons from the reaction mechanisms.

III. The reaction of 4-methylaniline with excess bromine gives the 2,6-dibromo-substituted product. In contrast, the reaction of 4-methylacetanilide with excess bromine gives the 2-bromo-substituted product. Explain this difference in the reactivity by drawing resonance structures for 4-methylaniline and 4-methylacetanilide.