Graduate Course of

Chemical System Engineering

(Major subjects for the Master's program admission)

ID number

Tuesday, August 28, 2018 9:00-12:00

You are expected to answer four problems selected from the seven problems below.

Problem No.	Subject	Pages
Problem 1	Physical Chemistry 1	1～ 2
Problem 2	Physical Chemistry 2	3～ 4
Problem 3	Inorganic Chemistry	5～ 6
Problem 4	Organic Chemistry	7～ 8
Problem 5	Chemical Engineering 1	9～10
Problem 6	Chemical Engineering 2	11～12
Problem 7	Mathematics	13～14

Note:

1. Five sheets of answer paper are given to each of you. In addition, two sheets of white paper are attached for draft writing and calculation. Use one answer sheet per problem. You may use the back of the answer sheets if necessary. When you answer to the problem 3, use the answer sheet specific to the problem 3.
2. Do not open the problem file until directed by the presiding officer.
3. Write down your ID number on each of all the five answer sheets. Do not write your name. Write down your ID number also on the sheets for draft writing and calculation.
4. Write the selected problem numbers on the answer sheets, even if you leave an answer paper blank.
5. Write the four problem numbers you answered on the Selected Problem Number sheet. Only the answers to the problems listed in this sheet are scored.
6. You cannot take any papers out of the examination room even after the examination is over.

Problem 1 (Physical Chemistry 1)

I. Answer the questions below related to entropy.

(1) Take the molar entropy of an ideal gas to be S_0 at temperature T_0 and volume V_0. Also, take the gas constant and heat capacity at constant volume to be R and C_V, respectively. Express the molar entropy S using S_0, C_V, T_0, V_0, T, V and R. Here, note that the relation between the change of internal energy dU, the change of entropy dS, the change of volume dV, and pressure p is $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$.

(2) Consider N_A atoms of element A and N_B atoms of element B forming a substitutional solid solution, $A_{N_A}B_{N_B}$. The change in lattice constant by forming the solid solution is assumed to be negligible, and the Boltzmann constant is taken to be k_B.

i) Calculate how many atomic arrangements there are in the solid solution.

ii) Give the entropy change in forming the solid solution. The following approximation, $\ln N! = N\ln N - N$, may be used.

(Continue on the next page)

II. Answer the questions below related to water.

(1) Regarding the phase equilibrium between water and ice, take the chemical potential, molar entropy, molar enthalpy and molar volume for both water and ice to be μ_ℓ, μ_s, S_ℓ, S_s, H_ℓ, H_s, V_ℓ, and V_s, respectively. Answer the questions below.

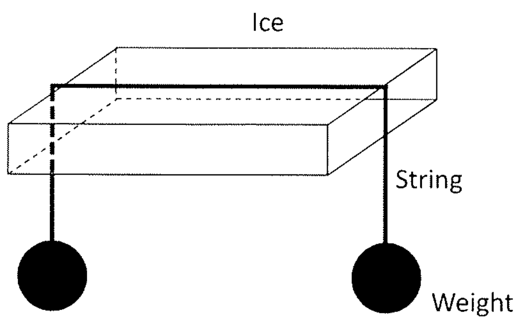
i) For water and ice in equilibrium at pressure p and temperature T, indicate what relationship exists involving the chemical potential.

ii) Derive the equation expressing the pressure dependence of the melting point, $(\mathrm{d}T_m/\mathrm{d}p)_{eq}$, using the equation, $\mathrm{d}\mu = V\mathrm{d}p - S\mathrm{d}T$, which holds when the pressure changes only slightly while equilibrium is maintained.

iii) Express the change in molar entropy ΔS_{melt} for melting of the ice using the temperature T_m and the molar heat of fusion ΔH_{melt}.

iv) Express $(\mathrm{d}T_m/\mathrm{d}p)_{eq}$ using the molar heat of fusion ΔH_{melt} and the results of ii) and iii).

v) As shown in the figure below, weights are hanged on ice using a sufficiently thin string in an environment at 0 °C under atmospheric pressure; consider what kind of phenomenon occurs. Using the results of i)–iv), briefly explain in about 50 words.



(2) The standard Gibbs energy of the dissociation reaction, $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$, is $118.1\,\mathrm{kJ\,mol^{-1}}$ at 2300 K. Give the degree of dissociation of H_2O at 1.000 bar and 2300 K. Note that the degree of dissociation may be taken to be sufficiently smaller than 1. The gas constant R is $8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Problem 2 (Physical Chemistry 2)

I. Answer the following questions.

(1) When light of wavelength 300 nm is irradiated on a metal, photoelectrons with energy of $3.20\times10^{-19}\,\mathrm{J}$ are emitted. Calculate the work function of this metal in eV units. Use light velocity $c = 3.00\times10^{8}\,\mathrm{m\,s^{-1}}$, Planck constant $h = 4.14\times10^{-15}\,\mathrm{eV\,s}$, and $1\,\mathrm{eV} = 1.60\times10^{-19}\,\mathrm{J}$.

(2) The band gap of gallium nitride, a typical semiconductor, is 3.40 eV. Convert this to temperature [K] and photon wavelength [nm] units. Use the Boltzmann constant $k_{\mathrm{B}} = 8.62\times10^{-5}\,\mathrm{eV\,K^{-1}}$.

(3) Discuss the results obtained in (2) in relation to carrier creation and optical functions in semiconductor devices in about 50 words.

II. Answer the following questions on energy levels.

(1) Explain what is energy-level-degeneracy in about 20 words.

(2) List two examples where degenerate states are changed to non-degenerate states, and explain in a simple manner the respective mechanisms.

(3) Give one analytical methodology which utilizes a transition from degenerate to non-degenerate states induced by external perturbation and explain its principle in about 30 words.

(4) Suppose six electrons each with mass m are in a one-dimensional potential well with a width of l. Give the absorbed energy when they transition from the ground state to the first excited state, using m, l, and h. Here, the energy levels are given by equation [1] with Planck constant h, and quantum numbers n. Repulsion among electrons is considered to be sufficiently small.

$$\varepsilon_n = \frac{h^2}{8m}\frac{n^2}{l^2} \qquad n = 1, 2, 3 \ldots \qquad [1]$$

III. The energy of a diatomic molecule, which is rotating around its center of gravity with a moment of inertia I, is given by equation [2].

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \qquad J\text{: Quantum number } (0,1,2,3,\ldots),\ h\text{: Planck constant} \qquad [2]$$

Answer the following questions.

(1) Utilizing the selection rules for absorption and emission, $\Delta J = \pm 1$, show that the infrared absorption lines with frequency ν as x-axis should occur at equally spaced intervals. Also, calculate the line interval $\Delta\nu$.

(2) Derive the equation to calculate the bond length r of a heteronuclear diatomic molecule AB, using the result of (1) and the reduced mass μ. Here, $\mu = M_A M_B/(M_A+M_B)$ with atomic weights M_A and M_B of atoms A and B.

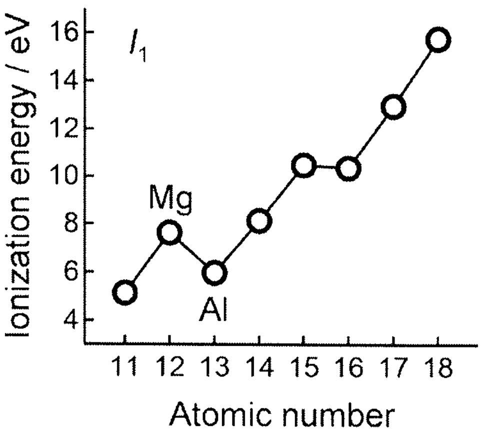
(3) The bond length cannot be obtained for a homonuclear diatomic molecule by applying the method described in (1) and (2). Explain the reason in about 20 words.

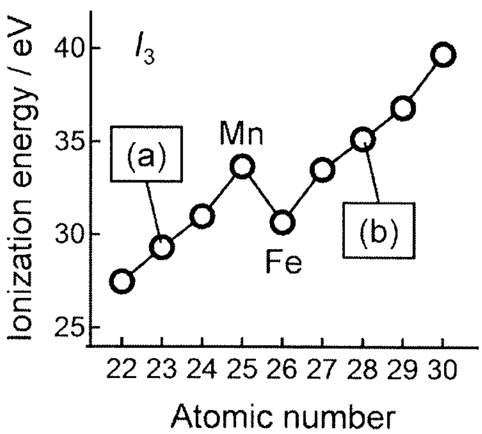
(4) Describe an experimental method to obtain the bond length of a homonuclear diatomic molecule in about 20 words.

Problem 3 (Inorganic Chemistry)

Put your solution in the answer sheet provided for Problem 3.

I. Answer the questions below related to the nth ionization energy, I_n.





(1) Write the chemical symbols for elements (a) and (b).

(2) Within a given period, there is generally a steady increase of I_n with increasing atomic number. Explain the reason.

(3) Contrary to the trend in (2), I_1 of Mg is larger than that of Al. Explain the reason.

(4) Contrary to the trend in (2), I_3 of Mn is larger than that of Fe. Explain the reason.

(5) Zr (atomic number: 40) and Hf (atomic number: 72) that are in the same group have similar I_3. Explain the reason.

II. Below is a statement about solid acids/bases. For the blanks (a) and (b), choose appropriate words from 'Brønsted acid', 'Brønsted base', 'Lewis acid', and 'Lewis base'. Also, explain the reason.

The surface of alumina is terminated with a hydroxyl group, which functions as a [(a)] site. However, after removing this hydroxyl group by heat treatment, the remaining surface Al site functions as a [(b)] site.

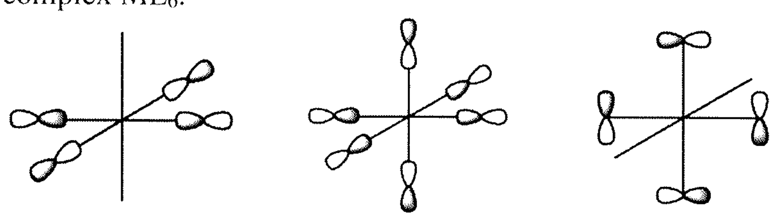
III. Write the chemical formulas and draw the chemical structures of the following coordination complexes. Provide all the geometrical and optical isomers if any.

(1) Hexaamminechromium(III) ion

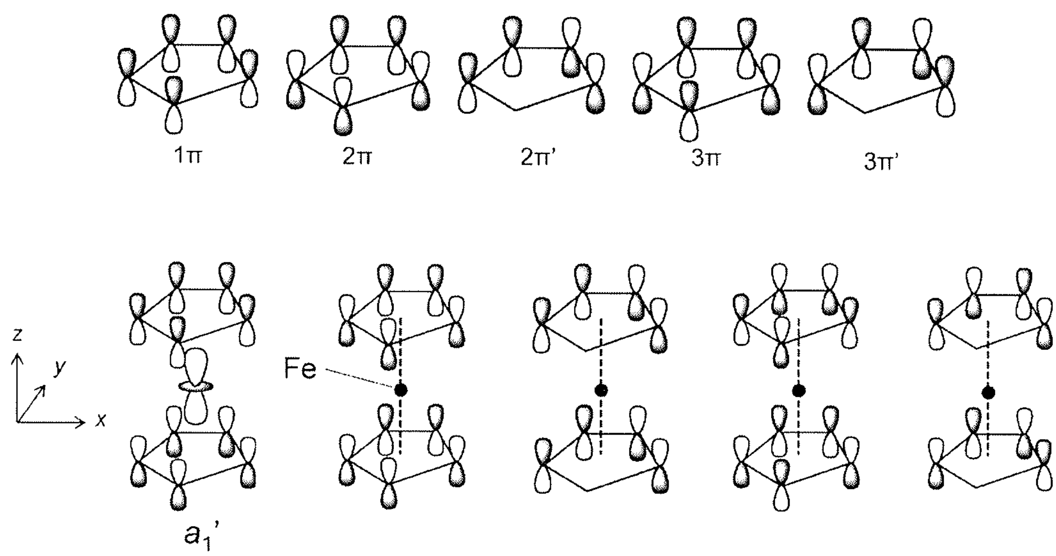
(2) Dichlorobis(ethylenediamine)cobalt(III) ion

IV. The *d* orbitals of a transition metal M in a coordination complex hybridize with the orbitals of ligands L. Answer the following questions.

(1) Draw the *d* orbitals that hybridize with the following *p* orbitals of ligands L in an octahedral coordination complex ML_6.

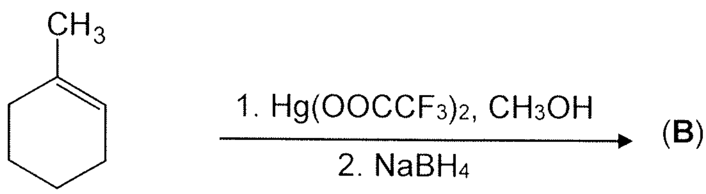


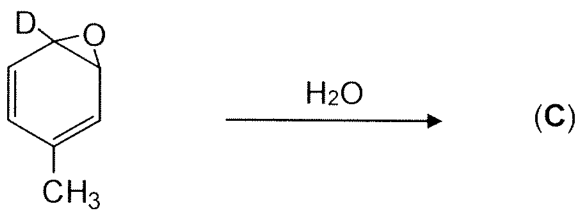
(2) A cyclopentadienyl group ($C_5H_5^-$), which is the ligand of ferrocene (formal chemical name: bis(η^5-cyclopentadienyl)iron(II)), has the following five π orbitals. The 1π orbitals hybridize with the d_{z^2} orbital of iron to form an a_1' orbital. Draw the *d* orbitals of iron that hybridize with the other π orbitals.

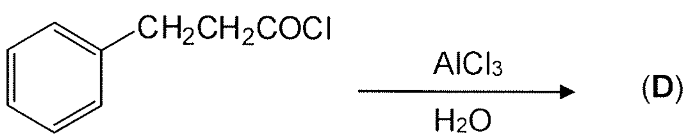


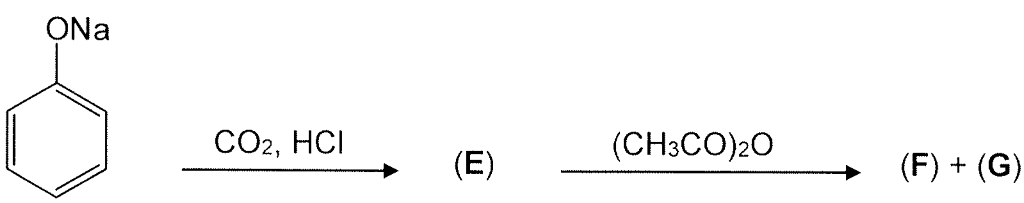
Problem 4 (Organic Chemistry)

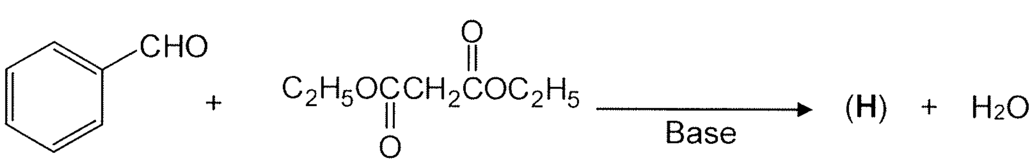
I. Draw the chemical formulas of the major products (**A**)–(**I**) in the following reactions.

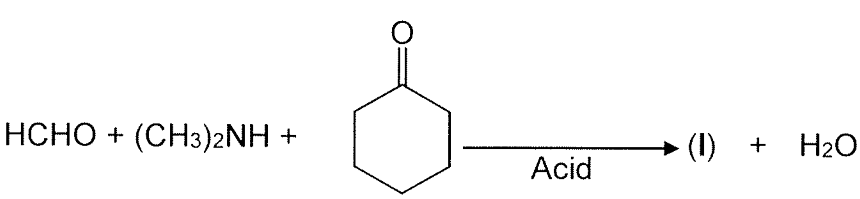












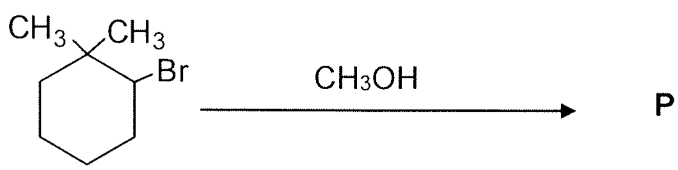
II. Answer the following questions regarding S_N2 and E2 reactions.

(1) For the example reaction of ethyl chloride and hydroxide ion, OH^-, draw the reaction coordinate, which represents the progress along the reaction pathway. Also, explain two main differences between the S_N2 and E2 reaction mechanisms.

(2) Explain differences when *tert*-butyl chloride is used instead of ethyl chloride in the above reaction, by use of the reaction coordinate.

(3) Hydroxide ion, OH^-, possesses the catalytic properties of a base. By referring to (1) and (2), explain the base catalysis.

III. Give two types of possible products, **P**, in the following reaction. Draw the reaction mechanism using curly arrows to show electron pair movements.



Problem 5 (Chemical Engineering 1)

The temperature of the earth's surface is determined by the balance of radiant heat from the sun and from the earth. Answer the following questions about the temperature of the earth's surface, T_E [K]. The following assumptions are made. The sun and the earth are spherical black bodies with uniform and steady temperatures. Outer space is an absolute zero Kelvin black body. The distance between the sun and the earth, L [m], is constant and the earth's radius, R_E [m], can be ignored compared with L. The size of the sun as seen from the earth is negligible. Use the following numbers, and calculate in four significant digits.

Stefan-Boltzmann constant	σ	=	5.670×10^{-8}	$\mathrm{W\ m^{-2}\ K^{-4}}$
Temperature of the sun's surface	T_S	=	5.780×10^{3}	K
Radius of the sun	R_S	=	6.960×10^{8}	m
Radius of the earth	R_E	=	6.378×10^{6}	m
Distance between the sun and the earth	L	=	1.496×10^{11}	m

(1) The amount of the radiation heat from the sun incident vertically on one square meter of area on the surface of the earth's atmosphere per second is called the solar constant S [$\mathrm{W\ m^{-2}}$]. Find the value of S.

(2) Assume that the earth's atmosphere does not exist. Express the heat balance equation on the earth's surface, and calculate T_E.

(3) A part of the radiation heat incident on the surface of the earth's atmosphere is reflected by clouds before reaching the earth's surface with reflectance α. When $\alpha = 0.3$, calculate T_E. Here, the effect of the atmosphere is ignored.

(4) Consider the influence of the atmosphere. As shown in Figure 1, a uniform atmospheric layer of negligible thickness exists over the earth's surface interposing an air layer whose thermal absorption and thermal transfer can be ignored. Above the atmospheric layer is outer space. The height of the atmospheric layer from the earth's surface can be ignored

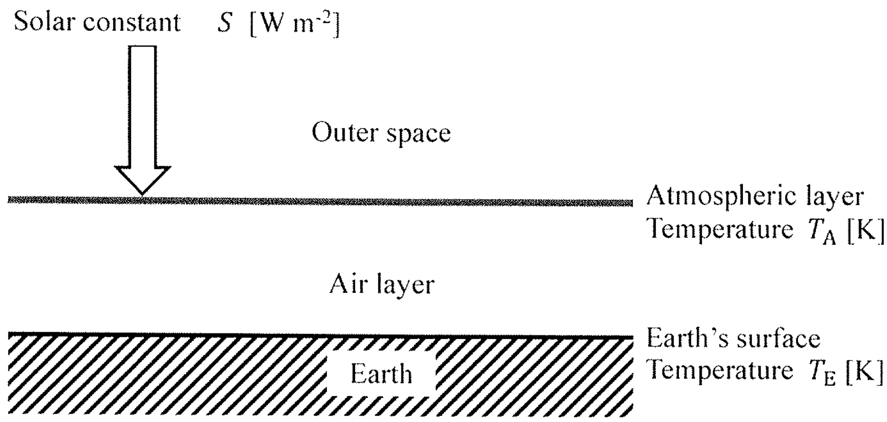


Figure 1

compared with the radius of the earth. The temperature of the atmospheric layer is T_A [K]. The emission from the earth's surface is infrared radiation and is absorbed in the atmospheric layer with absorbance ε. The emission from the sun is visible light and is reflected at the earth's surface with $\alpha = 0.3$. Visible light absorption by the air and atmospheric layers can be ignored. Answer the following questions.

i) Give the heat balance equations on the earth's surface and around the atmospheric layer, respectively. Note that the thermal emission rate and the absorption rate are equal, and there is equivalent radiation from the atmospheric layer to outer space and to the earth's surface.

ii) In case of $\varepsilon = 0.8$, calculate T_E and T_A, respectively.

iii) The status when $\varepsilon = 0.8$ is the earth's atmosphere 200 years before the present. Since then T_E has increased 1 K until the present. Calculate the value of the present ε.

iv) Describe the cause of the change in value of ε in these 200 years in about 30 words.

v) Describe the reason why the value of ε is about 0.8 in about 30 words.

vi) Enumerate the names of four substances existing in the atmospheric layer causing the change in ε.

vii) There is a theory that the rate of the T_E increase is accelerated when global warming is progressing. Describe one of the natural phenomena which can be grounds for the theory and one which can be evidence against the theory in about 30 words, respectively.

Problem 6 (Chemical Engineering 2)

Solid carbon in the form of a spherical particle reacts with oxygen in air according to $C + O_2 \rightarrow CO_2$. Figure 1 shows the particle, the gaseous boundary layer, and the concentration profile of oxygen. Oxygen diffuses from the gas phase through the boundary layer to the particle surface, and reacts with carbon on the surface. Carbon dioxide diffuses to the gas phase without affecting the diffusion of oxygen and the reaction. The radius of the particle R [m] decreases along with time t [s] from the initial radius R_0 [m] at $t = 0$. The molar density of the particle is ρ_m [mol m^{-3}], the kinematic viscosity of the gas phase is ν [m^2 s^{-1}], and the relative velocity of the particle to the gas phase is u [m s^{-1}]. The concentration of oxygen in the gas phase and that at the surface are C [mol m^{-3}] and C_S [mol m^{-3}], respectively. The diffusion coefficient of oxygen in the gas phase, and the mass transfer coefficient of oxygen in the boundary layer are D [m^2 s^{-1}] and k_G [m s^{-1}], respectively. The reaction rate r_S [mol m^{-2} s^{-1}] based on the surface area of the particle is expressed as $r_S = k_R C_S$ using reaction constant k_R [m s^{-1}]. The relation between Sherwood number Sh, particle Reynolds number Re, and Schmidt number Sc, which are the non-dimensional numbers around the particle, is expressed as $Sh = 2.0 + 0.60\, Re^{1/2}\, Sc^{1/3}$. The reaction is conducted at a constant temperature T [K], and the heat of reaction can be ignored. The parameters ν, ρ_m, C, D, and u are constant.

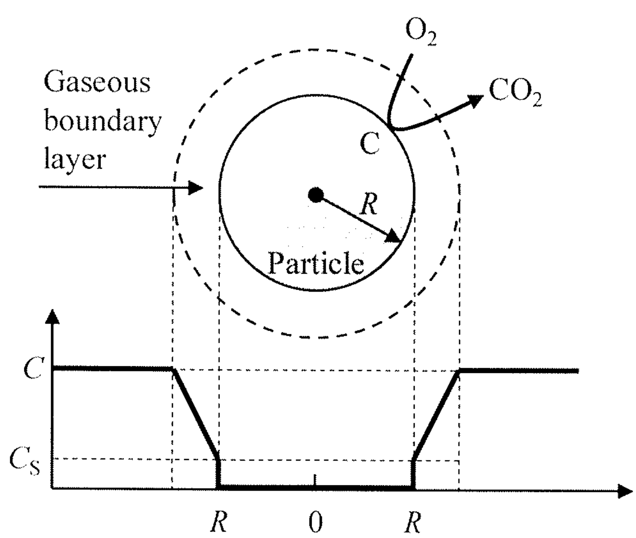


Figure 1

Answer the following questions.

(1) Express Re, Sc, and Sh using the given parameters.

(2) Consider oxygen. State what corresponds to the rate of oxygen diffusion to the surface.

(3) Express r_S using C, k_R, and k_G.

(4) Derive the differential equation that expresses the time change of R.

(5) Consider the case of $k_G >> k_R$. First, answer whether reaction or diffusion controls the time change of R, and state the reason. Then, express R as a function of t.

(6) Consider the case of $k_R >> k_G$. First, answer whether reaction or diffusion controls the time change of R, and state the reason. Then, express R as a function of t when $u = 0$.

(7) Present graphs with rough sketches of the features of $R(t)$ obtained in questions (5) and (6). Make separate graphs for each $R(t)$. In each graph, set R as the vertical axis and t as the horizontal axis, and indicate the intercepts using the given parameters.

(8) Under the condition of $u = 0$, particles with different R_0 were reacted at $T = 1000$ K and $T = 1600$ K. At each temperature, R decreased according to either of the graphs presented in question (7). The time τ [s] until $R = 0$ was obtained as shown in Tables 1 and 2 for 1000 K and 1600 K, respectively. Determine which is reaction controlled, and which is diffusion controlled, and state the reason.

Table 1

R_0 [m]	τ [s]
4.0×10^{-5}	3.7
5.0×10^{-5}	4.6
6.0×10^{-5}	5.6

Table 2

R_0 [m]	τ [s]
4.0×10^{-5}	4.1×10^{-2}
5.0×10^{-5}	6.4×10^{-2}
6.0×10^{-5}	9.2×10^{-2}

Problem 7 (Mathematics)

I. Obtain the general solutions for the following differential equations.

(1) $\dfrac{dy}{dx} = ay(b-y) \qquad (a > 0, b > 0)$

(2) $\dfrac{d^3y}{dx^3} + \dfrac{d^2y}{dx^2} + \dfrac{dy}{dx} + y = 0$

II. Calculate the values of the following integrals.

(1) $\displaystyle\int_{-a}^{a} \frac{b}{a}\sqrt{a^2 - x^2}\,dx \qquad (a > 0, b > 0)$

(2) $\displaystyle\int_{1}^{e} \frac{\log_e x}{x^2}\,dx \qquad$ (e: Euler's number)

III. The combustion reaction of a hydrogen/oxygen gas mixture proceeds by radical chain reactions. The occurrence boundaries for the combustion reaction are called explosion limits, and the explosion limit of a hydrogen/oxygen gas mixture at reduced pressure (the second explosion limit) can be estimated considering the following four main elementary reactions.

$$H + O_2 \xrightarrow{k_1} OH + O \qquad [1]$$

$$O + H_2 \xrightarrow{k_2} OH + H \qquad [2]$$

$$OH + H_2 \xrightarrow{k_3} H_2O + H \qquad [3]$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \qquad [4]$$

Here, M represents a third body. The time derivatives of the concentrations of the radical species can be described by the following equations.

$$\frac{d[O]}{dt} = k_1[O_2][H] - k_2[H_2][O] \qquad [5]$$

$$\frac{d[OH]}{dt} = k_1[O_2][H] + k_2[H_2][O] - k_3[H_2][OH] \qquad [6]$$

$$\frac{d[H]}{dt} = -k_1[O_2][H] + k_2[H_2][O] + k_3[H_2][OH] - k_4[O_2][M][H] \qquad [7]$$

Here, [O], [O_2], [OH], [H], and [H_2] represent the concentrations of the species O, O_2, OH, H, and H_2, respectively, k_1, k_2, k_3, and k_4 are the reaction rate constants of the reactions [1] - [4], respectively, and t represents time. Answer the following questions.

(1) The equations [5] - [7] can be written as the following equation [8] using $\mathbf{X} = \begin{pmatrix} [\mathrm{O}] \\ [\mathrm{OH}] \\ [\mathrm{H}] \end{pmatrix}$.

$$\frac{\mathrm{d}\mathbf{X}}{\mathrm{d}t} = \mathbf{AX} \qquad [8]$$

Obtain the matrix **A**, using $a = k_1[\mathrm{O_2}]$, $b = k_2[\mathrm{H_2}]$, $c = k_3[\mathrm{H_2}]$, and $d = k_4[\mathrm{O_2}][\mathrm{M}]$, where a, b, c, and d can be assumed to be positive constants.

(2) The solution of equation [8] can be given by equation [9].

$$\mathbf{X} = \mathbf{X}_0 \sum \xi_i \exp(\lambda_i t) \qquad [9]$$

Here, $\mathbf{X}_0$ is the value of $\mathbf{X}$ at $t = 0$, and ξ_i are coefficients.

Derive the equation, whose solutions are λ_i.

(3) If at least one of the solutions λ_i of the equation derived in question (2) is a positive real number, the concentration **X** will increase with time and diverge. It is considered that this corresponds to the occurrence of explosion.

According to this consideration, describe the condition for the occurrence of explosion using some of a, b, c, and d, as needed.