

Graduate Course of Chemical System Engineering

I D n u m b e r

(Major subjects for the Master's program admission)

Tuesday, August 27, 2019 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	8~10
Problem 5	Chemical Engineering 1	12~14
Problem 6	Chemical Engineering 2	15~16
Problem 7	Mathematics	17~18

Note:

1. Four 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.
2. Do not open the problem file until directed by the presiding officer.
3. Write down your ID number on each of all the four 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 concerning the reaction at constant pressure,



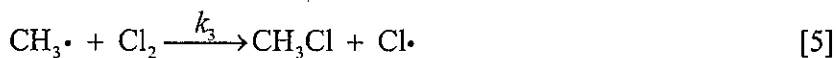
where k_r and k_r' are the first-order rate constants for the forward and backward reactions. Use the standard enthalpy of the reaction at 298 K, $\Delta_r H^\circ = -120 \text{ kJ mol}^{-1}$, the standard entropy of the reaction at 298 K, $\Delta_r S^\circ = -150 \text{ J K}^{-1} \text{ mol}^{-1}$, and the gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (1) Calculate the equilibrium constant K at 298 K.
- (2) Give the relationship between the equilibrium constant K and temperature T , and calculate K at 333 K. Assume that $\Delta_r H^\circ$ is constant at different temperatures.
- (3) When the temperature of the system at equilibrium is increased suddenly, the composition relaxes exponentially to a new equilibrium composition. Derive the equation, $x = x_0 \exp[-(k_r + k_r')t]$ where x_0 is the deviation of the concentration of A from the new equilibrium immediately after the temperature jump and x is the deviation from the new equilibrium at the new temperature after a time t .

II. Consider the gas-phase reaction of methane and chlorine,



which proceeds via the following elementary steps;



where k_i is the reaction rate constant for reaction i. Answer the questions below.

- (1) Give the time dependence of the concentrations of the chlorine radical $[\text{Cl}\cdot]$ and the methyl radical $[\text{CH}_3\cdot]$ using $[\text{CH}_4]$, $[\text{Cl}\cdot]$, $[\text{Cl}_2]$, $[\text{CH}_3\cdot]$ and the rate constants.
- (2) Give $[\text{Cl}\cdot]$ using the steady-state approximation for $[\text{CH}_3\cdot]$ and $[\text{Cl}\cdot]$.

- (3) When the approximation in (2) is applicable, give the formation rate of CH_3Cl . Obtain the reaction orders for methane and chlorine, and explain their physical meaning.
- (4) If the activation energies for reactions [3]-[6] are 58, 16, 4.0, 7.0 kJ mol^{-1} , respectively, does the rate go up or down with increasing temperature? Explain.

III. Answer the following questions regarding the mixing of gases. Assume that the gases always behave ideally, no heat is exchanged, and no reaction between the gases occurs. At pressure p and temperature T , the molar Gibbs energy can be described as equation 7:

$$\mu_i = \mu_i^\circ + RT \ln \left(\frac{p_i}{p^\circ} \right) \quad [7]$$

where R is the gas constant ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) and p° is the standard pressure.

- (1) Gas A (n_A mol, volume V_A) and gas B (n_B mol, volume V_B) are mixed in a volume V . Mole fractions of A and B are x_A and x_B , $V = V_A + V_B$, and $n = n_A + n_B$.

Using equation 7, derive the Gibbs energy of mixing as the following equation 8 when the mixing is carried out at constant pressure.

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B) \quad [8]$$

- (2) Explain why the mixing of the ideal gases is spontaneous.
- (3) Give the entropy of gas mixing $\Delta_{\text{mix}}S$ and the enthalpy of gas mixing $\Delta_{\text{mix}}H$.
- (4) A container is divided into three equal compartments with gas A (2.0 mol), gas B (3.0 mol) and gas C (5.0 mol) at 373 K (Figure 1). When the partitions are removed to mix gases A, B, C completely, calculate $\Delta_{\text{mix}}G$.

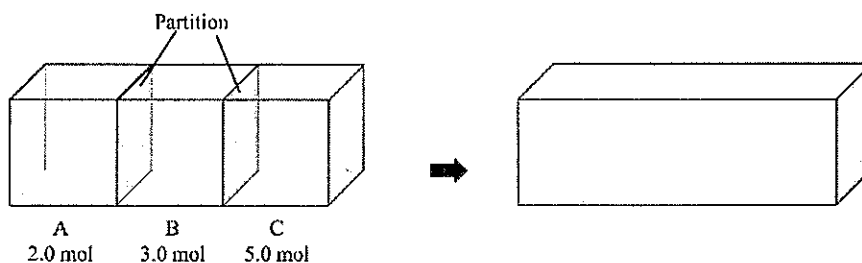


Figure 1

Problem 2 (Physical Chemistry 2)

I. Answer the questions below related to atomic orbitals.

Hydrogen atomic wave functions depend on the principal quantum number n , the azimuthal quantum number l , and the magnetic quantum number m . For example, the 1s orbital is designated by $(n, l, m) = (1, 0, 0)$ and its wave function is shown in the (r, θ, ϕ) coordinate system as follows (m_e : electron mass, ϵ_0 : vacuum permittivity, e : elementary charge, \hbar : reduced Planck constant).

$$\psi_{1,0,0}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} \exp\left(-\frac{r}{a_0}\right) \quad [1]$$

Note that $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$.

(1) Consider the 1s orbital.

- i) Give the magnitude of the orbital angular momentum.
- ii) Describe the radial distribution function $P(r)$. Here, the probability that an electron will be found in a spherical shell of thickness dr at a distance r from an atomic nucleus is expressed as $P(r)dr$.
- iii) Calculate the radius at which an electron will be most probably found.
- iv) Express the energy eigenvalue using a_0 , m_e , and \hbar . Here, the Hamiltonian \hat{H} of the hydrogen atom is given as follows.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad [2]$$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad [3]$$

- (2) List all combinations of quantum numbers (n, l, m) that designate the 3d orbitals.
- (3) For atoms other than hydrogen, explain the order of the energy levels of the 3s, 3p, and 3d orbitals from the standpoint of how the orbitals extend in space in about 50 words.

II. Answer the questions below related to molecular orbitals. Here, apply the Hückel method and assume that all overlap integrals between different carbon atoms are equal to zero, all Coulomb integrals are equal to α , all resonance integrals between neighboring carbon atoms are equal to β , and all resonance integrals between non-neighboring carbon atoms are equal to zero. Electron configuration obeys the Pauli Exclusion Principle and the Hund's rule. Here, the value of $|\beta|$ is large enough compared to spin correlation. For example, the π -electron configuration of benzene in the ground state is shown in Figure 1.

(1) Consider cyclobutadiene.

- i) Describe the secular determinant.
- ii) Calculate the π -orbital energies.
- iii) Draw the π -electron configuration in the ground state. Here, refer to Figure 1 and use up-down arrows to express different spin states.
- iv) Calculate the delocalization energy relative to the total π -electron energy of two ethylene molecules. Here, the total π -electron energy of an ethylene molecule is equal to $2\alpha + 2\beta$.
- v) Based on the results of iii) and iv), explain the stability and magnetic character of the molecule in about 50 words.

(2) Consider the cyclopentadienyl anion (Figure 2). Resolving the secular determinant gives the π -orbital energies of $\alpha + 2\beta$, $\alpha + 0.62\beta$, $\alpha + 0.62\beta$, $\alpha - 1.62\beta$, and $\alpha - 1.62\beta$.

- i) Briefly explain the stability of the cyclopentadienyl anion in about 30 words.
- ii) Based on the result of i), describe a peculiar property expected of cyclopentadiene.

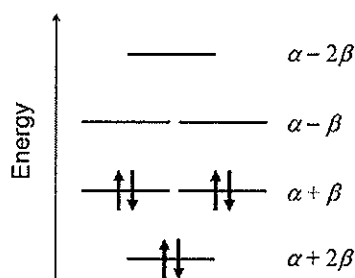


Figure 1

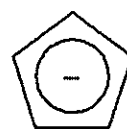


Figure 2

Problem 3 (Inorganic Chemistry)

I. Answer the following questions on pK_a .

- (1) Give the definition of pK_a and discuss it in about 20 words.
- (2) Place HClO and HClO_4 in order of decreasing pK_a value, and explain the reason in about 20 words.
- (3) Place HClO and HIO in order of decreasing pK_a value, and explain the reason in about 20 words.
- (4) Assume the pK_a of acetic acid is 4.7 and the self-ionization constant of water is 1.0×10^{-14} . Also, let all thermodynamic activity coefficients of chemical species in aqueous solution be taken as unity (the number 1).
 - i) Calculate the pH of a 0.10 mol/L acetic acid aqueous solution.
 - ii) Calculate the pH of a mixed aqueous solution of 50 mL of 0.050 mol/L acetic acid solution and 30 mL of 0.050 mol/L sodium acetate solution. You may assume the dissociation degree of acetic acid is sufficiently small and that of sodium acetate is sufficiently large.

II. Answer the questions below related to aluminum.

- (1) Aluminum is an amphoteric substance. Briefly explain the reason by showing representative chemical reactions.
- (2) An industrial method of manufacturing aluminum oxide is known as the Bayer process. In this process, a main ore containing aluminum, A, is treated with a hot solution of B. After the solution is filtered to remove impurities, the solution is cooled down to obtain a precipitate of C. Finally, aluminum oxide is obtained by calcining the precipitate.

Give A, B and C.

(3) An industrial method of manufacturing aluminum metal from aluminum oxide is known as the Hall-Héroult process.

i) Explain the features of the Hall-Héroult process by showing the difference between the Hall-Héroult process and the pig iron production process from iron ore in about 40 words.

ii) Indicate the reactions taking place at both cathode and anode in the Hall-Héroult process.

iii) Aluminum metal is known as a metal with high recycling rate. Discuss the reason in about 20 words.

(4) The most common forms of crystalline aluminum oxide are α -alumina with corundum structure and γ -alumina with spinel structure.

i) Describe what you know about the differences in the crystal structures in about 40 words.

ii) Explain which crystal structure is a stable phase.

iii) Give examples of material properties and applications of these two aluminum oxides in about 40 words.

III. Answer the following questions on half-life.

(1) Let the initial quantity of the substance, the quantity that still remains, and the decay constant be N_0 , N and λ , respectively, and let the decay be described as follows.

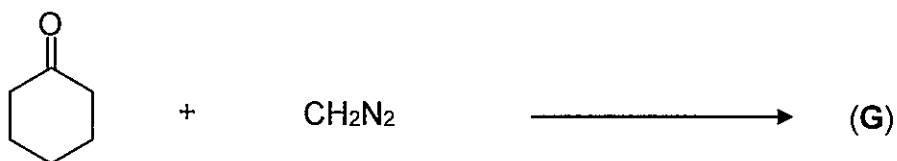
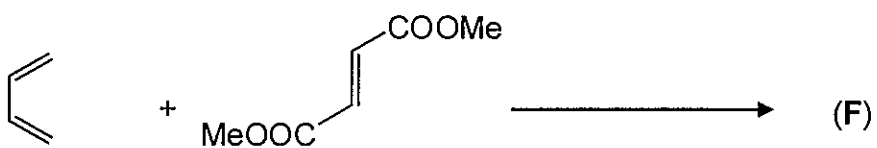
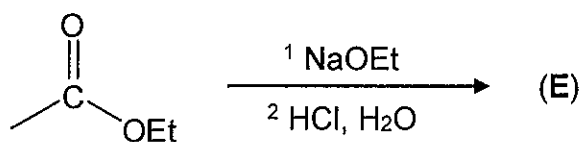
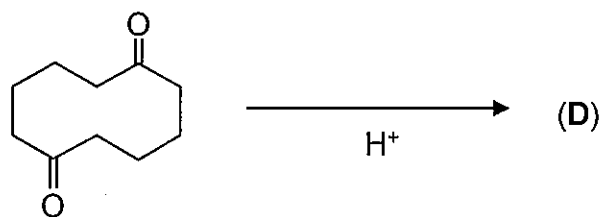
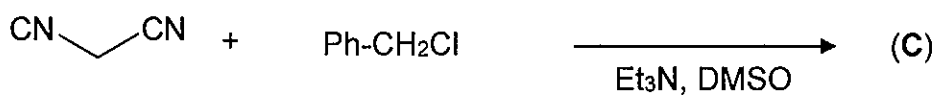
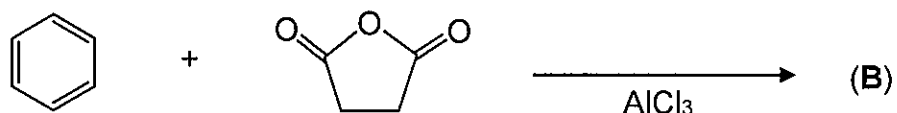
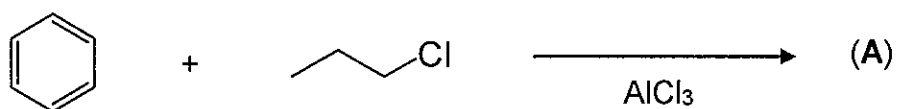
$$-\frac{dN}{dt} = \lambda N \quad [1]$$

Describe the time t for $\frac{N}{N_0} = \frac{1}{2}$ (half-life) using λ .

(2) Natural uranium, U, consists of two major isotopes, ^{235}U and ^{238}U . The half-lives of ^{235}U and ^{238}U are 0.70×10^9 and 4.5×10^9 years, respectively. The natural abundance ratio of ^{235}U is 0.0072 at present. Calculate the ratio of ^{235}U 4.6 billion years ago.

Problem 4 (Organic Chemistry)

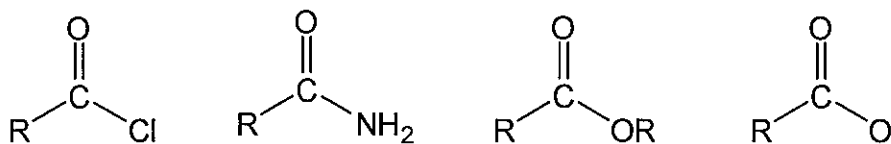
- I. Draw the chemical formulas of the major products (A)~(G) in the following reactions, and the reaction mechanism using curly arrows to show electron pair movements. If necessary, specify the stereochemistry.



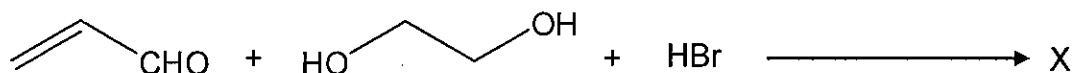
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II. Answer the following questions regarding the analysis of organic compounds.

- (1) The C=O stretching vibration band in the following carbonyl compounds and carboxylate ion appears at wavenumbers between 1600~1900 cm^{-1} . Draw the compounds and the ion in the order of descending wavenumbers. Also, explain the reason.

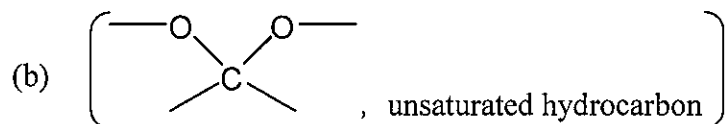
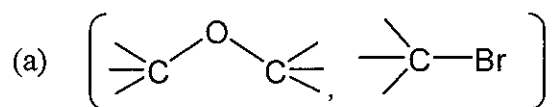


- (2) A compound X was obtained through the following reaction with 100% yield.



Consider that the atomic weights of hydrogen, carbon, oxygen, and bromine are 1, 12, 16, and 80.

- i) When X was analyzed by mass spectrometry, the highest m/z value was 181. Other signals at $m/z=73$ and 108 were also detected. Explain what you can tell about the structure from this result.
- ii) For the blanks (a)~(c), select the appropriate choice from the pair in parentheses. Analysis by ^{13}C NMR of compound X showed a resonance at chemical shift 70 ppm due to (a) . The NMR also showed another resonance at 100 ppm due to (b) . In addition, resonances at 40 and 30 ppm for (c) hydrocarbons were detected. The signal intensity of the band at 70 ppm was double those of the other bands.



(c) (saturated, unsaturated)

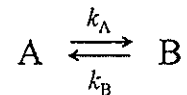
iii) Observation of compound X by infrared spectroscopy revealed that the absorption band between $1600\sim 1900\text{ cm}^{-1}$, which corresponds to carbonyl groups, and the one between $3000\sim 4000\text{ cm}^{-1}$, which can be assigned to groups, never appeared. For the blank (d), provide an appropriate word.

iv) Write the chemical formula and draw the chemical structure of compound X.

Provide all the candidates if more than one is possible.

Problem 5 (Chemical Engineering 1)

In a well-mixed reactor, for the species A and B, the reversible liquid-phase reaction below proceeds. The reaction rate constants are k_A [s^{-1}] and k_B [s^{-1}]. Assume the volume and temperature are constant and answer the following questions.



- (1) Consider the reaction occurring in a batch reactor. The reaction starts with an initial concentration of A of C_{A0} [mol m^{-3}], and at reaction time t [s], the concentrations of A and B, and the conversion of A are represented as C_A [mol m^{-3}], C_B [mol m^{-3}], and x_A . The volume of the reactor is V [m^3].
- Describe the differential equations that give the time changes of C_A and C_B .
 - Solve the equations described in i), and express C_A and C_B as functions of t .
 - Describe x_A as a function of t .
 - Obtain x_A at steady-state.

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(2) Consider the steady-state mass transfer across a membrane. As shown in Figure 1, solutions are separated by a semi-permeable membrane where only the species B can diffuse. The concentrations of B on both sides of the membrane are C_{B1} [mol m⁻³] and C_{B2} [mol m⁻³] in the bulk and C_{BS1} [mol m⁻³] and C_{BS2} [mol m⁻³] at the surfaces of the membrane.

- i) Draw the concentration distributions of the species B in the boundary films and in the semi-permeable membrane.
- ii) Derive the overall mass transfer coefficient K_O [m s⁻¹] using the boundary film mass transfer coefficients, K_1 [m s⁻¹] and K_2 [m s⁻¹], on both sides of the membrane; and the membrane permeability coefficient, K_M [m s⁻¹].

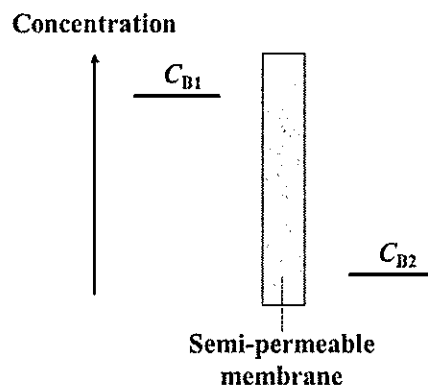


Figure 1

(3) Consider the reaction and diffusion in two continuous stirred-tank reactors separated by the same membrane. As shown in Figure 2, the volumes and flow rates of Tanks 1 and 2 are V_1 [m³], V_2 [m³], F_1 [m³ s⁻¹], and F_2 [m³ s⁻¹], respectively. A is provided to Tank 1 at a concentration of C_{AO} [mol m⁻³], but not to Tank 2. The concentrations of A and B in Tanks 1 and 2 are C_{A1} [mol m⁻³], C_{B1} [mol m⁻³], C_{A2} [mol m⁻³], and C_{B2} [mol m⁻³], respectively.

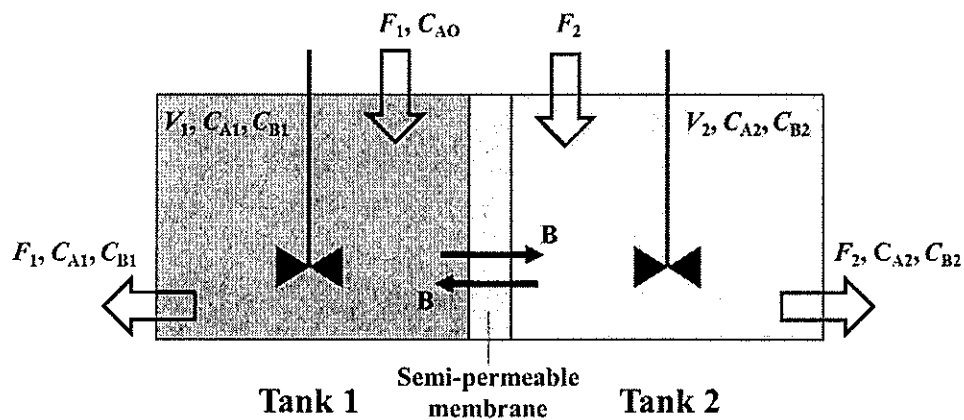


Figure 2

- i) Describe the differential equations that give the time changes of C_{A1} , C_{B1} , C_{A2} , and C_{B2} . Use the surface area S [m²] and the overall mass transfer coefficient K_O [m s⁻¹] of the semi-permeable membrane, if necessary.
- ii) At steady-state the reaction rate of A in Tank 1, x_{A1} , can be expressed in the partial fraction decomposition described below. First, taking $C_{B2} = aC_{A2}$, $C_{B1} = bC_{A2}$, and $C_{A2} = dC_{A1}$, express d using a and b . Second, express x_{A1} in a partial fraction decomposition using $(\frac{a}{b})$. Lastly, fill in the blanks from ① to ⑧ by eliminating a and b , and transforming the formula. Note that none of the blanks contains a partial fraction.

$$x_{A1} = 1 - \frac{\frac{F_1}{V_1 k_A}}{1 + \frac{\boxed{①}}{\boxed{②}} - \frac{1}{1 + \frac{\boxed{①}}{\boxed{③}} + \frac{\frac{1}{\boxed{③}}}{\frac{1}{\boxed{④}} + \frac{1}{\boxed{⑤}} + \frac{\boxed{⑥}}{\frac{\boxed{⑦}}{\boxed{⑤}} + \frac{1}{\boxed{⑧}}}}}}$$

- iii) Determine whether x_{A1} is greater when V_2 or F_2 each becomes infinite and explain the reasons in a few lines.

Problem 6 (Chemical Engineering 2)

Answer the following questions related to the motion of spherical particles (glass particles or cells) in a fluid. Assume that temperature is uniform and constant.

Use the following numbers, if needed.

Density of water $\rho_W = 9.97 \times 10^2 \text{ kg m}^{-3}$, Viscosity of water $\mu_W = 8.90 \times 10^{-4} \text{ Pa s}$

Density of glass $\rho_G = 2.40 \times 10^3 \text{ kg m}^{-3}$, Density of cells $\rho_C = 1.05 \times 10^3 \text{ kg m}^{-3}$

Acceleration of gravity $g = 9.81 \text{ m s}^{-2}$

(1) A particle of density ρ_p [kg m^{-3}] and diameter D_p [m] is settling at a velocity v [m s^{-1}] under the acceleration of gravity g [m s^{-2}] in a stationary fluid of density ρ_f [kg m^{-3}] and viscosity μ [Pa s]. Answer the following questions.

i) Describe the equation of motion for the particle. The resistance force R [N] acting on the particle from the fluid is given by the following equation [1]. C_D [dimensionless] is the drag coefficient.

$$R = C_D \left(\frac{\pi D_p^2}{4} \right) \left(\frac{1}{2} \rho_f v^2 \right) \quad [1]$$

ii) Describe the particle Reynolds number Re_p for the fluid flow surrounding the settling particle in which the characteristic length is the diameter of the particle D_p .

iii) When $Re_p < 2$, the fluid flow surrounding the settling particle is laminar and Stokes' law can be applied. In this case, C_D can be approximated as follows.

$$C_D = \frac{24}{Re_p} \quad [2]$$

Obtain the terminal velocity v_t [m s^{-1}] when the settling velocity of the particle becomes constant.

iv) Calculate v_t and Re_p at v_t of the settling spherical glass particle of $D_p = 50.0 \text{ }\mu\text{m}$ in still water.

v) Consider the case when minute glass particles of $D_p < 0.1 \text{ }\mu\text{m}$ are suspended in water. Describe the reason why v_t obtained in iii) no longer holds, and the suspended state continues for a long time in about 30 words.

- (2) As shown in Figure 1, a cylindrical container is fixed perpendicularly to a rotating shaft which rotates at constant angular velocity ω [rad s⁻¹]. Fluid motion, the radial distribution of particles, the effect of gravity, interactions between particles, the thickness of accumulated particles at the end of the container, and fluctuations at the start and stop of rotation can be ignored. Stokes' law can be applied for the frictional force acting on the particles. Answer the following questions.

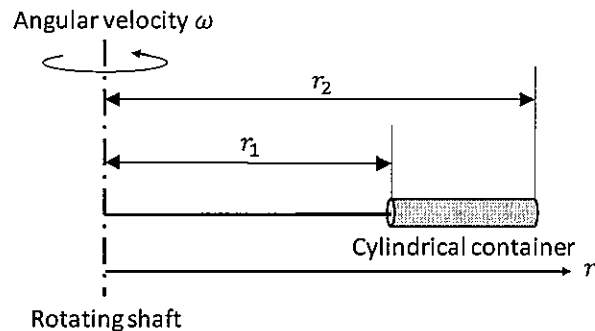


Figure 1

- i) Express the centrifugal force applied to a particle of density ρ_p [kg m⁻³] and diameter D_p [m] in the container in the r direction.
- ii) Describe the equation of motion of a particle in the container in the r direction. The density and the viscosity of the fluid are ρ_f [kg m⁻³] and μ [Pa s], respectively. The velocity of the particle rapidly reaches terminal velocity v_t [m s⁻¹] with the change in centrifugal force.
- iii) For a particle that is at $r = r_1$ at time $t = 0$ s, obtain the time t_r [s] to reach $r = r_2$.
- iv) The container is filled with water in which spherical glass particles having a distribution of diameters are suspended. The position of the container is $r_1 = 0.100$ m, $r_2 = 0.150$ m and the container is rotating at 180 rpm. Calculate the time required to recover all particles not less than $D_p = 50.0$ μm at the end of the container.
- v) The container is filled with water in which spherical cells having a diameter of $D_p = 10.0$ μm are suspended. The position of the container is the same as that described in iv). Calculate the rotational speed required to recover all cells in 180 s at the end of the container.
- vi) In the case of v), enumerate three measures to recover cells in a shorter time and describe the problems to implement each measure.

Problem 7 (Mathematics)

I. Answer the following questions.

(1) Obtain the eigenvalues and eigenvectors of the following matrix.

$$\begin{pmatrix} 1 & 1 & 2 \\ 0 & 2 & -1 \\ 0 & 0 & 3 \end{pmatrix}$$

(2) Solve the following differential equation.

$$\frac{d^2y}{dx^2} + 3\frac{dy}{dx} + 2y = \cos x$$

(3) Obtain the area of the enclosed part of the figure represented by the following equation.

$$x^{\frac{2}{3}} + y^{\frac{2}{3}} = a^{\frac{2}{3}}$$

II. Regarding the relationship between elapsed time t and concentration c of a product of a reaction, the following 10 values were observed for c at $t = 0.500$.

0.820 0.840 0.870 0.910 0.920 0.870 0.890 0.880 0.860 0.890

(1) Answer the following questions on the observed c at $t = 0.500$.

- i) Obtain the average, \bar{c} .
- ii) Define the i -th observed concentration as c_i and the number of observations as n , and give an expression for the standard deviation, σ .
- iii) Obtain σ for the observed 10 values above.

Then, additional observations were obtained for this chemical reaction; $c = 1.05$ at $t = 1.50$, $c = 1.15$ at $t = 2.50$, $c = 1.26$ at $t = 3.50$, and $c = 1.33$ at $t = 4.50$. Setting c at $t = 0.500$ as the average obtained in (1), answer the following questions.

(2) The concentration c can be expressed as a linear function of time t . The following equations give the factors a and b for a linear relationship, $y = a + bx$ ($x \in X$), for n observations at condition X and result Y , where y is the estimated value of Y . Note that the i -th measurement condition ($i = 1, 2, \dots, n$) and the observed results are denoted as X_i and Y_i , respectively.

$$a = \frac{\sum_{i=1}^n Y_i \sum_{i=1}^n X_i^2 - \sum_{i=1}^n X_i \sum_{i=1}^n X_i Y_i}{n \sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2}, \quad b = \frac{n \sum_{i=1}^n X_i Y_i - \sum_{i=1}^n X_i \sum_{i=1}^n Y_i}{n \sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2} \quad [1]$$

- i) Derive the equations [1] by minimizing the sum of squares of errors, $S = \sum_{i=1}^n (Y_i - y_i)^2$, with respect to the factors a and b .
- ii) Obtain the linear regression expression between c and t for this chemical reaction.
- iii) Calculate the coefficient of determination, R^2 , represented by the following equation, where \bar{Y} is the average of Y_i .

$$R^2 = 1 - \frac{\sum_{i=1}^n (Y_i - y_i)^2}{\sum_{i=1}^n (Y_i - \bar{Y})^2} \quad [2]$$

(3) Here, the representation, $c = t^{\frac{1}{5}}$, theoretically holds for this chemical reaction.

- i) Obtain the coefficient of determination, R'^2 , for the case of $c = t^{\frac{1}{5}}$ by equation [2].
- ii) Through the comparison of the obtained R'^2 with R^2 calculated in (2) iii), discuss which should be selected for the mathematical model for this chemical reaction, the linear expression in (2) ii) or the theoretical relationship $c = t^{\frac{1}{5}}$. Draw the curves of the linear expression in (2) ii) and $c = t^{\frac{1}{5}}$ schematically, and especially consider measurement errors and the characteristics of the statistical regression and the theoretical model.