

FY 2024

Department of

Chemical System Engineering

I D n u m b e r

(Major subjects for the Master's program admission)

Monday, August 28, 2023 13:00-15:30

You are expected to answer three problems selected from the five problems below.

Problem No.	Subject	Pages
Problem 1	Physical Chemistry 1	1~ 4
Problem 2	Physical Chemistry 2	5~ 6
Problem 3	Inorganic Chemistry	7
Problem 4	Chemical Engineering 1	9~11
Problem 5	Chemical Engineering 2	13~15

Note:

1. Three 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 booklet until directed by the presiding officer.
3. Write down your ID number on each of all the three 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 three 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 following questions (1) to (5) regarding heat and the change in internal energy in a closed system.

(1) Figure 1 shows the relation between pressure p and volume V (p - V diagram) of an ideal gas at different temperatures T_1 and T_2 . Derive the equations for the work done by 1.00 mol of the ideal gas, and the heat obtained by the gas in the paths ABC, and AC shown by the arrows in this figure, respectively. Use the necessary parameters among p_1 , p_2 , V_1 , V_2 , T_1 , T_2 , the gas constant, R , molar heat capacity at constant pressure, C_p , and molar heat capacity at constant volume, C_v . All the paths are reversible processes.

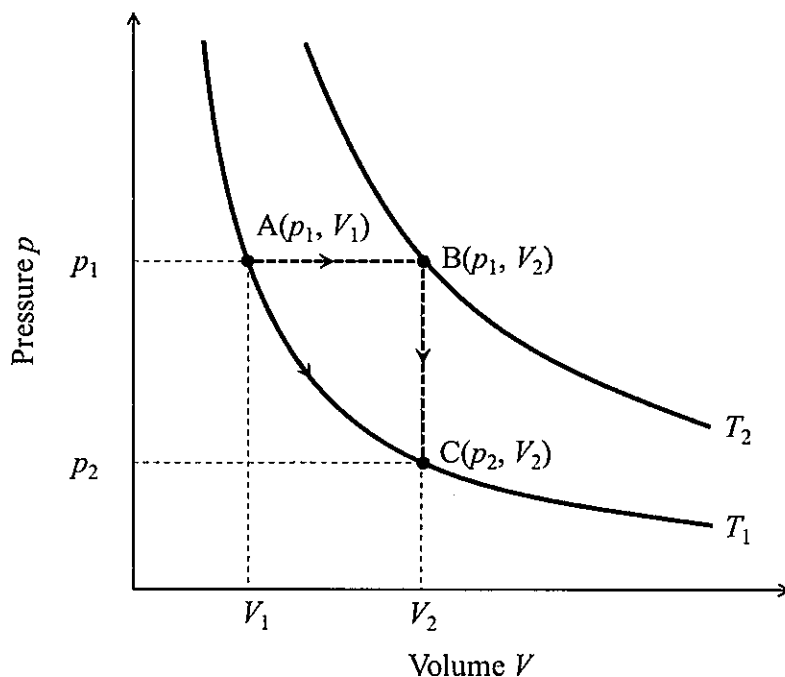


Figure 1

(2) Explain that the internal energy of an ideal gas is a function of state, based on the answers to question (1). Also, explain what conditions allow the ideal gas to expand without causing a temperature change.

- (3) Next, 1.00 mol of a van der Waals gas is isothermally and reversibly expanded. Assume that C_v is constant during this state change. Give an equation for the internal energy change dU . You may use the following equations: the equation of state for a van der Waals gas [1] (a and b are constants), and the relationship [2]. V_m is the molar volume.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad [1]$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad [2]$$

- (4) The p - V diagrams of a van der Waals gas under two different conditions are given as the bold curves in Figures 2(a) and (b). The figures also show the ideal gas behavior as the thin curves for comparison. Briefly describe the conditions required to achieve the van der Waals gas behavior shown in each figure.

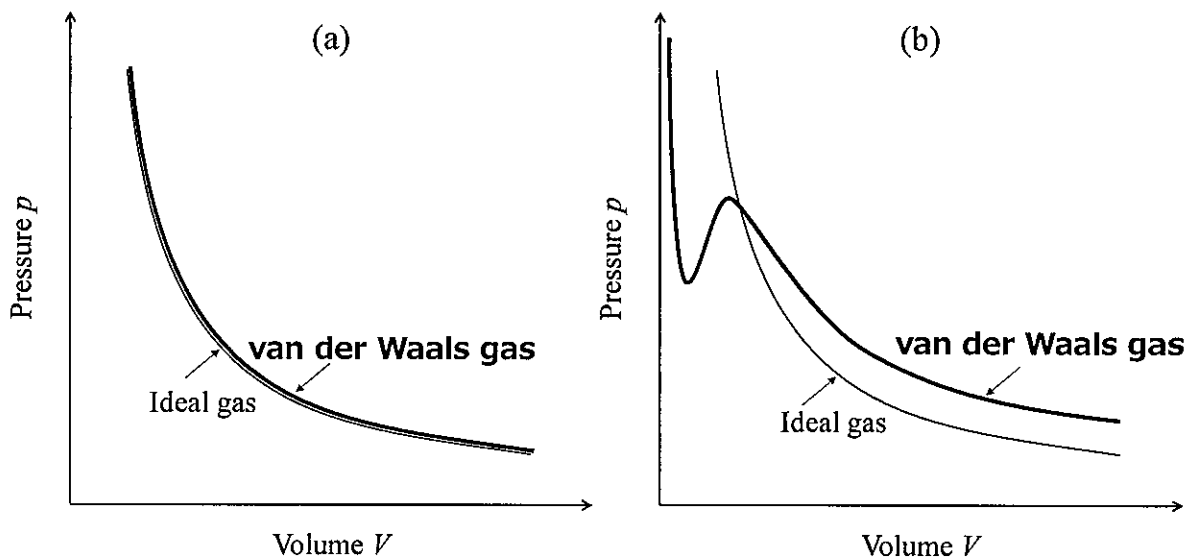


Figure 2

(Continue on the next page)

- (5) When a real gas was compressed, the p - V diagram in Figure 3 was obtained. Briefly explain what phenomena were involved.

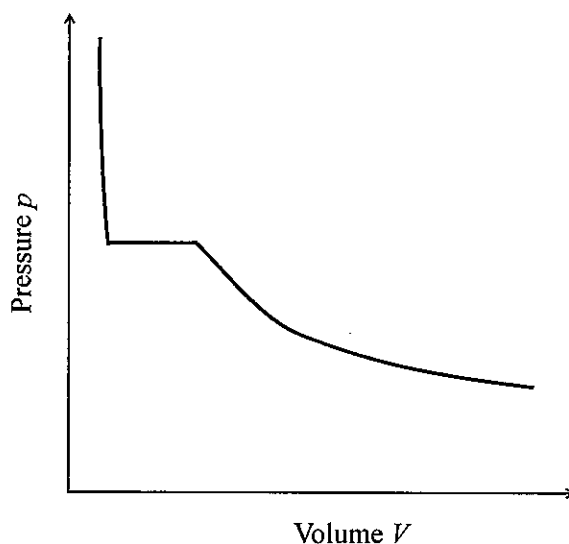


Figure 3

- II. Answer the following questions (1) to (6) regarding methane. You may use the value of the gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (1) Expansion work is performed by the complete oxidation of methane. Calculate the standard enthalpy change ΔH° and the standard entropy change ΔS° of the reaction at 298 K. You may use the thermodynamic data shown in Table 1 for the calculations.

Table 1 The standard enthalpy of formation and the standard entropy at 298 K.

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{CH}_4(\text{g})$	-74.4	186
$\text{H}_2\text{O}(\ell)$	-286	69.9
$\text{O}_2(\text{g})$	0	205
$\text{CO}_2(\text{g})$	-394	214

- (2) Calculate the maximum work per mole expected from this oxidation and the maximum efficiency.

- (3) Hydrogen production by methane steam reforming is governed by the following equilibrium reaction [3]. Calculate the standard free energy change of the reaction ΔG° at 298 K and find the pressure equilibrium constant K_p . You may use the thermodynamic data shown in Table 2 for the calculations.

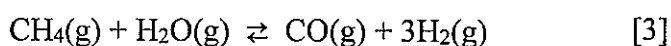


Table 2 The standard enthalpy of formation and the standard entropy at 298 K.

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
CH ₄ (g)	-74.4	186
H ₂ O(g)	-242	189
H ₂ (g)	0	131
CO(g)	-111	198

- (4) When methane steam reforming was performed using equal amounts of methane and steam as feedstock at a constant temperature and ambient pressure, the methane residuals became 8.00 vol% of the total gas and the system attained equilibrium. Calculate the K_p and the reaction temperature. The relationship shown in Eq. [4] may be used.

$$\ln \frac{K_{p2}}{K_{p1}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [4]$$

- (5) How many times does the amount of the produced hydrogen increase, when the mole of methane is increased by a factor of 10.0 at the same temperature as in question (4)?
- (6) For the methane steam reforming, propose three methods to produce more hydrogen without increasing the amount of methane, including the reasons.

Problem 2 (Physical Chemistry 2)

Answer the following questions on molecular vibrations.

- (1) How many normal vibrational modes does the CO₂ molecule have?
- (2) Select all molecules that have infrared active vibrational modes from the following:

H₂, He, CH₄, CO, CO₂, N₂, N₂O

- (3) To obtain energy levels of molecular vibration, consider the vibration of a diatomic molecule, which can be treated as a one-dimensional harmonic oscillator. The potential of the harmonic oscillator V^H is given by the following Eq. [1].

$$V^H = \frac{1}{2}kx^2 \quad [1]$$

Here, k is the spring (force) constant and x is displacement. Using Eq. [1], write down the time-independent Schrödinger equation. Use the reduced Planck constant \hbar , effective mass m , energy E , and wavefunction $\psi(x)$.

- (4) Starting from the Schrödinger equation obtained in question (3), derive Eq. [2] by using the following relationships: $\omega = \sqrt{\frac{k}{m}}$, $\xi = \sqrt{\frac{m\omega}{\hbar}}x$, $\lambda = \frac{2E}{\hbar\omega}$.

$$\frac{d^2\psi(\xi)}{d\xi^2} - (\xi^2 - \lambda)\psi(\xi) = 0 \quad [2]$$

- (5) Assuming that the wavefunction is $\psi(\xi) = f(\xi)\exp(-\frac{1}{2}\xi^2)$, its substitution into Eq. [2] yields the following Eq. [3].

$$\frac{d^2f(\xi)}{d\xi^2} - 2\xi \frac{df(\xi)}{d\xi} - (1 - \lambda)f(\xi) = 0 \quad [3]$$

$f(\xi)$ can be expressed in a power series as in Eq. [4]. Substitute it into Eq. [3] and find out the condition that λ must satisfy so that $\psi(\xi)$ does not diverge. Show the derivation steps.

Here, b_l are constants.

$$f(\xi) = b_0 + b_1\xi + b_2\xi^2 + \dots = \sum_{l=0}^{\infty} b_l\xi^l \quad [4]$$

- (6) Express the energy levels of the vibration of the harmonic oscillator using \hbar and the angular frequency, ω . In addition, express ω in terms of the wavenumber $\tilde{\nu}$, the speed of light c , and π .
- (7) Calculate the effective masses of $^{12}\text{C}^{16}\text{O}$ and $^1\text{H}^{35}\text{Cl}$. Calculate the wavenumber at which infrared absorption is observed for each molecule given that the spring constants of their vibration are 1855 N m^{-1} and 516 N m^{-1} , respectively. Neglect overtones. Use the atomic mass of each element as ^1H : 1.00, ^{12}C : 12.0, ^{16}O : 16.0, and ^{35}Cl : 35.0. The Avogadro constant is $6.02 \times 10^{23} \text{ mol}^{-1}$, $\pi = 3.14$, and the speed of light is $c = 3.00 \times 10^8 \text{ m s}^{-1}$.
- (8) In actual molecular vibrations, anharmonicity must be taken into account. In a diatomic molecule, an example of such anharmonic potential V^{M} can be expressed with a Morse oscillator as in Eq. [5]. Sketch the relationship between this potential energy V^{M} and the interatomic distance R .

$$V^{\text{M}} = 2\pi\hbar c\tilde{D}_e[1 - \exp\{-a(R - R_e)\}]^2, \quad a = \left(\frac{m\omega^2}{4\pi\hbar c\tilde{D}_e}\right)^{\frac{1}{2}} \quad [5]$$

Here, \tilde{D}_e is the depth of the potential minimum and R_e is the equilibrium bond distance.

- (9) For the Morse oscillator, solving the Schrödinger equation yields the energy levels E_n^{M} as expressed as Eq. [6].

$$E_n^{\text{M}} = E_n^{\text{H}} - \left(n + \frac{1}{2}\right)^2 \frac{\pi\hbar c\tilde{\nu}^2}{2\tilde{D}_e}, \quad n = 0, 1, 2, \dots, \quad E_{n+1}^{\text{M}} > E_n^{\text{M}} \quad [6]$$

Here, E_n^{H} are the energy levels of the harmonic oscillator. Present diagrams of the approximate energy levels of the harmonic and Morse oscillators, and explain the difference between them.

- (10) As an application of molecular vibrations and anharmonicity, consider the principle of a laser using a mixture of CO_2 and N_2 gases. Explain the reason why N_2 gas is used, considering energy levels of vibration.

Problem 3 (Inorganic Chemistry)

I. Answer the following questions (1) to (4) regarding symmetry of materials.

- (1) How many types of crystal systems and Bravais lattices exist? State the number for each.
- (2) Explain using illustrations why a base-centered cubic lattice is not a Bravais lattice.
- (3) Given the Miller indices $(h\ k\ l)$, express the extinction rules for diffraction from a face-centered cubic lattice using h , k , and l .
- (4) In X-ray diffraction patterns of powder samples of KCl and KBr with rocksalt-type structure, all diffraction peaks from a face-centered cubic lattice appear in the case of KBr, whereas in the case of KCl, the peaks appear to be from a simple cubic lattice. Give reason in about 50 words.

II. Answer the following questions (1) to (6) regarding iron and oxygen.

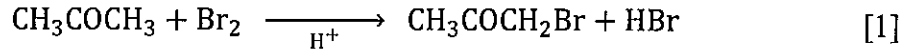
- (1) Give the atomic number of iron.
- (2) Give the number of unpaired electron(s) of Fe^{2+} and Fe^{3+} at the free ion state, respectively.
- (3) Give the name of the crystal structure of magnetite Fe_3O_4 . Also, give the valences of iron ions occupying the tetrahedral site and the octahedral site in the crystal, respectively.
- (4) Describe the ferrimagnetic state which is the magnetically ordered state for magnetite.
- (5) Based on molecular orbital theory, illustrate the electron configuration of an oxygen molecule O_2 at ground state.
- (6) O_2 accepts one electron to form a superoxide ion O_2^- . Give the bond order of the oxygen-oxygen bond of O_2^- .

III. Answer the following questions (1) to (3) regarding semiconductors.

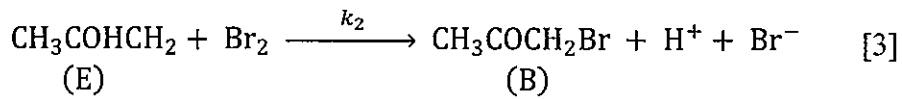
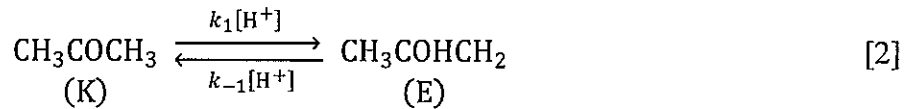
- (1) Based on band theory, compare intrinsic semiconductors with metals and insulators by using illustrations, and explain the differences among the three in about 80 words.
- (2) Give two examples for each of p-type and n-type semiconductors.
- (3) Give an example for an application utilizing p-n junctions and explain its working principle.

Problem 4 (Chemical Engineering 1)

Acetone produces bromoacetone by the acid-catalyzed bromination reaction shown in Eq. [1].



This reaction is assumed to consist of the following two elementary reactions: tautomerism of acetone between the keto form CH_3COCH_3 (called as K hereafter) and the enol form $\text{CH}_3\text{COHCH}_2$ (called as E hereafter) (Eq. [2]), and production of bromoacetone $\text{CH}_3\text{COCH}_2\text{Br}$ (called as B hereafter) via bromine addition to E (Eq. [3]).



Here, k_1 [$\text{s}^{-1} \text{mol}^{-1} \text{L}$], k_{-1} [$\text{s}^{-1} \text{mol}^{-1} \text{L}$], k_2 [$\text{s}^{-1} \text{mol}^{-1} \text{L}$] represent reaction rate constants. The concentrations of K, E, B, H^+ , and Br_2 are expressed as [K], [E], [B], $[\text{H}^+]$, and $[\text{Br}_2]$ [mol L^{-1}], respectively. The forward reaction rate of Eq. [2] is linearly proportional to $[\text{H}^+]$ and [K], whereas the backward reaction rate of that is linearly proportional to $[\text{H}^+]$ and [E]. The reaction rate of Eq. [3] is linearly proportional to [E] and $[\text{Br}_2]$. It is assumed that acetone before the reaction is composed of only the keto form, and the produced HBr is completely dissociated. All reactions proceed in the liquid phase and evaporation can be ignored.

When the initial concentration of bromine $[\text{Br}_2]_0$ [mol L^{-1}] was sufficiently high, the production rate of B, r [$\text{mol L}^{-1} \text{s}^{-1}$], was expressed as Eq. [4] using the overall reaction rate constant k_{A1} [$\text{s}^{-1} \text{mol}^{-1} \text{L}$]. On the other hand, when $[\text{Br}_2]_0$ was sufficiently low, r was expressed as Eq. [5] using the overall reaction rate constant k_{A2} [$\text{s}^{-1} \text{mol}^{-1} \text{L}$].

$$r = \frac{d[\text{B}]}{dt} = \begin{cases} k_{A1} [\text{K}] [\text{H}^+] & [4] \\ k_{A2} [\text{K}] [\text{Br}_2] & [5] \end{cases}$$

First, answer the following questions (1) to (4) regarding the reaction rate.

- (1) Based on Eqs. [2] and [3], express the differential equations showing the change of [E] and [B] with time, using the necessary parameters among k_1 , k_{-1} , k_2 , [K], [E], [B], $[H^+]$, and $[Br_2]$.
- (2) When $[Br_2]_0$ is sufficiently high, it can be assumed that the steady-state approximation can be applied to [E] and that the following relationship, $k_2[Br_2] \gg k_{-1}[H^+]$, holds. Express k_{A1} using the necessary parameters among k_1 , k_{-1} , and k_2 .
- (3) When $[Br_2]_0$ is sufficiently low, it can be assumed that the equilibrium in Eq. [2] is established instantaneously. Express k_{A2} using the necessary parameters among k_1 , k_{-1} , and k_2 .
- (4) From the viewpoint of rate limiting processes, explain the reason why the expression of r changed from Eq. [4] to Eq. [5] with the decrease in $[Br_2]_0$ (approximately 50 words).

Next, under the condition that $[Br_2]_0$ is sufficiently high, consider the production of B using a batch reactor. The initial concentration of K, $[K]_0$, is $5.0 \times 10^{-1} \text{ mol L}^{-1}$, whereas the initial concentration of H^+ , $[H^+]_0$, is $1.0 \times 10^{-1} \text{ mol L}^{-1}$. Under this condition, the reaction proceeded in a self-catalytic manner following Eq. [4], and the relationship between r and the conversion of K, x [-], was depicted as shown in Figure 1. It can be assumed that [E] is sufficiently lower than [K] and [B], and thus can be neglected. Answer the following questions (5) to (7).

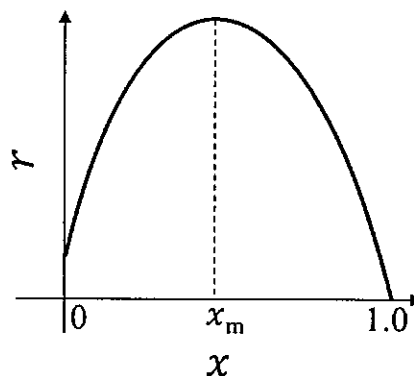


Figure 1

- (5) Explain the reason why r showed the convex upward curve against x in Figure 1 (approximately 50 words).
- (6) Based on Eq. [4], express r using x , k_{A1} , $[K]_0$, and $[H^+]_0$.
- (7) Calculate the value of x_m [-], the conversion of K that gives the maximum r .

Finally, also under the condition where r follows Eq. [4], consider the continuous production of B in a Continuous Stirred Tank Reactor (CSTR) and a Plug Flow Reactor (PFR). Using the precursor solution of $[K]_0 = 5.0 \times 10^{-1} \text{ mol L}^{-1}$ and $[H^+]_0 = 1.0 \times 10^{-1} \text{ mol L}^{-1}$, the target value of x_{out} [-], the conversion of K at the outlet of the reactor, is 9.5×10^{-1} . It can be assumed that $[E]$ is sufficiently lower than $[K]$ and $[B]$, and thus can be neglected. The volumetric flow rates at the inlet and outlet of the reactor are the same. Answer the following questions (8) and (9).

- (8) Express the space time τ [s] using $[K]_0$, r , and x_{out} for each of the following cases:
- (i) Use a single CSTR
 - (ii) Use a single PFR
- (9) Choose the most appropriate method to minimize the space time of the reactor (sum of the space time of all reactors if multiple reactors are used) from the following (a) – (d). In addition, explain the reason for the choice using a schematic illustration showing x at the horizontal axis and $[K]_0/r$ at the vertical axis (approximately 100 words).
- (a) Use a single CSTR
 - (b) Use a single PFR
 - (c) Connect a CSTR to a PFR in series in this order
 - (d) Connect a PFR to a CSTR in series in this order

Problem 5 (Chemical Engineering 2)

Figure 1 shows a steady-state particle collection process to clean air containing particles (called “air” hereafter), which involves capturing the particles using droplets through a tube. The air and the droplets enter at the inlet of the tube. The droplets collide with the particles in the tube. The cleaned air and the droplets containing the particles are ejected at the outlet of the tube. Figure 2 shows a magnified sketch of particle collision with one droplet in the tube. The diameter of the particles is sufficiently smaller than that of the droplets, and thus can be ignored. All the particles that collided with a droplet are captured in the droplet.

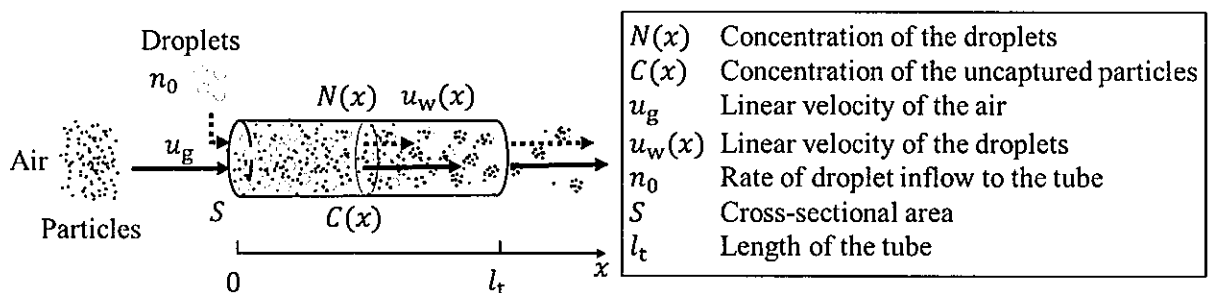


Figure 1

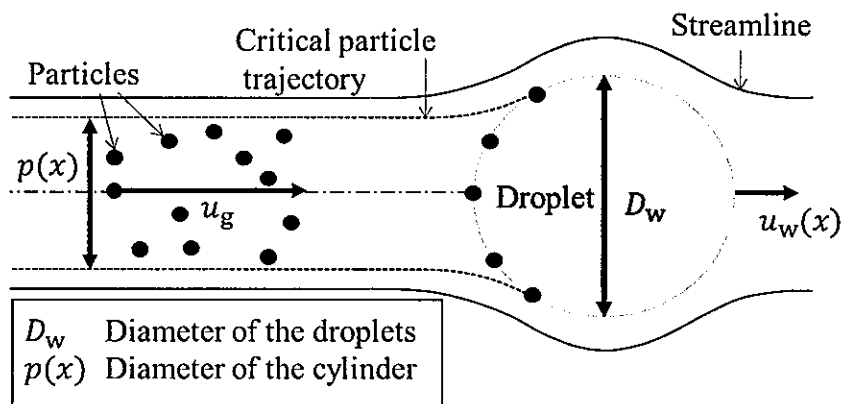


Figure 2

All relevant phenomena are described in a 1-dimensional coordinate system of x along the length of the tube, and variations in the radial direction can be neglected. The general expression $f(x)$ denotes a value that changes as a function of x . The particles move at the same speed of the air except in the neighborhood of the droplets. The effect of gravity is negligible. Droplet collision, splitting, and coalescence do not occur. The particle collection process by an

individual droplet is not affected by other droplets. The number of the droplets and the particles are expressed by the unit #; for example, 10 # means 10 particles or droplets. The air viscosity, $\mu = 1.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$, and the air density, $\rho_g = 1.2 \text{ kg m}^{-3}$, are constant. Answer the following questions (1)–(9).

First, consider the particle collection process by a single droplet shown in Figure 2. The droplet is spherical, and its diameter, D_w [m], is sufficiently smaller than that of the tube. The linear velocities of the air and the droplets are expressed as u_g [m s^{-1}] and $u_w(x)$ [m s^{-1}], respectively.

- (1) The droplet moves slower than the particles. The droplet collides with the particles in an air cylinder of diameter $p(x)$ [m], which is bounded by the critical particle trajectory. Express the volume of the air washed by one droplet in one unit of time, $Q_p(x)$ [$\text{m}^3 \text{ s}^{-1} \text{ \#}^{-1}$], in terms of $p(x)$, $u_w(x)$, and u_g .

Next, discuss the particle capture process in the tube as shown in Figure 1. The cross-sectional area and length of the tube are S [m^2] and l_t [m], respectively. The rate of droplet inflow to the tube at the inlet ($x = 0$) is n_0 [\# s^{-1}].

- (2) The air flows into the tube at $u_g = 80 \text{ m s}^{-1}$ at the inlet. The diameter of the droplets is $D_w = 8.0 \times 10^{-5} \text{ m}$, and the droplets enter the tube at $u_w(0) = 1.0 \text{ m s}^{-1}$ at the inlet. Calculate the particle Reynolds number, Re_p , of the droplets at the inlet.
- (3) Which is higher, Re_p of the droplets at the inlet or at the outlet ($x = l_t$)? Briefly discuss the reason in around 75 words.
- (4) Given that the droplet flux is always constant regardless of position x , express the concentration of the droplets, $N(x)$ [\# m^{-3}], in terms of S , n_0 , and $u_w(x)$.
- (5) The concentration of the uncaptured particles is expressed as $C(x)$ [\# m^{-3}]. At steady-state, consider the mass balance of the particles at an increment along the tube length, and express the relation of $C(x)$, $Q_p(x)$, S , n_0 , u_g , and $u_w(x)$ as a differential equation.

- (6) The volume of the air washed by a single droplet as it passes through the tube, R [$\text{m}^3 \#^{-1}$], is expressed by the following equation.

$$R = \int_0^{l_t} \frac{1}{u_w(x)} Q_p(x) dx \quad [1]$$

The particle penetration rate is defined as $C(l_t)/C(0)$ [-]. By solving the differential equation generated in problem (5), express $C(l_t)/C(0)$ in terms of R , n_0 , u_g , and S .

- (7) At a certain condition, the relation of $C(l_t)/C(0) = 0.10$ was found. How many times does $C(l_t)/C(0)$ change when n_0 is tripled without changing the other parameters?
- (8) Briefly discuss the effect of influential parameters on the particle penetration rate by referring to the answer of problem (6) in around 75 words.

Finally, the whole structure of a Venturi scrubber, which is widely known as a particle collector, is shown in Figure 3. The diameter of the Venturi tube decreases throughout the converging section, which connects to the throat section with a constant cross-sectional area. Throughout the diverging section, the diameter gradually increases and reaches the same diameter as that of the inlet of the converging section. Figure 1 shown before represents a magnified sketch of the throat section in Figure 3.

- (9) Briefly discuss the merits of using the Venturi tube for the particle capture process in around 75 words.

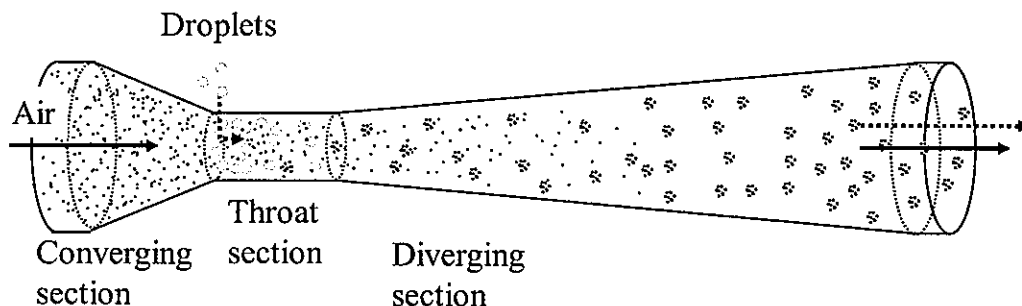


Figure 3