

CHAPTER 1

INTRODUCTION

1.1 Background

Chemical reactions applied in the chemical industry may involve raw materials in different phases, including solid, gas, and liquid phases. Therefore, chemical reactions in industrial processes may occur in a single phase (homogeneous) or in multiple phases (heterogeneous), such as binary or even ternary systems (Coulson, 1996). Before the chemical reaction takes place, one or more raw materials (reactants) may be transferred from their bulk flow toward an interfacial boundary or toward the bulk flow of another reactant present in a different phase.

Gas–liquid absorption is a heterogeneous process involving the transfer of a soluble gas component into an absorbent, which is typically a non-volatile liquid (Franks, 1967). Chemical reactions during the absorption process may occur in the gas film, interfacial region, liquid film, or even in the bulk liquid, depending on the concentration and reactivity of the reacting species. To facilitate these process steps, gas–liquid absorption is commonly carried out in stirred-tank reactors equipped with spargers, bubble columns, or columns containing a packed bed of inert particles (*packed bed columns*). Gas–liquid absorption can be applied to the purification of synthesis gas, in which valuable components can be recovered from gas streams, as well as in industries involving the dissolution of gases in liquids, such as H_2SO_4 , HCl , HNO_3 , formaldehyde, and others (Coulson, 1996). The absorption of CO_2 using a strong hydroxide solution is accompanied by a second-order chemical reaction between CO_2 and OH^- ions, forming CO_3^{2-} ions and H_2O . Meanwhile, the reaction between CO_2 and CO_3^{2-} to form HCO_3^- ions is generally neglected (Danckwerts, 1970; Juvekar & Sharma, 1972). However, when OH^- ions are present in excess such that their concentration changes negligibly during the absorption process, the reaction can be approximated as a pseudo-first-order reaction. Under these conditions, the OH^- concentration is assumed to remain constant, and the pseudo-first-order rate constant can be expressed as follows $k' = k_2[\text{OH}^-]$ (Sharma & Danckwerts, 1970; Lyu et al., 2017).

The design of chemical reactors is based on the modelling of reactor hydrodynamics and the chemical reactions occurring within them. A mathematical model represents a simplification of the actual processes inside

a reactor, which are typically highly complex (Levenspiel, 1972). Chemical reactions are usually studied through laboratory-scale batch processes, considering reactant requirements, ease of reaction control, equipment considerations, operational feasibility, analytical convenience, and accuracy.

1.2 Problem Formulation

1. How do operating variables affect the amount of CO_2 absorbed at various reaction times?
2. How do operating variables affect the value of the gas-phase CO_2 mass transfer coefficient (k_{GA})?
3. How do operating variables affect the value of the liquid-phase CO_2 mass transfer coefficient (k_{LA})?
4. How do operating variables affect the value of the overall mass transfer coefficient between CO_2 and H_2O (K_{OG})?

1.3 Objectives of the Experiment

After conducting this experiment, students are expected to be able to perform and/or explain the following:

1. Prepare and operate the absorption system, analyze samples, and process experimental data.
2. The effect of variables on the amount of CO_2 absorbed at various reaction times.
3. The effect of variables on the value of the gas-phase CO_2 mass transfer coefficient (k_{GA}).
4. The effect of variables on the value of the liquid-phase CO_2 mass transfer coefficient (k_{LA}).
5. The effect of variables on the value of the overall mass transfer coefficient between CO_2 and H_2O (K_{OG}).

1.4 Benefits of the Experiment

(Students are required to independently identify and obtain information regarding the benefits of the experiment).

CHAPTER II

LITERATURE REVIEW

2.1 Absorption

Absorption is one of the separation processes in the chemical industry in which a gas mixture is brought into contact with a liquid absorbent, allowing one or more components of the gas to dissolve in the liquid. The transfer of a gas component into the liquid phase occurs due to a difference between the concentration (or partial pressure) of the component in the gas phase and its equilibrium condition with respect to the liquid phase, thereby providing the driving force for mass transfer. During the absorption process, the gas component diffuses from the bulk gas phase toward the gas–liquid interface and subsequently passes through the liquid film until it reaches the bulk liquid phase. When absorption is accompanied by a chemical reaction, the dissolved gas component subsequently reacts with the absorbent in the liquid phase (McCabe et al., 1993). Absorption can occur through two mechanisms, namely physical absorption and chemical absorption.

2.1.1 Physical Absorption

Physical absorption is a process that involves the dissolution of a gas into an absorbing solution without being accompanied by a chemical reaction. Examples of this process include the absorption of H_2S gas by water, methanol, and propylene carbonate. Absorption occurs due to physical interactions between the gas and the liquid. The mechanism of physical absorption can be explained by several models, namely the two-film theory proposed by Whitman (1923), the penetration theory proposed by Danckwerts, and the surface renewal theory.

2.1.2 Chemical Absorption

Chemical absorption is a process that involves the dissolution of a gas into an absorbing solution accompanied by a chemical reaction. Examples of this process include the absorption of CO_2 gas using MEA (Mono Ethanol Amine), NaOH , K_2CO_3 (Potassium Carbonate), and others. Applications of chemical absorption can be found in the CO_2 gas absorption process in ammonia plants, as illustrated in Figure 2.1.

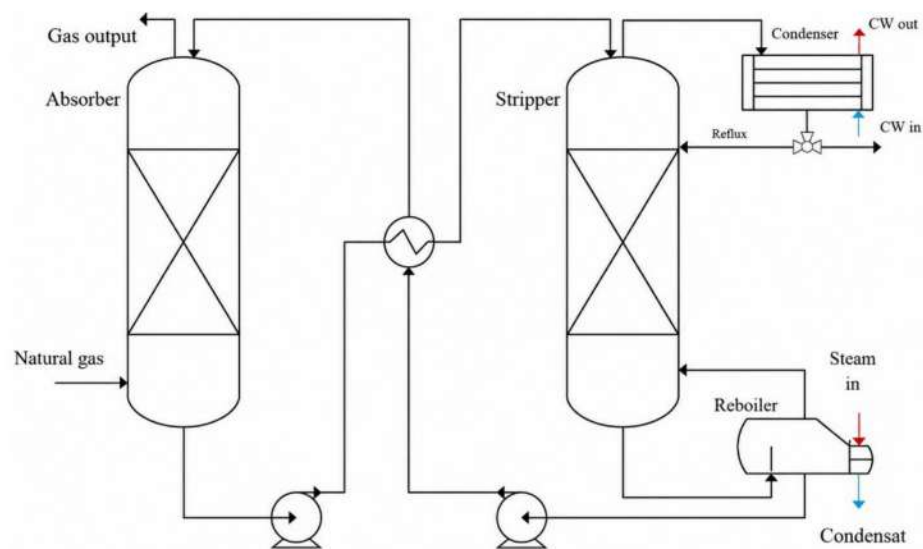


Figure 2.1 CO₂ absorption and desorption process using MEA solvent in an ammonia plant

The absorption process can be carried out in a stirred tank equipped with a sparger, a bubble column, a column packed with inert packing (packed column), or a tray column. The selection of absorption equipment is generally based on the reactivity of the reactants (gas and liquid), the corrosiveness of the absorbed component and the absorbent, operating temperature, pressure, capacity, and economic considerations.

2.2 Absorption Column

An absorption column is a column or vessel in which the absorption process of a substance passing through the column or vessel takes place. In this column or vessel, the absorption process occurs as the substance passes through the column and comes into contact with the absorbing phase. In general, absorption columns can be classified into four main types based on their configuration, namely spray columns, bubble columns, tray columns, and packed bed columns. Each type of absorption column has a different configuration for facilitating the contact between the gas and liquid phases.

2.2.1 Spray column

In a spray tower (Figure 2.2), the gas phase flows upward through a large open space, while the liquid phase is introduced using nozzles or other spraying devices. The liquid is fed in the form of fine droplets and flows downward countercurrently to the upward flow of the gas.

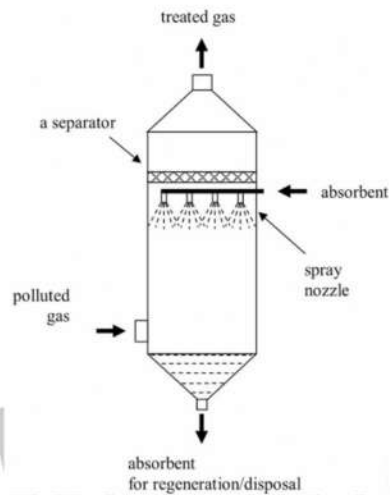


Figure 2.2 Spray column

2.2.2 Bubble column

A bubble column (Figure 2.3) consists of a large open space through which the liquid phase flows, while the gas is dispersed into the liquid phase through a sparger located at the bottom of the column in the form of fine bubbles. The small gas bubbles provide the desired interfacial contact area, while the rising bubbles induce mixing within the liquid phase, thereby reducing the liquid-phase resistance to mass transfer. Bubble columns are generally used in systems where the mass transfer resistance is dominated by the liquid phase, making enhanced mixing in the liquid phase an important factor.

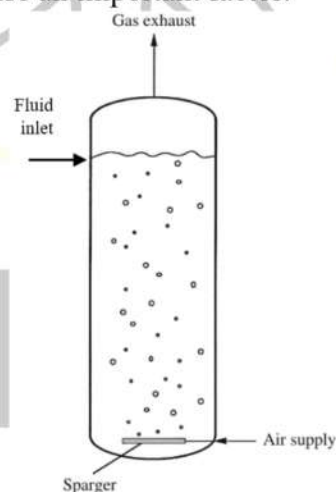


Figure 2.3 Bubble column

2.2.3 Plate column (tray column)

A plate column or tray column (Figure 2.4) is a type of column that has been widely used in industry. There are several types of trays, including sieve trays, valve trays, and bubble-cap trays. In a plate column, the liquid flows across each tray, passes over an outlet weir,

and enters the downcomer, which carries the liquid to the tray below by gravity. The gas flows upward through the openings in each tray and forms bubbles as it passes through the liquid on the tray, thereby generating foam (Seader et al., 1997).

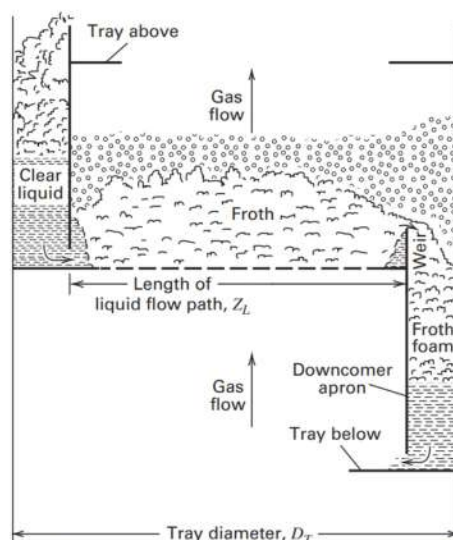


Figure 2.4 Plate column

2.2.4 Packed bed column

A packed column (Figure 2.5) is an absorption column filled with packing materials to increase the interfacial contact area between the gas and liquid phases, thereby improving mass transfer efficiency. In this column, the liquid flows downward over the surface of the packing, while the gas flows upward countercurrently through the void spaces between the packing materials. Packed towers contain two types of packing materials, namely random packing and structured packing.

In random packing, the packing materials are randomly arranged within the column. Random packing is available in various materials, including ceramic, metal, plastic, and carbon. The selection of packing material is based on the properties of the liquid and the operating temperature. Ceramic materials are generally used for corrosive liquids but are not suitable for use with strong alkalis. Plastic materials are generally susceptible to certain organic solvents and can only be used at moderate temperatures (Towler & Sinnott, 2008). Meanwhile, metal materials are more recommended for operating conditions that tend to be unstable, such as drastic changes in pressure, flow rate, and temperature, because ceramic and plastic materials tend to undergo damage under such conditions (Ludwig, 1997; Towler & Sinnott, 2008).

In contrast, in structured packing, the packing materials have a fixed and orderly arrangement within the column, with the materials positioned in a predetermined and organized manner. Structured packing materials are made of wire mesh or perforated metal sheets, which are used as the main materials for constructing the packing. These materials are folded and arranged in an orderly geometry within the column to provide a high surface area. Structured packing materials are available in several materials, including metal, plastic, and ceramic. The cost of structured packing is generally much higher than that of random packing; however, structured packing offers higher efficiency compared with random packing (Towler & Sinnott, 2008).

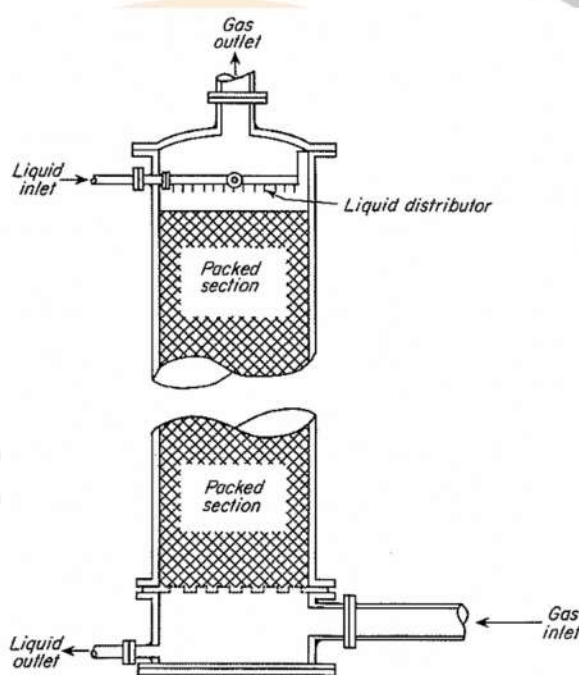


Figure 2.5 Packed column

Packed towers operated at high gas velocities may experience back mixing, in which the gas flow affects the movement of the liquid within the column. As the gas velocity continues to increase, the upward force exerted by the gas becomes greater than the gravitational force driving the liquid downward, resulting in liquid accumulation within the column, a condition known as flooding. This condition causes the operation of the column to become unstable and subsequently reduces the efficiency of mass transfer between the gas and liquid phases. Conversely, if the gas velocity is too low, contact between the gas and liquid phases becomes less effective because the packing surface is not optimally wetted by the liquid, resulting in poor wetting conditions. Consequently, the interfacial contact area between the gas and liquid phases decreases, leading to a lower mass transfer rate (Silla, 2003).

2.3 Analysis of Mass Transfer and Reactions in Gas Absorption by Liquids

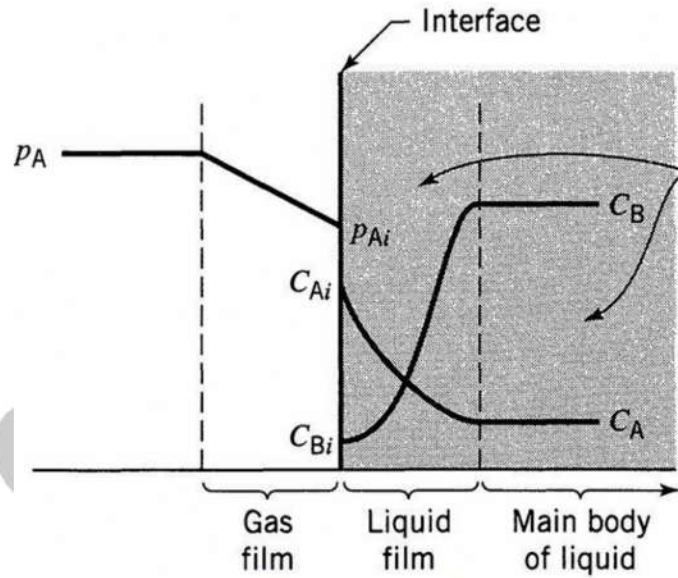


Figure 2.6 Mechanism of CO₂ gas absorption in NaOH solution

In general, the absorption process of CO₂ gas into a NaOH solution accompanied by a chemical reaction proceeds through four stages, namely the mass transfer of CO₂ through the gas film toward the gas-liquid interface, the equilibrium between CO₂ in the gas phase and in the liquid phase, the mass transfer of CO₂ from the interfacial layer into the bulk NaOH solution, and the reaction between dissolved CO₂ and hydroxyl (OH⁻) groups. The schematic of this process is shown in Figure 2.6.

The rate of CO₂ mass transfer through the gas film:

$$R_a = k_{GA} (p_A - p_{Ai}) \quad (2.1)$$

The equilibrium between CO₂ in the gas phase and in the liquid phase:

$$C_{Ai} = H \times p_{Ai} \quad (2.2)$$

p_{Ai} = Partial pressure of gas A at the gas-liquid interface (atm)

p_A = Partial pressure of gas A in the gas phase (atm)

k_{GA} = Gas-phase mass transfer coefficient (mol/atm·min)

H = Henry's law solubility coefficient (g·mol/cm³·atm)

C_{Ai} = Concentration of A in the liquid phase at the gas-liquid interface

At a temperature of 30 °C, the value of H is 2.88×10^{-5} g·mol/(cm³·atm).

The rate of CO₂ absorption into the NaOH solution accompanied by a chemical reaction is expressed as:

$$R_a = [A^*] a \sqrt{D_A k_2 [\text{OH}^-]} \quad (2.3)$$

where A^* is the equilibrium concentration of CO₂ at the gas-liquid interface. This quantity represents the concentration of dissolved CO₂ under conditions where the gas and liquid phases are in equilibrium according to Henry's law.

Boundary condition:

$$(a). \frac{\sqrt{D_A \cdot k_2 \cdot [OH^-]}}{k_L} \gg 1$$

$$(b). \frac{\sqrt{D_A \cdot k_2 \cdot [OH^-]}}{k_L} \ll \frac{[OH^-]}{z \cdot A^*} \sqrt{\frac{D_B}{D_A}}$$

where z is the chemical reaction coefficient between CO_2 and $[OH^-]$, which is equal to 2. In the liquid phase, the reaction between CO_2 and the NaOH solution occurs through several process stages:



Steps d and e usually proceed very rapidly because they are ionic reactions; therefore, the absorption process is generally controlled by the dissolution of CO_2 into the NaOH solution, particularly when CO_2 is fed as a mixture with other gases, or is jointly controlled by the chemical reaction occurring in step c (Juvekar & Sharma, 1973).

The concentration of the NaOH solution affects the absorption mechanism. At high NaOH concentrations, the reaction between CO_2 and OH^- ions occurs very rapidly, so the absorption rate tends to be controlled by mass transfer. Conversely, in more dilute NaOH solutions, the concentration of OH^- ions may decrease along the film layer due to the reaction, making the effect of the chemical reaction on the absorption rate more significant.

Elimination of A^* from Equations 2.1, 2.2, and 2.3 yields:

$$R_a = \frac{a \cdot H \cdot p_A \cdot \sqrt{D_A \cdot k_2 \cdot [OH^-]}}{1 + \frac{a \cdot H \cdot \sqrt{D_A \cdot k_2 \cdot [OH^-]}}{k_{GA}}} \quad (2.9)$$

If the value of k_L is very large, then: $\frac{\sqrt{D_A \cdot k_2 \cdot [OH^-]}}{k_L} \approx 1$ thus, the above equation becomes:

$$R_a = \frac{a \cdot H \cdot p_A \cdot \sqrt{D_A \cdot k_2 \cdot [OH^-] + k_L^2}}{1 + \frac{a \cdot H \cdot \sqrt{D_A \cdot k_2 \cdot [OH^-] + k_L^2}}{k_{GA}}} \quad (2.10)$$

If boundary condition (b) is not satisfied, this indicates the occurrence of depletion of $[OH^-]$ in the solution. This results in:

$$\frac{\sqrt{D_A \cdot k_2 \cdot [OH^-]}}{k_L} \approx \frac{[OH^-]}{z \cdot A^*} \sqrt{\frac{D_B}{D_A}} \quad (2.11)$$

Accordingly, the rate of CO₂ gas absorption into the NaOH solution will follow the equation:

$$R_a = \frac{a.H.p_A.\Phi.k_L}{1 + \frac{a.H.\Phi.k_L}{k_{GA}}} \quad (2.12)$$

Where Φ is the enhancement factor, which represents the ratio of the CO₂ mass transfer coefficient in the liquid phase when absorption is accompanied by a chemical reaction to that when absorption occurs without a chemical reaction, as formulated by Juvekar and Sharma (1973):

$$\Phi = \frac{\sqrt{D_A.k_2.[OH^-]}}{k_L} \cdot \left[1 + \frac{[OH^-]D_B}{z.A^*D_A} \Phi \right]^{\frac{1}{2}} \quad (2.13)$$

The effective diffusivity (D_A) of CO₂ in NaOH solution at a temperature of 30 °C is $2.1 \times 10^{-5} \text{ cm}^2/\text{s}$ (Juvekar & Sharma, 1973).

The value of k_{GA} can be calculated based on physical absorption by considering the overall mass transfer of CO₂ into the NaOH solution occurring over a certain time interval in the absorption apparatus. In dimensionless form, k_{GA} can be calculated using the following equation (Kumoro & Hadiyanto, 2000):

$$Sh = a \times Re^b \times Sc^c \quad (2.14)$$

$$\frac{k_{GA}.dp^2}{D_{AB}} = 4,0777 \times \left(\frac{\rho_{CO_2}.v.dp}{\mu_{CO_2}} \right)^{1,4003} \times \left(\frac{\mu_{CO_2}}{\rho_{CO_2}.D_{AB}} \right)^{\frac{1}{3}} \quad (2.15)$$

$$\frac{k_{GA}.dp^2}{D_{AB}} = 4,0777 \times \left(\frac{\rho_{CO_2}.Q.dp}{A.\mu_{CO_2}} \right)^{1,4003} \times \left(\frac{\mu_{CO_2}}{\rho_{CO_2}.D_{AB}} \right)^{\frac{1}{3}} \quad (2.16)$$

$$\text{With } A = \frac{\pi.D^2}{4}$$

Theoretically, the value of k_{GA} should satisfy the following equation:

$$k_{GA} = \frac{\text{mol}(\text{CO}_2, \text{liq})}{A.Z.\epsilon.P_{lm}} = \frac{\text{mol}(\text{CO}_3^{2-})}{A.Z.\epsilon.P_{lm}} \quad (2.17)$$

If the operating pressure is sufficiently low, P_{lm} can be approximated as:

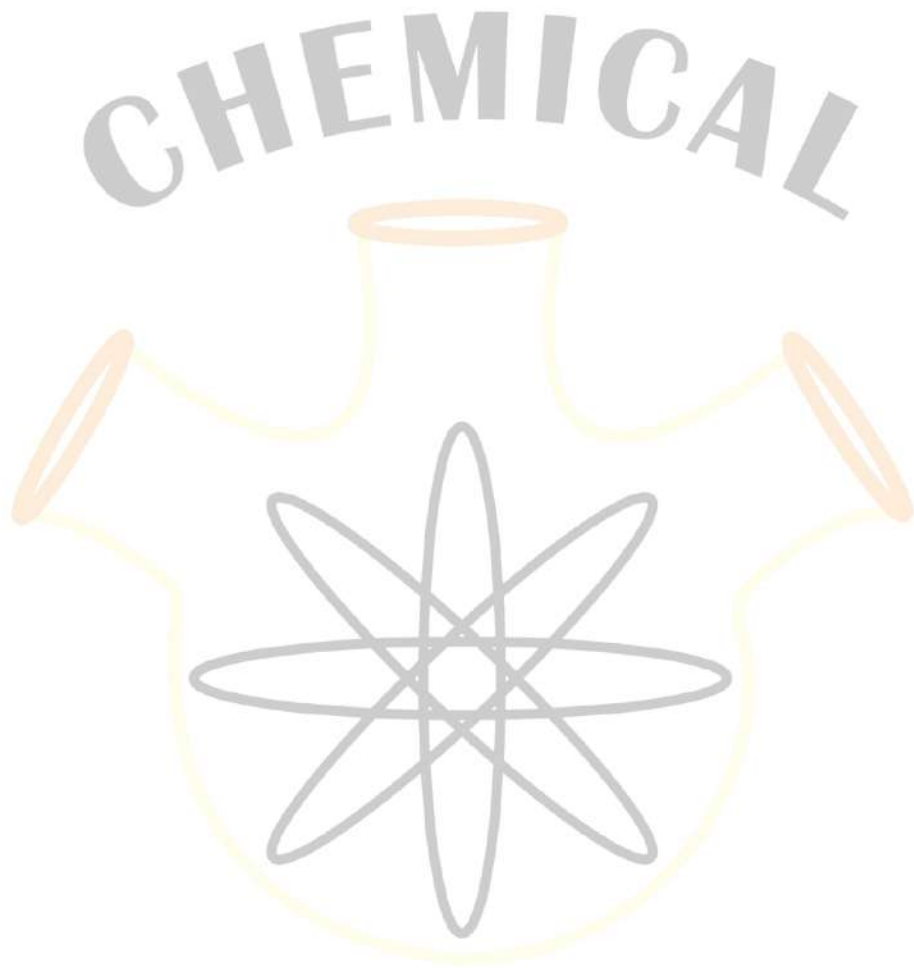
$$\Delta P = P_{in} - P_{out} \quad (2.18)$$

Meanwhile, the value of k_{LA} can be calculated empirically using the following equation (Zheng & Xu, 1992):

$$\frac{k_{LA}.dp}{D_A} = 0,2558 \times \left(\frac{\rho_{NaOH}.Q_{NaOH}.4.dp}{\pi.\mu_{NaOH}.D_c^2.\epsilon} \right) \times \left(\frac{\mu_{NaOH}}{\rho.D_A} \right)^{0,5} \quad (2.19)$$

If the rate of Na₂CO₃ formation is much greater than the rate of CO₂ diffusion into the NaOH solution, then the concentration of CO₂ at the boundary between the liquid film and the bulk liquid is zero. This is due to the very rapid consumption of CO₂ during the reaction along the film. Therefore, the film thickness (δ) can be determined using the following equation:

$$\delta = \frac{D_A(P_{in}-P_{out})}{\text{mol}(\text{CO}_3^{2-}).R.T} \quad (2.20)$$



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CHAPTER III

PRACTICUM METHOD

3.1 Trial Design

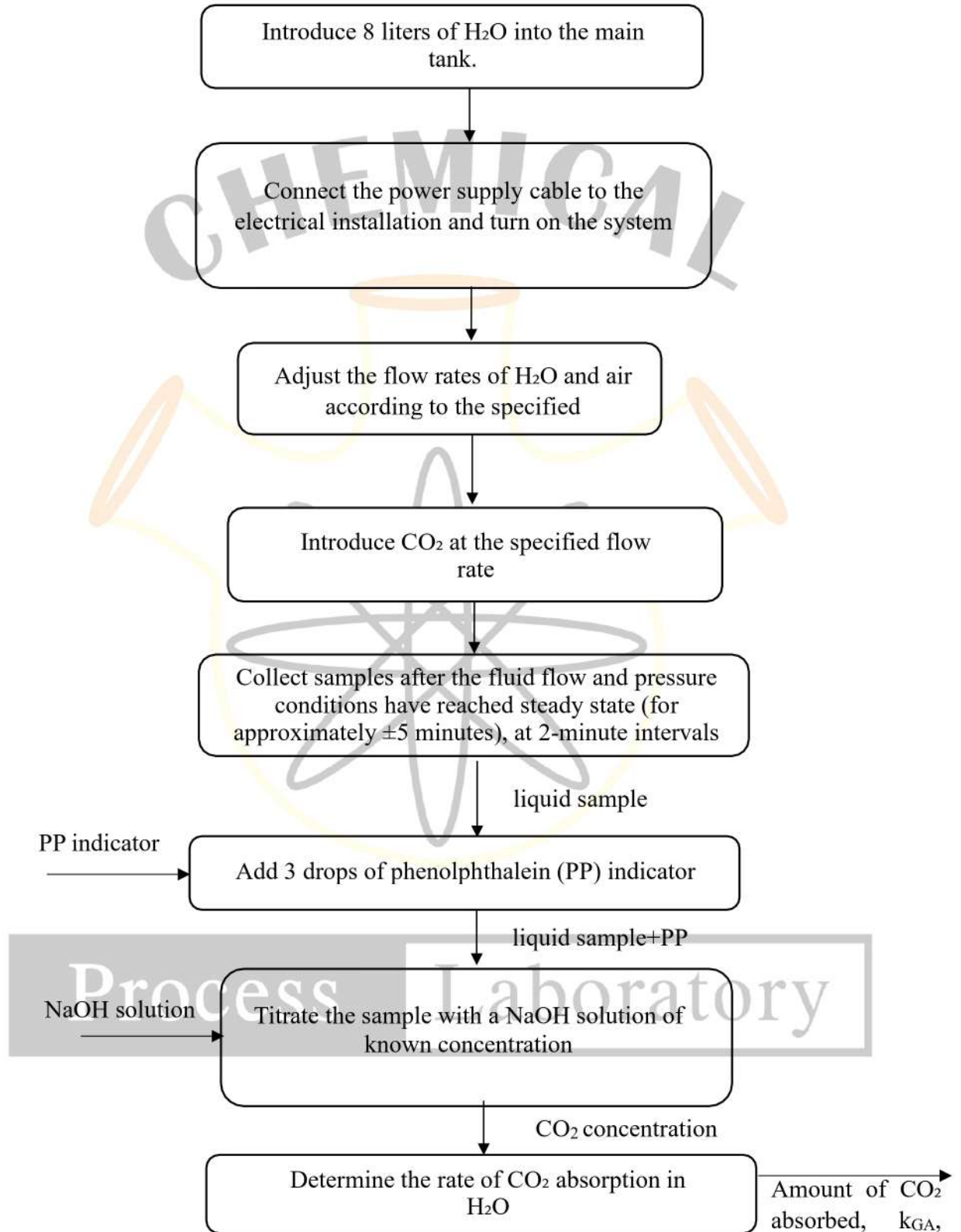


Figure 3.1 Experimental setup schematic of the laboratory experiment

3.1.1 Determination of variables

- A. Constant variables:
- B. Independent variables:

3.2 Materials and Equipment Used

1. Materials

- 1. Sodium hydroxide (NaOH) crystals with a purity of 98% w/w
- 2. Carbon dioxide (CO₂) in liquid phase stored in a pressurized cylinder
- 3. Air
- 4. Aquadest (H₂O)
- 5. Phenolphthalein (PP) indicator

2. Equipment

The experimental absorption apparatus is shown in Figure 3.2.

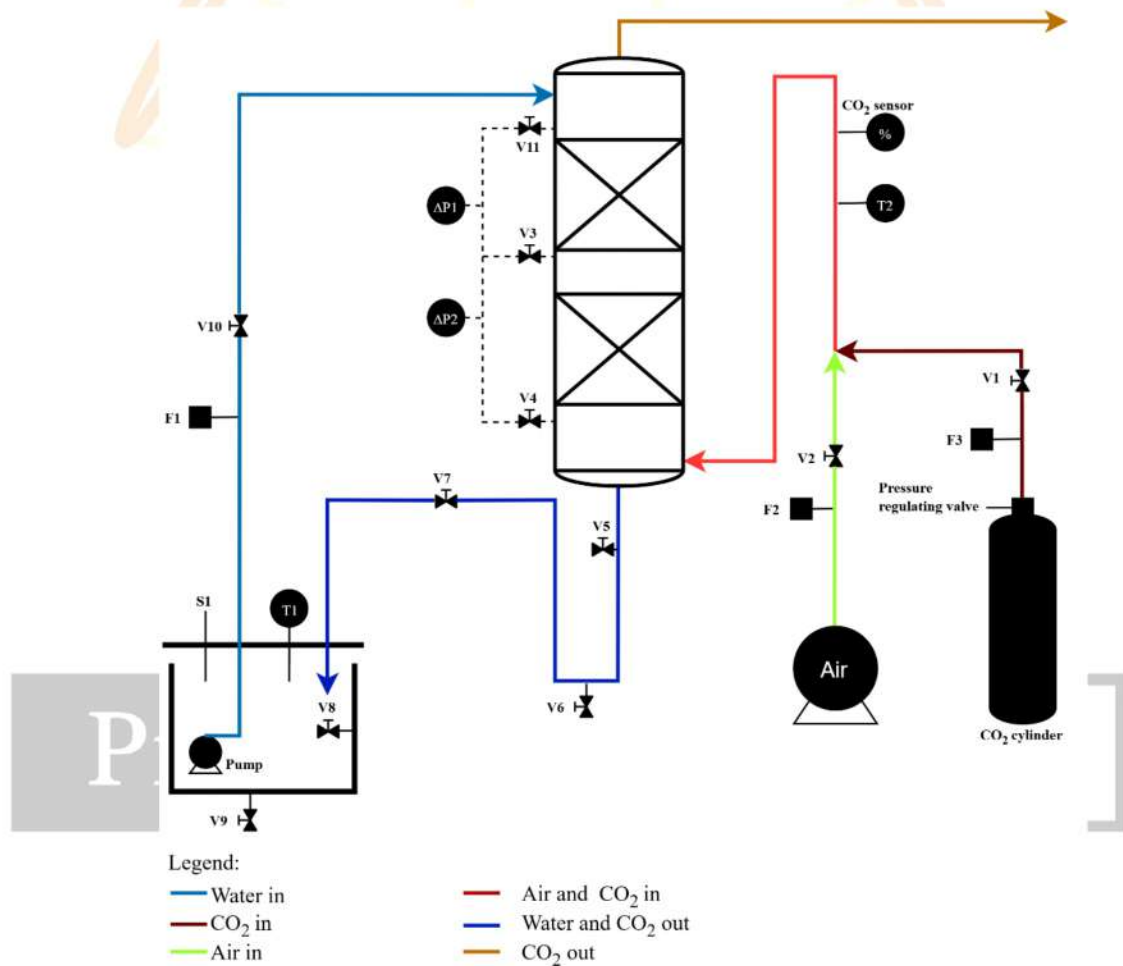


Figure 3.2 Main experimental apparatus setup

3.3 Test Response

Carbonate ion (CO₃²⁻) concentration in the sample solution and the amount of CO₂ absorbed.

3.4 Experimental Procedure

A. Equipment Preparation

First, the power cable is connected to the electrical power source, followed by turning the ON/OFF switch, and the instrument monitor will turn on. The main water supply to the tank is opened and the tank is allowed to fill. Ensure that the water outlet line from the column is connected to the pipe that returns the water to the tank. With gas flow valves V_1 and V_2 closed, the liquid pump is turned on. The water flow through the column, as indicated by flowmeter F_1 , is adjusted using valve V_{10} . The compressor is turned on and valve V_2 is adjusted to provide an air flow. The pressure-regulating valve on the CO_2 cylinder is opened, and valve V_1 is adjusted to set the reading on flowmeter F_3 . After 5 minutes (when fluid flow and pressure conditions have reached steady state), 25 mL of liquid sample is withdrawn through the outlet valve at the bottom of the absorber column at 2-minute intervals for 14 minutes, and the pressure difference displayed on the monitor is recorded. The liquid samples are analyzed for dissolved carbon dioxide content in the form of carbonate ions according to the procedure described in Section B.

B. Determination of Dissolved CO_2

Two to three drops of PP indicator are added to the liquid sample. If a red color forms immediately, this indicates the absence of free CO_2 in the sample. The sample is then titrated with a standard NaOH solution according to the specified variables until a pale pink color persists for 30 seconds. The volume of titrant required during the titration is recorded and used to calculate the amount of carbon dioxide dissolved in the sample.

The amount of CO_2 dissolved in the water sample is calculated from:

$$\text{gmol/liter CO}_2 = \frac{V_{\text{titrant}} \times N_{\text{titrant}}}{\text{Sample volume}} = \text{Cd}$$

3.5 Observation Sheet

3.5.1 Operating Variables

- Constant variables:
- Independent variables:

3.5.2 Data

Table 3.1 Data for variable 1

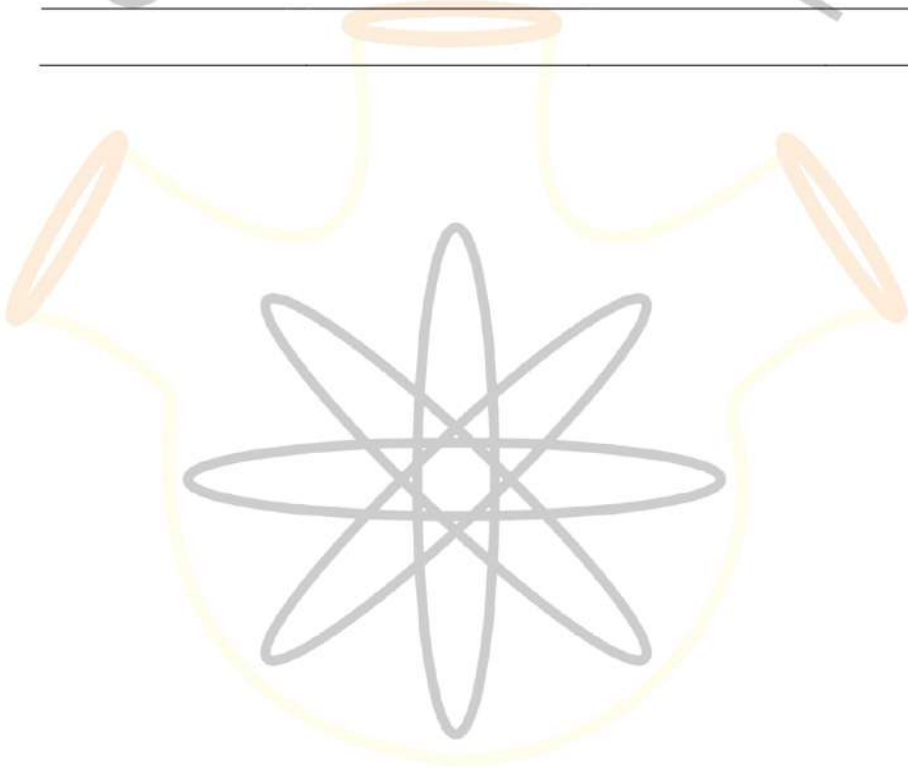
Time (minutes)	Va out (mL)	ΔP_1	ΔP_2

Table 3.2 Data for variable 2

Time (minutes)	Va out (mL)	ΔP_1	ΔP_2

Table 3.3 Data for variabel 3

Time (minutes)	Va out (mL)	ΔP_1	ΔP_2



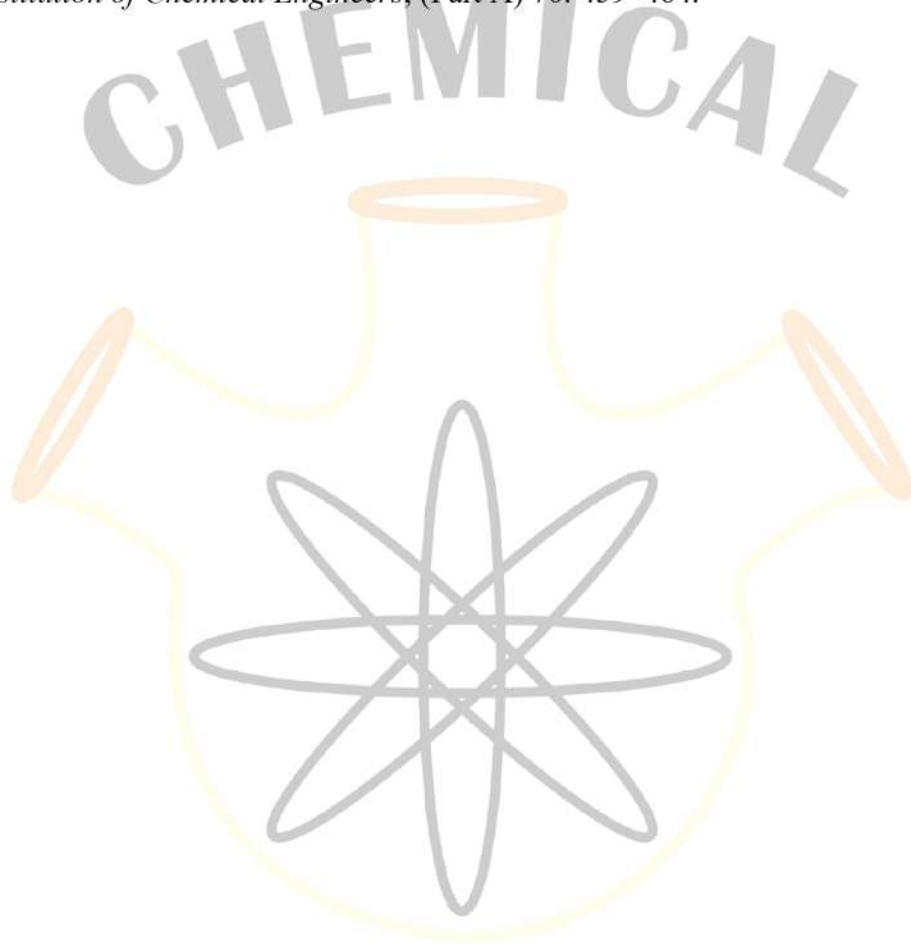
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