CHAPTER I
INTRODUCTION

1.1 Background

Chemical reactions applied in the chemical industry can involve raw materials in different forms, either in the form of solids, gases, or liquids. Therefore, chemical reactions in an industry can occur in single phase (homogeneous) or double phase (heterogeneous), for example binary or even tertiary (Coulson, 1996). Before a chemical reaction takes place, one or more of the raw materials (reactants) will move from its main flow to the interphase / boundary layer or to the main flow of other raw materials that are in a different phase.

Gas-liquid absorption is a heterogeneous process that involves the transfer of soluble gaseous components to an absorbent that is usually a non-volatile liquid (Franks, 1967). Chemical reactions in the absorption process can occur in the gas layer, the interphase layer, the liquid layer, or even the main body of the liquid, depending on the concentration and reactivity of the reacted . To facilitate these process stages, the absorption process is usually carried out *in* a sparged stirred tank reactor (mass flow sprayer), *bubble* column, or *packed bed column*. The gas-liquid absorption process can be applied to the purification of synthesis gases that are still useful in flue gases or even in industries that involve dissolving gases in liquids, such as H_2SO_4, HCl, HNO_3, formadehyde, and others (Coulson, 1996). Absorption of CO_2 gas with a strong hydroxide solution is an absorption process accompanied by a 2nd order chemical reaction between CO_2 and OH^- ions to form CO_3^{2-} and H_2O ions. While the reaction between CO_2 and $CO_{(3}^{)(2-)}$ to form HCO_3^- ions is usually ignored (Danckwerts 1970; Juvekar & Sharma, 1972). However, according to Rehm *et al.* (1963) this process is also commonly considered to follow a 1st order reaction if the concentration of NaOH solution is low enough (dilute).

The design of chemical reactors is based on modeling the hydrodynamics of the reactor and the chemical reactions that occur in it. A mathematical model is a simplified form of the actual process in a reactor which is usually very complicated (Levenspiel, 1972). Chemical reactions are usually studied in a laboratory-scale *batch* process by considering the need for reactants, ease of reaction control, equipment, ease of running reactions and analysis, and accuracy.

1.2 Problem Formulation

1. How do the variables affect the amount of CO_2 adsorbed at various reaction times?
2. How do the variables affect the value of the gas phase CO_2 mass transfer constant (k_{Ga})?
3. How do the variables affect the value of the liquid phase CO_2 mass transfer constant (k_{La})?
4. How do the variables affect the value of the total mass transfer constant between CO_2 and H_2O ($K_{(OG)}$)?

1.3 Experiment Objective

After conducting this experiment, students are able to explain the following:

1. Students are able to prepare, operate the absorption process and analyze samples and process experimental data.
2. Able to prepare and operate absorption systems and analyze samples and process experimental data.
3. Effect of variables on the amount of CO_2 adsorbed at various reaction times.
4. Effect of variables on the value of the gas phase CO_2 mass transfer constant (k_{Ga}).
5. Effect of variables on the value of the liquid phase CO_2 mass transfer constant (k_{La}).
6. Influence of variables on the value of the total mass transfer rate between CO_2 and H_2O (K_{OG}) and compare it with the reaction rate data in the literature.

1.4 Benefits of the Experiment

Students are able to understand the reactions that occur in gaseous and liquid reactants (heterogeneous) and apply them in reactor design research and related process equipment.

CHAPTER II
LITERATURE REVIEW

2.1 Absorption

Absorption is one of the separation processes in the chemical industry where a gas mixture is contacted with an absorbent liquid so that one or more components of the gas dissolve in the liquid. 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 in an absorbent solution, but is not accompanied by a chemical reaction. Examples of this process are the absorption of H_2S gas with water, methanol, and propylene carbonate. Absorption occurs due to physical interaction between the gas and the liquid. The mechanism of the physical absorption process can be explained by several models: the *two films* theory by Whitman (1923), the penetration theory by Dankcwerts, and the renewed surface theory.

2.1.2 Chemical Absorption

Chemical absorption is a process that involves the dissolution of gas in an absorbent solution accompanied by a chemical reaction. Examples of this event are the absorption of CO_2 gas with a solution of MEA (Mono Ethanol Amine), NaOH, K_2CO_3 (Potassium Carbonate) and so on. Applications of chemical absorption can be found in the CO_2 gas absorption process at the Ammonia plant as shown in Figure 2.1.

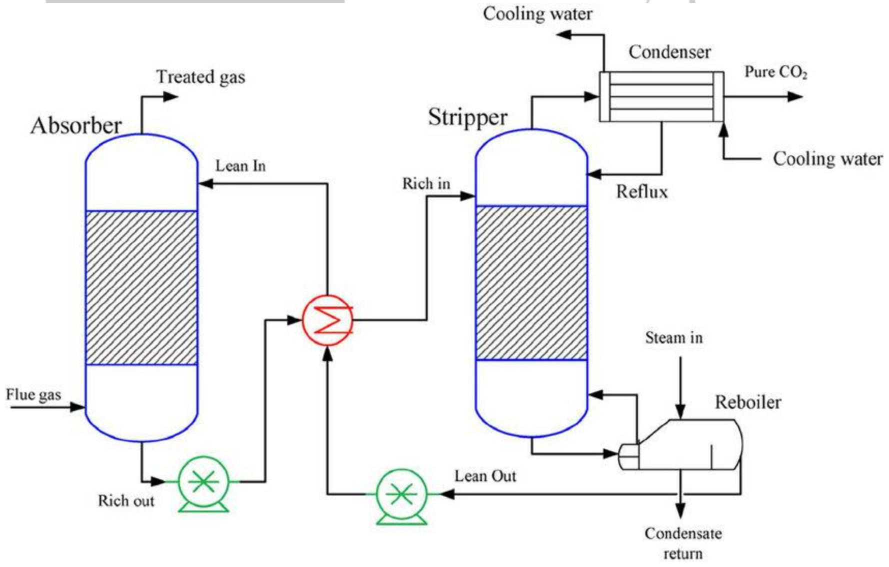

Figure 2.1 CO_2 absorption and desorption process with MEA solvent at Ammonia plant

The absorption process can be carried out *in* a stirred tank equipped with a *sparger*, *bubble column*, *packed column*, or *tray column*. The selection of absorption process equipment is usually based on the reactivity of the reactants (gases and liquids), the corrosivity of the absorbed material and the absorbent, temperature, pressure, capacity, and economy.

2.2 Absorption Column

Absorption column is a column or tube where the absorption process of substance passed in the column / tube occurs. In general, there are four types of absorption columns, namely: *spray column*, *bubble column*, *tray column*, and *packed bed column*.

2.2.1 ***Spray*** **tower (*spray column*)**

In a *spray* tower the gas phase flows up through a large open space and the liquid phase is introduced by means of a *nozzle* or other atomizer. The liquid is fed in the form of fine drops, falling in the opposite direction to the upward flow of gas.

2.2.2 ***Bubble*** **Tower (*bubble column*)**

bubble tower consists of large open spaces through which the liquid phase flows and into which gas is dispersed into the liquid phase in the form of fine bubbles. Small gas bubbles will provide the desired contact area, rising bubbles cause a mixing action in the liquid phase, thus reducing the resistance of liquid phase to mass transfer. Bubble towers are used with systems where the liquid phase usually controls the mass transfer rate.

2.2.3 ***Plate*** **tower (*tray column*)**

Plate towers or *tray columns* are towers that have been widely used in industry. This tower consists of several types, namely: *Sieve Tray, Valve Tray*, and *Bubble Cup Tray*.

2.2.4 ***Packing*** **Tower (*packed bed column*)**

The *packing* tower is a tower filled with filler material. The function of the filler material is to expand the contact area between the two phases. In this tower, the liquid will flow downward through the bottom surface of the filler, while the gas will flow upward in the opposite direction, through the empty space between the fillers.

2.3 Analysis of Mass Transfer and Reaction in Gas Absorption Process by Liquid

In general, the absorption process of CO_2 gas into NaOH solution accompanied by chemical reactions takes place through four stages, namely the mass transfer of CO_2 through the gas layer to the gas-fluid interphase layer, the equilibrium between $CO_{(2)}$in the gas phase and in the solution phase, the mass transfer of CO_2 from the gas layer to the main body of the NaOH solution, and the reaction between dissolved CO_2 and hydroxyl groups ($OH^{-)}$. process scheme can be seen in Figure 2.2.

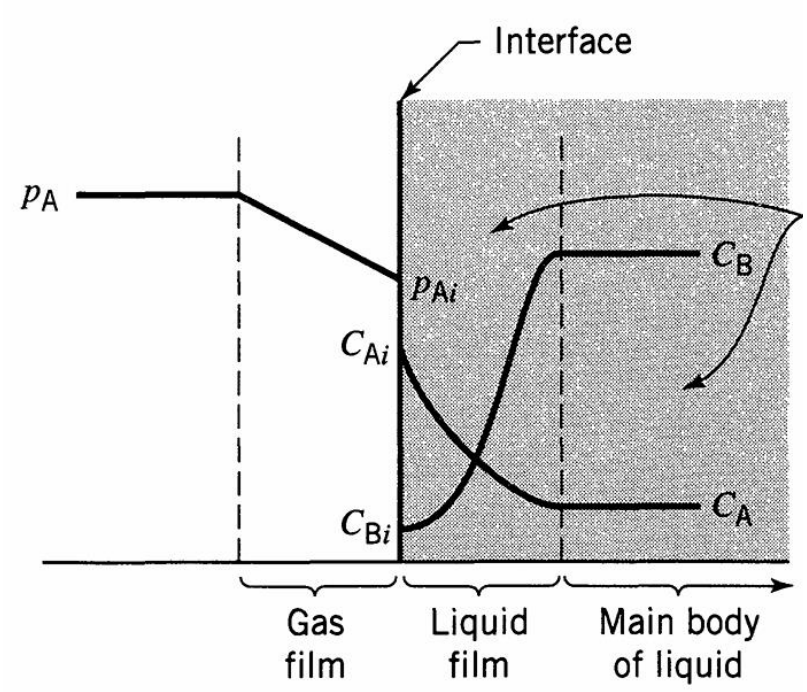

Figure 2.2 Absorption mechanism of CO_2 gas in NaOH solution

Mass transfer rate of CO_2 through the gas layer:

$R_a = k_{ga} (p_g - p_{ai})$ (2.1)

Equilibrium between CO_2 in the gas phase and in the solution phase:

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

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

p_{ag} = Partial pressure of gas A in the gas phase (atm)

k_{ga} = Coefficient of mass transfer in the gas phase (mol/atm.min)

H = equilibrium constant of gas A (atm/L.mol)

C_{Ai} = concentration of A in the liquid phase at the gas-liquid interphase with H at 30°C = $2.88.10^{-5}$ g.mol/cm^3. atm.

The mass transfer rate of CO_2 from the gas layer to the main body of NaOH solution and the reaction between dissolved CO_2 and hydroxyl groups:

$R_a = [A^*]a \sqrt{D_A k_A\ [OH-]}$

Boundary state:

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

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

where z is the chemical reaction coefficient between $CO_{(2}{}^{)}$and $[OH^-]$, which = 2. In the liquid phase, the reaction between $CO_{(2}{}^{)}$and NaOH solution occurs through several stages of the process:

$$NaOH_{(aq)} \rightleftarrows Na^{+}{}_{(aq)} + OH^{-}{}_{((aq}{}^{))} \qquad (a)$$

$$CO_{2(g)} \rightleftarrows CO_{2(aq)} \qquad (b)$$

$$CO_{(2(aq}{}^{)})+ OH^{-}{}_{(l)} \rightleftarrows HCO_3{}^{-}{}_{(l)} \qquad (c)$$

$$HCO_3{}^{-}{}_{(l)} + OH^{-}{}_{(l)} \rightleftarrows H_2O_{(l)} + CO_3{}^{(2-}{}_{)((l))} \qquad (d)$$

$$CO_{(3}{}^{)(2-)}{}_{(l)} + 2Na^{+}{}_{(l)} \rightleftarrows Na_2CO_{3(aq)} \qquad (e)$$

Steps d and e usually proceed very quickly because they are ionic reactions, so the absorption process is usually controlled by the dissolution event of CO_2 into the NaOH solution especially if CO_2 is fed in mixed form with other gases or controlled together with the chemical reaction in step c (Juvekar & Sharma, 1973).

Elimination of A* from equations 1, 2, and 3 yields :

$$R_a = \frac{a.H.pg.\sqrt{D_A.k_2.[OH^-]}}{1+\frac{a.H.\sqrt{D_A.k_2.[OH^-]}}{k_{Ga}}} \qquad (2.4)$$

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

$$R_a = \frac{a.H.pg.\sqrt{D_A.k_2.[OH^-]+k_L{}^2}}{1+\frac{a.H.\sqrt{D_A.k_2.[OH^-]+k_L{}^2}}{k_{Ga}}} \qquad (2.5)$$

If boundary condition (b) is not met, there is a dissolution of $[OH^-]$ in solution. This results in:

$$\frac{\sqrt{D_A.k_2.[OH^-]}}{k_L} \approx \frac{[OH^-]}{z.A*}\sqrt{\frac{D_A}{D_B}} \qquad (2.6)$$

Thus, the absorption rate of CO_2 gas into NaOH solution will follow the equation:

$$R_a = \frac{a.H.pg.\phi\ k_L}{1+\frac{a.H.\phi\ k_L}{k_{Ga}}} \qquad (2.7)$$

With ϕ is the *enhancement* factor which is the ratio between the mass transfer coefficient of CO_2 in the liquid phase if absorption is accompanied by chemical reactions and not accompanied by chemical reactions as formulated by Juvekar and Sharma (1973):

$$\Phi = \frac{\sqrt{D_A.k_2.[OH^-]}}{k_L}.\left[\frac{1+\frac{[OH^-]D_B}{z.A*\,D_A}\Phi}{\frac{[OH^-]}{z.A*}.\frac{D_B}{D_A}}\right]^{\frac{1}{2}} \qquad (2.8)$$

The effective diffusivity (DA) of CO_2 in NaOH solution at $30^{(o)}$C is 2.1 x 10^{-5} cm^2/det (Juvekar & Sharma, 1973).

The value of k_{Ga} can be calculated based on physical absorption by reviewing the total mass transfer of CO_2 into NaOH solution that occurs at a certain time interval in the absorption device. In the form of dimensionless number, k_{Ga} can be calculated according to the equation (Kumoro & Hadiyanto, 2000):

$$\frac{k_{Ga} dp^2}{D_A} = 4.007 \text{ x} \left(\frac{\rho_{CO_2}.Q_{CO_2}}{\mu_{co_2} a}\right)^{1,4003} x \left(\frac{\mu_{CO_2}}{\rho_{CO_2} D_A}\right)^{\frac{1}{3}} \qquad (2.9)$$

With a $=\frac{6-(1-\epsilon)}{dp}$ and $\epsilon = \frac{V_{void}}{V_T}$

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

$$k_{Ga} = \frac{mol\ (Co_2,liq)}{A.Z.\epsilon\ P_{lm}} = \frac{mol\ ({CO_3}^{2-})}{A.Z.\epsilon\ P_{lm}} \qquad (2.10)$$

If the operating pressure is low enough, then p_{lm} can be approximated by

$$\Delta p = P_{in} - P_{out}$$

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

$$\frac{K_{La}.dp}{D_A} = 0.2558 \text{ x x} \left(\frac{\rho_{N_aOH}.Q_{N_aOH}}{\mu.a}\right) \left(\frac{\mu}{\rho.D_A}\right)^{0,5} \qquad (2.11)$$

If the reaction rate of Na_2CO_3 formation is much greater than the diffusion rate of CO_2 into the NaOH solution, the concentration of CO_2 at the boundary of the liquid film with the liquid body is zero. This is due to the very fast consumption of CO_2 during the reaction along the film. Thus the film thickness (δ) can be determined by the equation:

$$\delta = \frac{D_A(P_{in} - P_{out})}{mol\ ({CO_3}^{2-}).R.T} \qquad (2.12)$$

CHAPTER III

PRACTICUM METHOD

3.1 Trial Design

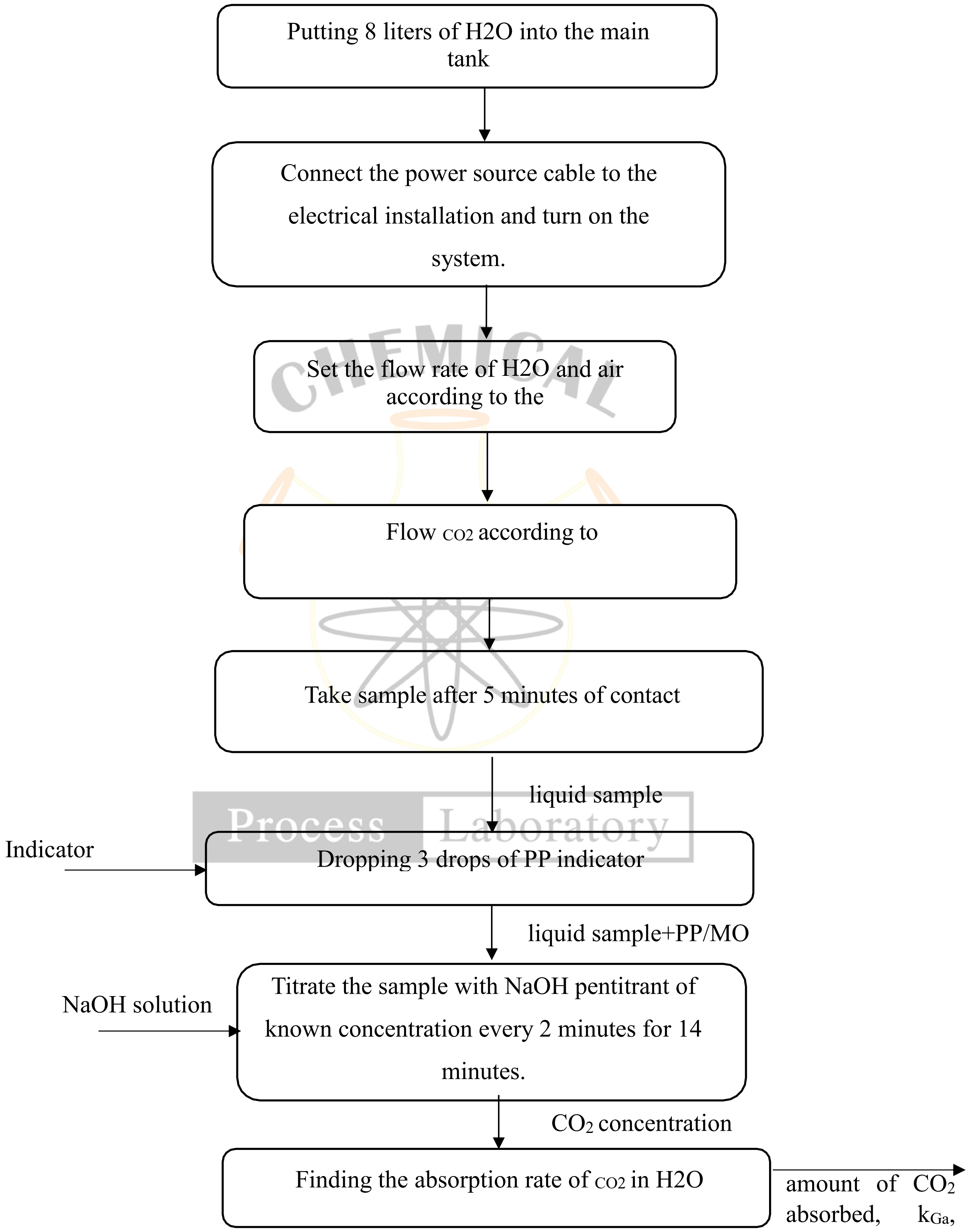

Figure 3.1 Schematic design of the practicum

3.1.1 Variable Assignment

A. Fixed variable

B. Variable changes

3.2 Materials and Tools Used

1. Materials used
    1. Sodium hydroxide (NaOH) crystals
    2. Carbon dioxide (CO_2) in liquid phase stored in pressurized tubes
    3. Air
    4. Distilled water (H_2O)
    5. *Phenolphthalein* (PP) indicator @3 drops
2. Tools used

    The absorption laboratory circuit is shown in Figure 3.2.

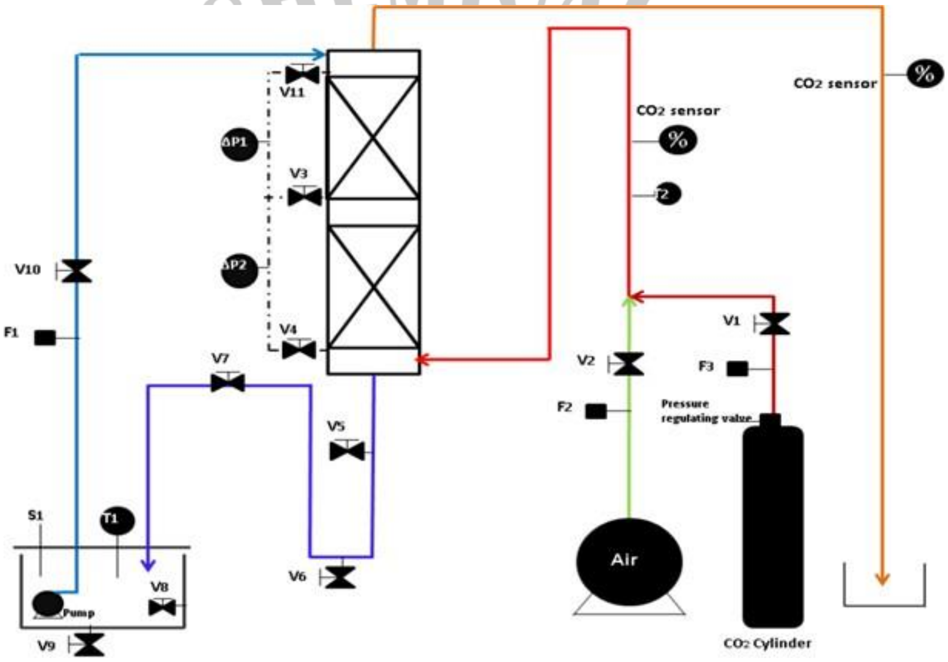

Figure 3.2 Main tool circuit

3.3 Test Response Results

Concentration of $CO_{(3}^{)(2-)}$ ions in sample solution and CO_2 adsorbed

3.4 Practicum Procedure

A. Tool preparation

First, the power cord is plugged into the power source, then the ON/OFF button is turned and the monitor turns on. The main water supply to the basin tank is turned on and allow the tank to fill. Ensure the water outlet from the column is plugged into the pipe that returns the water to the tank. With gas flow *valves* V1 and V2 closed, the liquid pump is turned on.

Then, the water flow through the column at *flowmeter* F1 is adjusted using valve $V_{10.}$ The compressor is turned on and *valve* V_2 is adjusted to provide air flow. The pressure regulating *valve* on cylinder CO_2 was opened, and valve V_1 was adjusted to give a value to flow meter F_3. After 5 min of stabilization, samples were taken at 2 min intervals for 14 min from the *inlet valve* and *outlet valve*. Samples were taken at 25 ml at known times in each case. Analyze the samples according to the procedure.

B. Determination of dissolved CO_2

Samples were taken as much as 25 ml each. Dropped 2-3 drops of PP / MO indicator, if a red color is formed immediately then there is no free CO_2. Titrate the sample with standard NaOH solution according to the variable until a pink color is formed that does not disappear 30 seconds. Record the volume of titrant needed.

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

$$\text{gmol/liter } CO_2 = \frac{\text{V titran X N titran}}{\text{volume sampel}} = \text{Cd}$$

3.5 Observation Sheet

3.5.1 Operation Variables

a. Fixed variable

b. Variable changes

3.5.2 Data

Table 3.1 Data on variable

Time (minutes)	Va in (mL)	Va out (mL)

Table 3.2 Data on variable 2

Time (minutes)	Va in (mL)	Va out (mL)

Table 3.3 Data on variable 3

Time (minutes)	Va in (mL)	Va out (mL)

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