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Gas absorption with chemical reaction is an important unit operation in the chemical and petroleum industries for the selective removal of components from industrial gas streams. Apart from choosing absorption media, the most difficult problems facing the design engineer are the sizing and performance prediction of the absorption tower due to the scarcity of fundamental design data, especially when novel absorption media and/or packings are used.

The solubility of carbon dioxide in 2 and 3 M solutions of 2-amino-2-methyl-1-propanol (AMP), which is a newly introduced absorbent, was determined at 20, 40, 60 and 80 °C and for CO₂ partial pressures ranging from approximately 1 to 100 kPa. The results were interpreted with a modified Kent-Eisenberg model which predicted the present and previous experimental results well. The absorption capacities of AMP and monoethanolamine (MEA) solutions were also compared.

Detailed concentration and temperature measurements were reported for the absorption of carbon dioxide from air into NaOH, MEA and AMP solutions. A full-length absorber (0.1 m ID, packed with 12.7 mm Berl Saddles up to heights of 6.55 m) was used. It was operated in countercurrent mode and at 30 to 75 % flooding velocities which are typical for gas
absorber operations. The following ranges of operating conditions were employed: superficial gas flow rate 11.1 to 14.8 mol/m² s; superficial liquid flow rate 9.5 to 13.5 m³/m² h; feed CO₂ concentration 11.5 to 19.8 %; total absorbent concentration 1.2 to 3.8 kmol/m³; liquid feed temperature 14 to 20 °C; total pressure 103 kPa. The measurements for the CO₂-NaOH and CO₂-MEA systems were compared with predictions from a previously developed mathematical model. Generally good agreement was obtained except at high CO₂ loadings of MEA solutions. Compared with MEA, AMP was found to have superior CO₂ absorption capacities and inferior mass transfer rates.

A new procedure, called the Pilot Plant Technique (PPT), for designing gas absorbers with chemical reactions has been developed. The PPT is primarily intended for designing absorbers for which fundamental design information is lacking. It is based on the premise that full-length absorption columns can be sized by making a minimum number of tests using a small-scale pilot plant. Two special features of the PPT are (i) the details of hydrodynamic parameters (i.e. mass transfer coefficients, effective interfacial area and liquid hold-up) and the physico-chemical information of the system (e.g. reaction mechanism, reaction rate constants) need not be known and (ii) complex calculations are avoided.
Using the PPT to size the height or to predict the performance of a given full-length absorber, the specific absorption rate, which is the essential information, can be measured directly using the pilot plant model (PPM) column if both columns have the same hydrodynamic conditions. This can be achieved by using the same type and size of packing in the PPM and the full-length columns and ensuring that the end and wall effects are negligible. The PPM column must also be operated at the same superficial fluid velocities as those of the full-length column. The specific absorption rate was then obtained from the gradient of the fluid composition profile along the PPM column. The validity of the PPT was demonstrated by determining the height and predicting the performance of the full-length column in which carbon dioxide was absorbed from air by aqueous solutions of NaOH and AMP at various operating conditions; good agreement was obtained.
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Figure 7.26: Column temperature measured from the full-length (solid circles) and PPM column (open squares) for Run T27. Operating conditions: gas flow rate = 11.1 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.0%; inlet liquid loading = 0.021 mol CO₂/mol AMP

Figure 7.27: Column temperature measured from the full-length (solid circles) and PPM column (open squares) for Run T30. Operating conditions: gas flow rate = 11.1 mol/m² s; liquid flow rate = 13.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.0%; inlet liquid loading = 0.29 mol CO₂/mol AMP
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CHAPTER 1
INTRODUCTION

Most natural gas processing plants, petroleum refineries, and many chemical production plants use gas absorption processes for removing acid gases (such as CO₂, H₂S) from their streams [1-12]. Some major industrial processes that need acid gas treating are listed in Table 1.1 [12] and typical compositions of some corresponding gas streams are shown in Tables 1.2 to 1.4. As can be seen from these tables, substantial amounts of acid gases have to be removed before the streams can be utilized or marketed.

In the case of natural gas, which is one of the world's most extensive and cleanest energy sources, the majority of raw gases contain significant amounts of CO₂ and H₂S. According to statistics published in 1990 in the Oil & Gas Journal [121, 122], more than 0.14 trillion m³ (5.04 trillion ft³) and 2.0 trillion m³ (70.0 trillion ft³) of natural gas are being produced annually in Canada and worldwide, respectively. (The proven natural gas reserves worldwide (excluding communist countries) and of Canada are
Table 1.1: Major industrial processes requiring acid gas treating [12].

<table>
<thead>
<tr>
<th>Process</th>
<th>Acid gases to treating $^a$</th>
<th>Common cleanup targets (% acid gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen manufacture</td>
<td>CO$_2$</td>
<td>&lt;0.1% CO$_2$</td>
</tr>
<tr>
<td>Petroleum desulfurization</td>
<td>CO$_2$ + H$_2$S + COS</td>
<td>10 ppm H$_2$S</td>
</tr>
<tr>
<td>Coal liquefaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia manufacture (H$_2$/N$_2$ mixture)</td>
<td>CO$_2$</td>
<td>&lt;16 ppm CO$_2$ + CO</td>
</tr>
<tr>
<td>Natural gas purification</td>
<td>CO$_2$ + H$_2$S + COS</td>
<td>0.01 ppm H$_2$S</td>
</tr>
<tr>
<td>Pipeline gas</td>
<td>H$_2$S, CO$_2$, COS, RSH, etc.</td>
<td></td>
</tr>
<tr>
<td>LNG feedstock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syn gas for chemicals (H$_2$/CO)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal gasification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNG (high Btu gas)</td>
<td>CO$_2$, H$_2$S, COS</td>
<td>500 ppm CO$_2$; 0.01 ppm H$_2$S</td>
</tr>
<tr>
<td>Intermediate Btu gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Btu gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil desulfurization</td>
<td>H$_2$S</td>
<td>100 ppm H$_2$S</td>
</tr>
<tr>
<td>Refinery fuel gas treating</td>
<td>H$_2$S, CO$_2$, COS</td>
<td>100 ppm H$_2$S</td>
</tr>
<tr>
<td>Ethylene manufacture (steam cracker gas treating)</td>
<td>H$_2$S, CO$_2$</td>
<td>~1 ppm H$_2$S, 1 ppm CO$_2$</td>
</tr>
<tr>
<td>Flue gas desulfurization</td>
<td>SO$_2$</td>
<td>90% removal</td>
</tr>
<tr>
<td>Utilities (electric)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refineries, etc.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.2: Typical composition of Canadian, Thai and American natural gases (dry basis, mole %).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Canada*</th>
<th>Thailand**</th>
<th>US***</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ft. St. John</td>
<td>East Calgary</td>
<td>Erawan &quot;B&quot; Structure</td>
</tr>
<tr>
<td>C₁</td>
<td>85.34</td>
<td>54.40</td>
<td>63.34</td>
</tr>
<tr>
<td>C₂</td>
<td>4.50</td>
<td>0.35</td>
<td>10.61</td>
</tr>
<tr>
<td>C₃</td>
<td>1.50</td>
<td>0.12</td>
<td>5.17</td>
</tr>
<tr>
<td>iC₄</td>
<td>0.25</td>
<td>0.01</td>
<td>1.07</td>
</tr>
<tr>
<td>nC₄</td>
<td>0.48</td>
<td>0.04</td>
<td>0.89</td>
</tr>
<tr>
<td>C₅</td>
<td>0.83</td>
<td>0.00</td>
<td>0.81</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.41</td>
<td>13.77</td>
<td>17.20</td>
</tr>
<tr>
<td>H₂S</td>
<td>4.37</td>
<td>29.12</td>
<td>0.00</td>
</tr>
<tr>
<td>N₂</td>
<td>0.00</td>
<td>2.13</td>
<td>0.90</td>
</tr>
<tr>
<td>H₂</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* from Younger [149]
** from Meisen [3]
*** from Astarita et al. [12]
Table 1.3: Typical composition of product gas from natural gas steam reforming process [12].

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole % (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>58.3</td>
</tr>
<tr>
<td>N₂</td>
<td>18.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>20.4</td>
</tr>
<tr>
<td>CO</td>
<td>1.0</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.7</td>
</tr>
<tr>
<td>Ar</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 1.4: Typical composition of product gas from a coal gasification process, Flexicoker [12].

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole % (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>18.2</td>
</tr>
<tr>
<td>N₂</td>
<td>50.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>11.4</td>
</tr>
<tr>
<td>CO</td>
<td>17.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.4</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.0</td>
</tr>
<tr>
<td>CÔS</td>
<td>0.02</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.06</td>
</tr>
</tbody>
</table>
2.7 and 68.6 trillion m$^3$, respectively[121, 122].) For a typical gas processing plant which processes natural gas containing 10 to 20% of acid gases, the capital and operating costs of acid gas removal can be as high as one quarter to one half of the total cost [147].

In the manufacture of hydrogen, very large volumes of CO$_2$ must be removed from the product stream before it can be marketed or used as a feedstock for other chemicals such as ammonia. The CO$_2$ removal requirements depend largely on the process used and the plant feedstocks which are mostly light or heavy hydrocarbons or coal. For example, in the production of synthesis gas (a mixture of H$_2$ and N$_2$ for producing NH$_3$), the CO$_2$ removal requirement ranges from 1.22 tons CO$_2$/ton of synthesis gas produced from steam reforming of natural gas to 2.49 tons CO$_2$/ton of synthesis gas made by the partial oxidation of heavy fuel oil. The amounts of CO$_2$ to be removed are significant, ranging up to over 20,000 tons/day for large plants [19]. According to Weinberg et al. [100], worldwide annual production of H$_2$ and NH$_3$ are well over 160 billion m$^3$ and 100 million tons, respectively. Furthermore, their production rates are still growing at more than 10% per year. Stratton and Teper [148] have estimated the capital cost associated with the CO$_2$
separation unit for commercial synthesis gas plants to be up to 40% of the total cost (c.f. Table 1.5). As can be seen from these figures, a significant portion of the processing efforts is directly associated with CO$_2$ separation in producing basic chemical products.

For coal gasification plants producing high-Btu synthetic natural gas, acid gas removal systems also account for a sizeable percentage of the total plant investment. According to Penner et al. [83], about 30% of the plant investment is allocated to purification processes; the gasification section requires only 10 to 15%. Furthermore, the operating costs for the purification processes are substantial.

It is therefore clear that acid gas separation is one of the most important processing steps in the productions of a variety of basic chemicals. To summarize the importance of gas treating, the statement by Astarita, Savage and Bisio [12] may be quoted:

"...The major traditional uses of gas treating for CO$_2$ and H$_2$S removal in hydrogen manufacture, ammonia production, petroleum refining, and natural gas purification are expected to experience significant growth in
the coming decades. The importance of gas treating will grow faster than industrial activity as a whole, owning to the growing use of heavier more sulfurous petroleum, coal, shale, and tar sands as feedstocks and fuels. Large quantities of acid gases will have to be removed from these new energy sources. Moreover, the complexity of gas treating will increase since the acid gases will contain large quantities of CO$_2$, significant amounts of H$_2$S, and troublesome levels of other sulfur contaminants such as COS. These changes will require improved energy-efficient treating technology for both simultaneous and selective gas treating.

In the case of natural gas, new gas finds are expected to be at greater depths and in more remote locations than was the case in the past. New natural gas is expected to be more highly contaminated with H$_2$S and CO$_2$. These gases will require extensive treating to make them suitable for pipelining or conversion to LNG, methanol, or gasoline. Remote production of gas (e.g. offshore or on permafrost) will require improved technology with emphasis on small size units of light weight and high reliability."
Table 1.5: Capital cost breakdown for a commercial scale plant producing synthesis gas (N₂+3H₂) from steam reforming for making ammonia [148].

<table>
<thead>
<tr>
<th>Plant section</th>
<th>Capital cost as % of the total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary and secondary reforming</td>
<td>51.4 %</td>
</tr>
<tr>
<td>Shift and Methanation</td>
<td>8.6 %</td>
</tr>
<tr>
<td>CO₂ removal</td>
<td>40.0 %</td>
</tr>
</tbody>
</table>
1.1 ACID GAS ABSORPTION BY CHEMICAL SOLVENTS

Even though many acid gas removal processes are available, over 90% of existing plants use chemical absorption [3, 4, 6, 10, 11]. Its popularity stems from high separation rates and capacities which lead to relatively low overall costs [8]. The most commonly used chemical solvents are listed in Table 1.6 [12].

Amine solutions are employed in more than 60% of the existing plants, especially in natural gas processing plants. The second major group is based on aqueous potassium carbonate solutions with inorganic or organic additives [11]. Sodium hydroxide solutions are generally only used as a final treatment step [12].

A typical flow sheet of an industrial acid gas removal system utilizing a chemical absorbent is shown in Figure 1.1. The sour gas, which enters the unit through an inlet separator where entrained liquid and solid particulates are removed, flows from the bottom of the absorber upwards against a counter-current stream of the lean solution. The acid gases are absorbed and the treated (or "sweet") gas leaves the top of the absorber.
Table 1.6: Common alkaline reagents used as chemical solvents [12].

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>( \text{N} - \text{H} ) \text{C} - \text{C} - \text{OH}</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>( \text{N} - \text{H} ) \text{C} - \text{C} - \text{OH} ), ( \text{OH} )</td>
</tr>
<tr>
<td>Diisopropanolamine (DIPA)</td>
<td>( \text{N} - \text{H} ) \text{C} - \text{C} - \text{C} - \text{OH}</td>
</tr>
<tr>
<td>( \beta, \beta' ) Hydroxyaminoethylether (DGA)</td>
<td>( \text{N} - \text{H} ) \text{C} - \text{C} - \text{O} - \text{C} - \text{C} - \text{OH}</td>
</tr>
<tr>
<td>Potassium carbonate (with promoters)</td>
<td>( \text{K}_2\text{CO}_3 )</td>
</tr>
<tr>
<td>Potassium glycinate</td>
<td>( \text{NaOH} )</td>
</tr>
<tr>
<td>Caustic</td>
<td>( \text{NaOH} )</td>
</tr>
</tbody>
</table>
Figure 1.1: Typical flowsheet for gas sweetening by chemical reaction [13].
The acid gas loaded ("rich") solution flows from the bottom of the absorber and passes through the lean-rich heat exchanger where it is heated by the hot, recycled lean solution. It then enters the top of the stripper column. In some cases, a flash tank is installed upstream of the heat exchanger to desorb dissolved hydrocarbons and some of the acid gases by letting down the pressure of the rich stream.

Upon entry into the stripper, some of the absorbed acid gases are flashed. The solution then flows downward against a counter-current flow of water vapor generated in the reboiler. The stripping vapor removes most of the remaining acid gases from the rich stream.

The overhead mixture leaves the stripper through a condenser where most of the water vapor is condensed and returned to the stripper as reflux. The lean solution, which leaves the bottom of the stripper, exchanges heat with the rich solution in the lean-rich heat exchanger and then passes through a cooler before being pumped to the absorber.
1.2 DESIGN OF CHEMICAL GAS ABSORPTION COLUMNS

In general, the most important design problem of a gas absorption process is posed by the absorption column because it has the greatest effect on the capital and operating cost of the process. Although many different types of gas-liquid contactors have been developed, only packed and tray columns have found significant industrial use as gas absorbers. More recently, packed towers are gaining an increasing share of the market due to the development of high-capacity, high-efficiency packings [19]. These new packings are also used to retrofit existing units in order to improve column capacities.

Industrial design methods for sizing packed absorption towers are given by the NGPSA Engineering Data Book [13], Maddox [4], and Kohl and Riesenfeld [15]. In addition, the latest data and methods for the selection and design of industrial gas treating processes have been compiled by Newman [16]. Theoretical design approaches are presented by Astarita [17] and Danckwerts [18]. Recently, both the industrial and theoretical design approaches were combined by Astarita, Savage and Bisio [19].
Nevertheless, the design of many gas absorbers using, for example, amines or activated hot potassium carbonate is still largely based on experience or "rules of thumb" [14, 22, 124] despite the fact that absorption with chemical reaction has been studied for over sixty years. (Hatta's work [23] was first published in 1928.) The main reason for this is the lack of fundamental design data, i.e. mass transfer coefficients, interfacial areas, reaction kinetics, and physico-chemical properties. Another reason is the lack of confidence in the theoretical design procedures [15, 24] which are often complex or based on doubtful assumptions [4, 22]. For instance, using the theoretical method recommended by Danckwerts [18] and the data given by Beddome [21], DeCoursey showed that the height of absorbers would be overestimated by as much as a factor of four [20]. This indicates that considerable discrepancies may exist between theoretical predictions and actual requirements [25]. To quote from Maddox [4], "Fixing the number of trays, either theoretical or actual, in the absorber is not a simple task. As a matter of fact, many authors feel that computation of the number of trays required is an exercise in futility. The calculation of rates and efficiencies of a simple absorption process is complicated enough. In the case of absorption followed by chemical reaction, the calculations
become exceedingly difficult". A similar statement also applied to designing packed towers.

Evidence supporting this observation is provided in Figure 1.2 which is based on typical industrial data [15]. As can be seen, most of the absorber (approximately 60%) does not perform a useful duty and represents an over design of the column.
Figure 1.2: Concentration and temperature profiles of a typical industrial absorber [15].
1.3 RESEARCH OBJECTIVES

In the past few years, much progress has been made in the basic understanding of chemical absorption processes [22, 84]. For some systems like CO₂–NaOH and CO₂–conventional amines, accurate, steady state simulation of gas absorption with chemical reaction has become possible provided the fundamental design data (i.e. mass transfer coefficients, reaction kinetics, physico-chemical properties, etc.) are available. Unfortunately, comprehensive data on absorber performance under industrial conditions are rarely published in the open literature. Most of the published data are incomplete or insufficient to permit sound comparisons with theoretical predictions [15, 123]. Therefore, good full-length absorber data are required to validate the theoretical predictions and to give confidence to industrial design.

Furthermore, improvements in chemical absorption processes are still progressing at a fairly fast rate. New and higher capacity chemical solvents (e.g. mixture of amines, sterically hindered amines) and high-efficiency mass transfer equipment (e.g. structured packings) are introduced every year. Enormous amounts of fundamental design data
would be needed to permit the complete simulation of such absorbers.

The principal objective of this thesis is to develop a new design concept for industrial absorbers with chemical reaction. This new design concept is subsequently called the "Pilot Plant Technique" or PPT. The concept depends only on laboratory-scale, pilot plant experiments and requires a minimum knowledge of the absorption system. This new design concept is subsequently validated by applying it to a full-length absorber (6.6 m high) in which CO₂ was removed from air using aqueous solutions of sodium hydroxide and 2-amino-2-methyl-1-propanol (AMP), which is a sterically hindered amine. These absorption systems were selected because they are industrially important and used extensively [17, 18, 76]. To narrow the scope of the study, the research was restricted only to packed columns.

This dissertation also reports extensive experimental data on gas and liquid concentrations as well as temperature profiles for CO₂ - NaOH, CO₂ - MEA and CO₂ - AMP absorbers of various heights. In addition, comparisons between the experimental data and theoretical predictions are presented
for the CO$_2$-NaOH and CO$_2$-MEA systems because their fundamental design data are available.

Since the CO$_2$-AMP system is one of the systems used to validate the PPT concept, the solubility of CO$_2$ in AMP solutions had to be determined. Previously reported solubility data were too limited and did not cover the typical operating ranges of absorbers.

This thesis is divided into nine chapters. Chapter 2 is a general literature review of subjects related to gas absorption with chemical reaction. The details of the theoretical absorber design procedure, which is based on previously published work, and the development of the Pilot Plant Technique are given in Chapter 3. Chapter 4 is a self contained chapter and reports the study of CO$_2$ solubility in AMP solutions. Chapter 5 presents the details of the experimental equipment and the related operating procedures. In Chapter 6 the results, which were obtained from the full-length absorber and the theoretical design procedure given in Chapter 3, are discussed. Chapter 7 presents the verification results of the Pilot Plant Technique. Conclusions drawn from this research project are summarized
in Chapter 8. The thesis terminates with a summary of suggestions for future work in Chapter 9.
CHAPTER 2
LITERATURE REVIEW

The contents in this chapter are general reviews of the subjects related to the design aspects of gas absorbers with chemical reaction. In the later chapters, more specific reviews are also given where necessary.

2.1 GAS ABSORPTION WITH CHEMICAL REACTION

Gas absorption with chemical reaction occurs when a reactant in the gas phase and another reactant in the liquid phase are brought into contact. Let A denote a reactant from the gas phase and B denote a reactant in the liquid phase. According to Astarita [17] and Danckwerts [18], the following major steps occur during absorption (also see Figure 2.1):

(i) Transfer of A from the gas phase by diffusion to the gas/liquid interface and dissolution into the liquid film.

(ii) Simultaneous diffusion and chemical reaction in the liquid phase.
Gas Absorption with Chemical Reaction

Figure 2.1: Schematic of gas absorption with chemical reaction system.
(iii) Diffusion of all components in the liquid due to concentration gradients.

(iv) Heat transfer from the liquid phase to the gas phase due to the temperature gradient which is caused by the heats of solution and reaction.

Steps (ii) to (iv) take place simultaneously after step (i). The overall absorption rate is significantly affected by the chemical reaction since the reactant acts as a sink for the solute A. As a result, chemical absorption processes have much higher rates and capacities than physical absorption processes.

In general, the chemical reaction in the liquid film can be simplified by recognizing characteristic reaction regimes [1, 17-19, 20, 23, 26]. These regimes, which are described in detail by Levenspiel [30,31] and Godfrey [32], are summarized below. Starting from the instantaneous chemical reaction regime and proceeding to the extremely slow reaction regime, their corresponding concentration profiles are presented in Figure 2.2.
Figure 2.2: Interface behavior for gas absorption with chemical reaction [30].
Regimes A and B. When the reaction is instantaneous or very fast, the reaction plane lies either within the liquid film if the concentration of B, \( C_B \), is not too high (regime A), or at the gas liquid interface if \( C_B \) is high enough (regime B). The absorption rate is determined primarily by the rate of diffusion of components A and B for the regime A. For the regime B, the diffusion of A through the gas film controls the overall absorption rate.

Regimes C and D. When the reaction is not extremely fast, but is fast enough so that reactant A is completely consumed within the liquid film, the reaction zone occurs either within the liquid film in case of low \( C_B \) values or near the gas liquid interface in case of high \( C_B \) values.

Regime E and F. In these cases the reaction and mass transfer rates are of the same magnitude. The reaction zone extends from the gas-liquid interface to within the bulk of the liquid.

Regime G. The reaction is slow and the amount of dissolved gas held up in the film is small. The mass transfer rate of A in the film is still important but the overall process is such that it can be visualized as one of physical absorption
followed by chemical reaction within the bulk of the liquid phase.

*Regime H.* The reaction is extremely slow in this case. The mass transfer resistances in the fluid film are negligible due to a low consumption rate of A by the reaction in the liquid phase. As a result, the entire liquid phase becomes uniform in concentration of A at the concentration corresponding to the partial pressure above the liquid. The rate of absorption is simply equal to the rate of reaction within the bulk liquid.

For a given system and set of operating conditions, the faster the reaction rate, the shorter the distance between the interface and the reaction plane (or the higher the liquid mass transfer coefficient). In a chemical absorption column, the reaction regime can change significantly along the column from instantaneous reaction at the top to slow reaction at the bottom because of the variation of reactant composition in both phases. This causes the effective mass transfer coefficient of the liquid film to change significantly along the column and therefore makes chemical absorption more complex than physical absorption. The effect of reaction in the liquid film on the overall absorption
rate is often presented in the term of an "enhancement factor" which is defined as the ratio of the liquid film coefficient for absorption with chemical reaction to the liquid film coefficient for the purely physical absorption [18].
2.2 REACTION OF CO$_2$ IN CAUSTIC AND AMINE SOLUTIONS

Since the absorption of carbon dioxide into caustic and amine solutions is of major industrial importance, the subject has been extensively reviewed [18], [19]. The industrial aspects of these processes are discussed by Kohl and Riesenfeld [15]. Since these two systems will be used in the present thesis, their reaction kinetics are briefly described in the following section.

2.2.1 REACTION CHEMISTRY OF THE CAUSTIC - CO$_2$ SYSTEM

Absorption of carbon dioxide into aqueous solutions of caustic is probably the most widely studied system. Before the reaction occurs, CO$_2$ is physically dissolved in the solution and OH$^-$ ions are from the dissociation of the caustic. Once CO$_2$ enters the solution, two reaction steps can occur:

\[
\begin{align*}
\text{a) } & \quad \text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \\
\text{b) } & \quad \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}
\end{align*}
\]

According to Astarita [17], reaction (b) may be regarded as instantaneous, whereas reaction (a) proceeds at a finite
rate. When a substantial amount of free hydroxide is present, the reaction equilibrium lies far to the right since the equilibrium constant of reaction (b) is large ($5.9 \times 10^3$ m$^3$/kmol at 20 °C). The bicarbonate concentration may be assumed to be zero whenever the hydroxide concentration exceeds $10^{-2}$ kmol/m$^3$ [17].

The overall reaction which takes place may therefore be written as:

$$\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$$

(c)

the rate of which is given by

$$\text{rate} = k_2 [\text{CO}_2][\text{OH}^-]$$

Pohoreck and Moniuk [111] recently reported new rate constant data for this system. They also reviewed the data previously published in the open literature. They found that the rate constant is not only a function of the activation energy, but also the concentration of the ionic species in solution.
2.2.2 REACTION CHEMISTRY OF CO\textsubscript{2} - AMINE SYSTEM

According to Astarita et al. [19] as well as other researchers, the reactions governing the CO\textsubscript{2}-aqueous amine system are remarkably complex and are not fully understood even though they have been studied for more than half a century. It is believed that there are three principal steps governing the system:

Carbamate formation:
\[
\text{CO}_2 + 2\text{R}\text{NH} = \text{R}\text{NCOO}^- + \text{R}\text{NH}_2^+ \quad (d)
\]

Bicarbonate formation:
\[
\text{CO}_2 + \text{RNH} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{R}\text{NH}_2^+ \quad (e)
\]

Carbamate reversion:
\[
\text{R}\text{NCOO}^- + \text{H}_2\text{O} = \text{HCO}_3^- + \text{R}\text{NH} \quad (f)
\]

where R stands for -C\textsubscript{2}H\textsubscript{4}OH and R denotes -H and -C\textsubscript{2}H\textsubscript{4}OH for primary and secondary amines, respectively. For primary amines, Danckwerts [18] and Astarita et al. [19] suggested that the carbamate formation reaction predominates when the CO\textsubscript{2} loading is less than about 0.5 moles of CO\textsubscript{2} / mole of amine. On the other hand, the carbamate reversion predominates when the CO\textsubscript{2} loading exceeds about 0.5 moles of
CO₂ per mole of amine. The relative importance of the bicarbonate formation depends on the stability of the carbamate; the importance of bicarbonate formation is inversely proportional to the stability of carbamate.

For the CO₂-MEA system, the rate of bicarbonate formation is relatively unimportant since the MEA carbamate is quite stable[71]. Danckwerts [18] as well as other researchers concluded from their experimental results that the overall rate of reaction can be approximated as first order with respect to both CO₂ and amine when the loading is less than 0.5 moles of CO₂ per mole of amine, i.e.

\[ \text{rate} \propto [\text{CO}_2][\text{RNH}_2] \]

For other systems such as secondary amines and sterically hindered amines*, the reaction mechanisms are more complex. Their carbamate stability varies from moderate to low by comparison with that of MEA. Therefore, the overall reaction rate depends on all three reactions. The understanding of the effect of each reaction on the overall reaction rates for these systems is still unclear with respect to the

*A sterically hindered amine is defined as a primary amine in which the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino group is attached to a secondary or a tertiary carbon atom [71].
reaction mechanisms and rate constants [19, 43, 120, 145]. For more details on the reaction chemistry of these systems, References [18], [19] and [87] should be consulted.

2.3 DESIGN OF PACKED ABSORBERS WITH CHEMICAL REACTION

Packed absorbers are vertical columns filled with packings of large surface areas (Figure 2.3). The operation may be either co-current or counter-current. However, most packed absorbers are operated counter-currently to obtain maximum concentration driving forces. In counter-current packed absorbers, the absorbent is distributed over and trickles down through the packings thereby creating a large surface for contacting with the gas.

The main design objectives are to find the diameter and height of the tower. The main steps for designing gas absorbers with chemical reaction are shown schematically in Figure 2.4. Routes 1, 2 and 3 in Figure 2.4 refer to Empirical design method, Theoretical design method and design methods based on laboratory models, respectively.
Figure 2.3: Packed absorber [86]
DEFINITION OF PROCESS CONDITIONS
- Total flow rates of gas and liquid
- Inlet and outlet conditions

SPECIFY GAS-LIQUID CONTACTING SYSTEM
- Type and details of packings

OBTAIN PHYSICAL INFORMATION
- Densities and viscosities
- Gas-liquid equilibrium data

DETERMINATION OF SUPERFICIAL VELOCITIES
- Liquid side
- Gas side

OBTAIN PHYSICAL GAS ABSORPTION PARAMETERS
- Mass transfer coefficients
- Interfacial area
- Liquid hold-up

OBTAIN ADDITIONAL INFORMATION
- Diffusivities
- Solubilities
- Reaction kinetics

DETERMINATION OF ENHANCEMENT FACTOR

DETERMINATION OF (K_{G^2v})_{ave}

DETERMINATION OF ABSORPTION RATE

DETERMINATION OF COLUMN HEIGHT

Figure 2.4: Major design procedures for gas absorbers with chemical reaction.
The details of each method will be described in Sections 2.3.1 to 2.3.3.

Once the specific design problem is defined in terms of the total flow rate of each phase, inlet and outlet conditions, a suitable gas-liquid contacting system can be selected. In general, there is no specific criterion for selecting the packing type and size. However, Treybal [86] suggested that good packings should have the following characteristics:

1. Large effective gas-liquid contacting area.
2. Large voidage.
3. Chemically inertness.
4. Structural strength to permit easy handling and installation.
5. Low cost.

The next design step is to obtain physical information such as density and viscosity of both phases in order to determine their superficial velocities and the column diameter; this is normally based on pressure drop or flooding conditions. These calculations can be performed
using techniques suggested by Fair [85] or Treybal [86]. The techniques will be described in some detail in Chapter 5.

Before the detailed calculation of the absorber height can be undertaken, it is necessary to know the vapor-liquid equilibrium data of the system. The equilibrium information is needed to determine if there is a pinch (or equilibrium) condition in the column. If such a condition exists, the column will not be able to perform as expected. Therefore, adjustments of the process conditions (e.g. flow rates, compositions of gas and liquid etc.) are necessary. The equilibrium information is also need to determine the concentration driving force in order to calculate the absorber height.

Extensive equilibrium data have been reported for the CO₂ - amine systems. Particularly noteworthy is the work conducted at the University of Alberta by Otto, Mather and their co-workers. Among their many studies on solubility, some of these data are in References [95], [96] and [101]. These data as well as the data previously published by other researchers were well summarized in Kohl and Riesenfeld's book, "Gas Purification" [15]. Recently, Austgen et al. [88] and Chakravarty [119] have proposed rigorous mathematical
models to predict the equilibrium behavior of acid gases in amine solutions. However, the deviations between their model predicted solubility and previously reported experimental results can be as high as ± 60 %. Austgen et al. [88] and Chakravarty [119] suggested that the wide variation in the solubility data reported by different research groups is one of the causes of the deviation. Figure 2.5 shows typical vapor-liquid equilibrium curves for CO₂ absorption into commonly used solvents [138]

The next design step is to determine the column height. Figure 2.6 shows a schematic diagram of a packed column together with the nomenclature that will be used in developing the design equations. According to Sherwood et al. [26], the mass flux of A at steady state may be expressed in terms of the mass transfer coefficients and driving forces for each phase:

\[ \dot{N}_A = k_G(p_{y_A} - y_{A,i}) \]  \hspace{1cm} (2.1)
\[ \dot{N}_A = k_L(C_{A,i} - C_A^*) \]  \hspace{1cm} (2.2)

where
\[ \dot{N}_A = \text{mass transfer flux of the absorbed component A} \]
\[ k_G = \text{gas-side mass transfer coefficient} \]
Figure 2.5: Typical vapor-liquid equilibrium curves at 40 °C of CO₂-Chemical solvents [138].
Figure 2.6: Schematic of a packed absorber.
\( \text{P} = \text{total pressure} \)
\( y_A = \text{mole fraction of A in the bulk gas} \)
\( y_{A,i} = \text{mole fraction of A on the gas-side of the gas-liquid interface} \)
\( k_L = \text{effective liquid-side mass transfer coefficient} \)
\( C_A^* = \text{concentration of A in the bulk liquid} \)
\( C_{A,i} = \text{concentration of A on the liquid-side of the gas-liquid interface.} \)

The relationship at the gas-liquid interface is assumed to obey Henry's law:

\[
C_{A,i} = H \text{P} y_{A,i}
\]

(2.3)

where \( H \) denotes Henry's constant. Although the above assumption may not be applied for nonideal systems, the effects of system nonidealities can however be lumped into the values of \( H \) as detailed in Section 6.2.1.

The mass flux can also be written in terms of the overall mass transfer coefficient, \( K_G \), and the overall driving force by rearranging Equations 2.1 and 2.2:

\[
N_A = K_{G \text{P}}(y_A - y_A^*)
\]

(2.4)
\( K_G \) is given by

\[
1/K_G = 1/k_G + 1/(Hk_L) = 1/k_G + 1/(Hk_L^o)
\]

where \( I \) denotes the enhancement factor

\[
I = k_L/k_L^o
\]

\( k_L^o \) denotes the liquid-side mass transfer coefficient \emph{without} chemical reaction. The mass balance for an element of column with height \( dZ \) can be written as:

\[
N_Aa_v dZ = G_I d[y_A/(1-y_A)] \\
= K_Ga_v P(y_A - y_A^*) dZ
\]

where \( G_I \) is the inert gas molar flow rate, \( a_v \) is the effective interfacial area per unit volume of packing, and \( y_A^* \) is the vapor-phase mole fraction of component \( A \) which is in equilibrium with the concentration in the liquid phase.

Rearranging and integrating Equations 2.5 and 2.6 gives

\[
Z_t = G_I \int \frac{d y_A}{[K_G a_v P(1-y_A)] (y_A - y_A^*)} \\
Y_{A,in} \leq \frac{y_A}{y_{A,out}} \leq Y_{A,in}
\]

\( Y_{A,out} \) and \( Y_{A,in} \)
In the traditional design method for packed columns, Equation 2.5 is sometimes rearranged as the product of the "height of a transfer unit (HTU)" and the "number of transfer unit (NTU)" , i.e.

\[ Z_t = (\text{HTU}) \times (\text{NTU}) \]

where

\[ \text{HTU} = \frac{G_I}{K_G a_v P} \]

and

\[ \text{NTU} = \frac{y_{A,\text{out}}}{\int dy_A / [(1-y_A)^2(y_A-y_A^*)]} \]

\[ y_{A,\text{in}} \]

The HTU is an inverse measure of the packing efficiency; the lower its value, the more efficient the packing. The NTU represents the total number of the transfer units required for a given absorption duty. It should be noted that these definitions are only valid provided \( K_G, a_v \) and \( P \) are constant.

According to Danckwerts [18], Equation 2.7 can also be written as
where $R_a$ is defined as the specific rate of absorption per unit interfacial area. (The detailed expression of $R_a$ will be derived in Section 2.3.2.)

Solving Equations 2.7 or 2.8 is usually difficult because $I$ is a complex function of the column hydrodynamics, fluid properties and concentrations, which can vary significantly along the column. The details of theoretical calculations of the enhancement factor will be explained on page 50 to 57.

The following sections are reviews of three different approaches for determining the column height.

2.3.1 **Empirical Design Method**

Empirical design approach (see Route# 1 of Figure 2.4) is based on the concepts developed for the design of distillation and physical absorption columns. By using this
approach, the overall volumetric mass transfer coefficient \( (K_{Ga_v}) \) is assumed to be constant along the packed column and has to be obtained experimentally using a column which is filled with the same packing as the full-length column to be designed. The experimental data are usually collected in the form of the average \( K_{Ga_v} \) values on the basis of a log-mean driving force:

\[
(K_{Ga_v})_{ave} = \frac{G_I [y_{A,B}/(1-y_{A,B}) - y_{A,T}/(1-y_{A,T})]}{Z_e P (y_A - y_{A*})_{lm}}
\]

where \( Z_e \) is the height of the experimental column and \( (y_A - y_{A*})_{lm} \) denotes the log mean driving force,

\[
(y_A - y_{A*})_{lm} = \frac{[(y_A - y_{A*})_B - (y_A - y_{A*})_T] / \ln[(y_A - y_{A*})_B/(y_A - y_{A*})_T]}{1}
\]

Subscript \( B \) and \( T \) represent the bottom and top conditions, respectively. The values of \( (K_{Ga_v})_{ave} \) obtained this way are usually correlated as empirical functions of the operating parameters (such as flow rates). The height of an absorber can then be calculated by using Equation 2.7.

Numerous studies using this approach have been reviewed by Kohl and Riesenfeld [15] and Edwards [24].
Although the empirical approach has been used extensively for the design of distillation and physical absorption columns, it usually leads to problems in the case of absorption with chemical reaction. When the extent of chemical reaction is high, which is usually the case, the enhancement factor and therefore \((K_{Ga_v})\) change appreciably along the column. Astarita et al. [19] and Joshi et al. [65] recently pointed out this problem. To quote from Astarita et al. [19],

"........ the assumptions that the mass transfer is constant and independent of fluid concentrations are certainly not justified in the case of chemical absorption. It follows that the values of \((K_{Ga_v})_{ave}\) obtained in this way will strongly depend on all operating parameters in rather unpredictable ways and cannot be extrapolated to conditions different from the ones for which they have been obtained. .....".

In supporting this statement, Astarita et al. [19] further showed that using this empirical approach would lead to large errors in predicting column heights. As illustrated by Figure 2.7, the \((K_{Ga_v})_{ave}\) values of the \(K_2CO_3-CO_2\) system reported by Benson et al. [139] vary by more than an order of magnitude. Since the calculated height (c.f. Equation
depends directly on the values of \( K_{Ga_v} \), the uncertainty associated with the height prediction is similar to that associated with the \( K_{Ga_v} \) values. As a result, a "safety factor" of 1.5 to 2.5 is commonly applied to this design method in order to overcome the uncertainty associated with the \( (K_{Ga_v})_{ave} \) data [124, 125]. This may lead to excessively oversized columns resulting in unnecessary expenditures of capital and operating costs.

It is therefore difficult to have confidence in the empirical design approach for gas absorption with chemical reaction systems.
Figure 2.7: $K_{GaV}$ values of CO$_2$-$K_2$CO$_3$ system [65].
2.3.2 THEORETICAL DESIGN METHOD

The height of an absorber with chemical reaction may also be calculated by using Equation 2.8 provided that the values of the specific absorption rate, \( R_a \), along the absorber are known. However, to evaluate these values theoretically, information regarding the column hydrodynamics and physico-chemical properties of the system (diffusivities, solubilities and reaction kinetics) must be known (see Route# 2 in Figure 2.4).

THEORETICAL DETERMINATION OF \( R_a \)

Even though some of the following equations were presented before, they are repeated here for convenience sake. The mass transfer rate of \( A \) at any point of the absorber may be written as:

\[
R_a v \, dz = k_G P (y_A - y_A, i) a_v \, dz = I k_L^0 (C_A, i - C_A^*) a_v \, dz
\]  

Equations 2.9 and 2.10 can be rearranged as:
\[ k_{GP}(y_A - y_{A,i}) = I_k L^0(C_{A,i} - C_A^*) \] (2.11)

Substituting \( C_{A,i} = H P y_{A,i} \) into Equation 2.11 and rearranging gives;

\[ y_{A,i} (I_k L^0 H P + k_{GP}) = k_{GP} y_A + I_k L^0 C_A^* \] (2.12)

\[ y_{A,i} = (k_{GP} y_A + I_k L^0 C_A^*) / (I_k L^0 H P + k_{GP}) \] (2.13)

From Equation 2.9, the concentration of \( A \) at the interface can also be written as:

\[ y_{A,i} = y_A - R_a / (P_k G) \] (2.14)

Substituting Equation 2.13 into Equation 2.14 and rearranging gives

\[ R_a = k_{GP} y_A - \{k_{GP} [I_k L^0 C_A^*] / (I_k L^0 H P + k_{GP})]\} \]

\[ R_a = \{(k_{GP} y_A)(I_k L^0 H) + (k_{GP} y_A)(k_G) - (k_G)(k_{GP} y_A) \]

\[ - (k_G)(I_k L^0 C_A^*)\} / (I_k L^0 H + k_G)\} \] (2.16)

Therefore,
\[ R_a = \{k_{L}^{0}(HPy_A - C_A^*)/[1 + I_H(k_{L}^{0}/k_G)]\} \] (2.17)

To find \( R_a \), an iterative method must be used since the enhancement factor depends on the concentrations at the interface which are not known and cannot be measured. As a result, Equations 2.14 and 2.17 are coupled and need to be solved simultaneously. For example, \( y_{A,i} = y_A \) may be taken as a first approximation. \( C_{A,i} \) and the enhancement factor are then calculated. Equation 2.17 is then used to evaluate \( R_a \). The second approximation for \( y_{A,i} \) is then obtained from Equation 2.14. The calculations are repeated until \( y_{A,i} \) of the current iteration closely approximates that of the previous iteration.

**ENHANCEMENT FACTOR CALCULATION**

One of the most important calculation steps is to determine the enhancement factor, \( I \), which is a function of the physical and chemical properties of all components in the liquid film. To calculate the enhancement factor in general, a set of partial differential equations which represent simultaneous diffusional mass transfer and
chemical reaction along the liquid film, need to be solved. According to Astarita [17], the diffusion equations which represent these phenomena within the liquid phase may be written in the following form:

\[ D_j \nabla^2 C_j = u \nabla C_j + \frac{\partial C_j}{\partial t} + r_j \]  (2.18)

\( r_j \) denotes the reaction rate of species \( j \) inside the liquid film. In general, the reaction rate depends on the local concentrations of the reactants and the reaction products. To obtain the enhancement factor, the diffusion equations for all species in the liquid have to be solved.

The type of chemical absorption system which has received the most attention in the literature is the one in which component \( A \) from the gas phase reacts with component \( B \) in the liquid by an irreversible second-order reaction. This system will be used to illustrate the enhancement factor calculation. The reaction is represented by

\[ A + \nu_{AB}B = C \]

and the rate expression is given by:

\[ r_{AB} = k_2 C_A C_B \]
It must be noted that there is not necessarily any relationship between the stoichiometric coefficient, \( \nu_{AB} \), of the reaction and the order of the reaction [18]. According to Astarita [17], Equation 2.18 can be simplified by making the following assumptions: (i) the gas-liquid interface is plane, (ii) the film theory is valid, which means the surface element behaves rigidly during its life \((u=0)\), (iii) steady state conditions prevail in the liquid film. The mass transfer phenomena across a gas-liquid interface could also be described by the penetration and surface renewal theory. However, all three theories give virtually the same results as far as the numerical results are concerned [26]. Since the film theory is relatively easy to understand, it has been more widely used and will be used in the following discussion.

The effect of the reaction product, \( C \), on the physical and chemical properties of components A and B are assumed to be insignificant. Therefore, the differential equations for components A and B can be rewritten as:

\[
D_A \left( \frac{\partial^2 C_A}{\partial x^2} \right) - k_2 C_A C_B = 0 \tag{2.19}
\]
\[
D_B \left( \frac{\partial^2 C_B}{\partial x^2} \right) - \nu_{AB} k_2 C_A C_B = 0 \tag{2.20}
\]
where \( x \) is the distance in the liquid film from the interface. The boundary conditions for Equations 2.19 and 2.20 are:

At \( x = 0 \)
\[
C_A = C_{A,i}
\]
\[
\partial C_B / \partial x = 0
\]
At \( x = \delta \)
\[
C_A = 0
\]
\[
C_B = C_B^*
\]

where \( \delta \) denotes the liquid film thickness. The enhancement factor is equal to the ratio of the actual interface concentration gradient of A to the gradient which would be established in purely physical absorption:

\[
I = \{-(\partial C_A / \partial x)_{x=0}\} / (C_{A,i}/\delta)
\]

At the present time, there is no exact analytical solution for this set of equations [18, 59]. However Van Kevelen and Hoftijzer [44, 67] provided an approximate analytical solution which relates the actual enhancement
factor, \( I_i \), to the enhancement factor for the instantaneous reaction, \( I_{\infty} \):

\[
I = \left[ M \left\{ \frac{(I_{\infty} - I)/(I_{\infty} - 1)}{a} \right\} \right]^{0.5} \tanh \left[ M \left\{ \frac{(I_{\infty} - I)/(I_{\infty} - 1)}{a} \right\} \right]^{0.5}
\]  \hspace{1cm} (2.21)

where

\[
M = \frac{(D_A k_2 C_B^*)}{(k_L^o)^2}
\]

and

\[
I_{\infty} = 1 + \frac{(D_B C_B^*)}{(\nu_{AB} D_A C_A, i)}
\]

However, this equation is implicit and can be solved only by an iterative method. To improve the computational efficiency, several explicit equations have been proposed.

Porter [68]:
\[
I = 1 + (I_{\infty} - 1)\left\{ 1 - \exp\left[ -(\sqrt{M} - 1)/(I_{\infty} - 1) \right] \right\}
\]  \hspace{1cm} (2.22)

Kishinevskii [69]:
\[
I = 1 + \left\{ \sqrt{\frac{M}{\beta}} \right\} \left\{ 1 - \exp\left[ -0.65\sqrt{M} \right] \right\}
\]  \hspace{1cm} (2.23)

where \( \beta = \sqrt{M/(I_{\infty} - 1)} + \exp\left\{ (0.68/\sqrt{M}) - (0.45/\sqrt{M/(I_{\infty} - 1)}) \right\} \)

DeCoursey [90]:
\[
I = \left[ \left( \frac{M^2}{4(I_{\infty} - 1)^2} \right) + I_{\infty} M/(I_{\infty} - 1) + 1 \right]^{0.5}
- \left[ M/(2(I_{\infty} - 1)) \right]
\]  \hspace{1cm} (2.24)
Wellek et al. [89]:

\[ I = 1 + \left[ 1 + \left( \frac{I_\infty - 1}{I_1 - 1} \right)^{1.35} \right]^{1/1.35} \]  

(2.25)

where \( I_1 = \sqrt{\frac{M}{\tanh v}} \)

Alper [70] and Wellek et al. [89] also made a comprehensive comparison of these equations with precise numerical solutions over wide ranges of conditions. They found that the maximum differences among the results were less than 10%. The above equations can therefore be used to estimate the enhancement factor for slow to instantaneous reaction (\( I \approx 1 \) to \( I \approx I_\infty \)). In laboratory equipment (i.e. stirred cells, sphere columns, etc.) which has a well-defined gas-liquid contacting area, the precise prediction of the experimental results can be obtained from these equations provided all fundamental data are available. Some of these results were summarized by Danckwerts [18]. Alper [70] gave a typical plot of \( I \) as functions of \( I_1 \) and \( \sqrt{M} \) (Figure 2.8). Some typical values of \( I \) obtained from well-defined absorbers for the CO\(_2\)-MEA system are shown in Figure 2.9 [131].

For systems in which one or more components in the gas phase react reversibly with one or more liquid reactants, the enhancement factor calculation is even more complex.
Figure 2.8: A typical plot of $I$ as functions of $I_\infty$ and $M$ parameters [70].
Figure 2.9: Variation of the enhancement factor for CO$_2$-MEA system obtained from laboratory absorbers [131]. (Points were from experimental measurements and lines were from theoretical predictions.)
DETERMINATION OF COLUMN HEIGHT

After the values of \( R_a \) are determined theoretically at various points along the column, the column height can be obtained by integrating Equation 2.8 numerically or graphically.

Surprisingly, no detailed comparisons have been published on the concentration and temperature profiles obtained from theoretical predictions and pilot plant measurements. Therefore, such detailed comparisons are made for the CO\(_2\)-NaOH and CO\(_2\)-MEA systems in Chapter 6.
2.3.2.1 INFORMATION REQUIRED IN THEORETICAL CALCULATIONS

As can be seen from the previous section, several kinds of information are required before the specific absorption rate, and therefore the tower height, can be determined theoretically.

PHYSICAL GAS ABSORPTION PARAMETERS

For the physical gas absorption extensive experimental results have been reported on $k_G$, $k_{L^o}$ and $a_v$ in the 1950's and 1960's for conventional packings like ceramic Raschig rings and Berl Saddles. These data were correlated in terms of dimensionless parameters such as Reynolds number (Re), Schmidt number (Sc). These data and their correlations are well documented in Perry's Chemical Engineers' Handbook [85]. However, the uncertainties (errors) associated with these data and correlations are substantial as pointed out by many researchers including Hudgins and Reilly [126]. For example, Figure 2.10, reproduced from Perry's Handbook, shows that the gas-side mass transfer coefficient has a two- to three-fold variation at a given gas flow rate [126]. This type of uncertainty has also been observed for the case of
liquid-side mass transfer coefficients and effective interfacial areas [36].

A major reason for the uncertainties is that the flow behavior and mass transfer phenomena in packed absorbers are complex and cannot be accurately predicted by simply using correlations of dimensionless parameters. To quote from Sherwood et al. [26], "... it seems doubtful that the complicated phenomena involved in flow in packings will ever be satisfactorily correlated by using classical dimensionless parameters such as Re, Sc etc. .... ".

For the newer, high-efficiency packings, which are favoured by industry [37], very little information is available in the literature regarding their mass transfer coefficients and effective interfacial area. Figures 2.11 and 2.12 show some of the high-efficiency random and structured packings, respectively. The classical correlations obtained for the conventional packings should not be used to predict the physical gas absorption properties of high-efficiency packings since the latter
Figure 2.10: Gas-side mass transfer coefficient, $k_G$, as a function of gas flow rate [126].
Figure 2.11: High-efficiency random packing [19].
Figure 2.12: Structured packing [38].
packings have much more complex configuration resulting in different flow and mass transfer phenomena. The high-efficiency packings usually have much higher effective interfacial areas and lower pressure drops compared with conventional ones.
PHYSICO-CHEMICAL PROPERTIES

For the case of absorption with chemical reaction, physico-chemical data such as solubility, diffusivity and reaction rate constants are needed in order to calculate the enhancement factor. These data are highly specific and have to be obtained for each system at the prescribed conditions. The reaction kinetics of a given reaction system can only be obtained by performing experiments which are often difficult, time-consuming and inaccurate.

For the case of CO₂ absorption into amine solutions other than MEA, the understanding of the reaction kinetics is still inadequate [40-51, 87] although it has been studied for more than half a century. For instance, there is no general agreement on the reaction mechanism for the CO₂ absorption into diethanolamine (DEA) which is a secondary alkanolamine. Although prominent researchers in the field agree on the reaction mechanism to be second order reaction, they found that the rate constants, under certain conditions, differ by as much as a factor of four [52] (see Figure 2.13).
Figure 2.13: Apparent rate constant of CO₂ - DEA system reported by various researchers [43].
For the new, high-capacity solvents such as sterically hindered amines, very little information is available on their reaction mechanism and rate constants.

To measure diffusivities and physical solubilities for gas absorption with chemical reaction systems also presents further difficulties due to the simultaneous diffusion and reaction which take place in the liquid phase. It is not possible to obtain these properties directly and indirect methods must therefore be used. A commonly used method is to deduce these data from corresponding, but nonreacting systems.

In view of its similar configuration, molecular volume, and electronic structure, N₂O is often used as the nonreacting gas to estimate the diffusivity and physical solubility of CO₂ in amine solutions. Laddha et al. [127] and Versteeg and Swaaij [128] investigated the solubility of N₂O and CO₂ in aqueous solutions of amines and other organic compounds. They found that the ratio of the solubilities of N₂O and CO₂ was constant. Therefore, the "N₂O analogy" may be applied to estimate the physical solubility of CO₂ in aqueous alkanolamine solutions according to:
(Physical solubility of CO₂ in amine)

\[ C_j = \frac{C_j (\text{N}_2\text{O solubility in amine})}{C_j (\text{CO}_2 \text{ solubility in water})} \]

where

\[ C_j = \frac{\text{CO}_2 \text{ solubility in water}}{\text{N}_2\text{O solubility in water}} \]

Versteeg and Swaaij [128] and Versteeg et al. [129] also used this approach to estimate CO₂ diffusivities in aqueous alkanolamine solutions. Their experimental results covering industrial operating conditions have been published recently [128, 129]. They found that their results agree well with the previously reported findings.

Estimation methods for solubilities and diffusivities of gases in liquids for both reacting and nonreacting systems have recently been reviewed and summarized by Morsi and Charpentier [39], Versteeg and Swaaij [128] and Versteeg et al. [129].
2.3.2.2 WEAK POINTS OF THEORETICAL DESIGN METHOD

As have been shown above, there are two major difficulties in predicting the height of a gas absorber with chemical reaction using the theoretical approach. Firstly, it involves complex calculations. Secondly, it needs detailed information regarding the hydrodynamic properties of the absorber and the physico-chemical properties of the system. It is therefore very important to develop alternative design procedures which are free of these two major restrictions.
2.3.3 DESIGN METHODS BASED ON LABORATORY MODELS

Since many difficulties are encountered in the process of obtaining the physico-chemical information and in computing the enhancement factors as mentioned in the previous section, Danckwerts and Alper [18, 36, 55, 56] and Charpentier and Laurent [58-60] proposed two laboratory models for designing gas absorbers with chemical reaction. The laboratory models (see Route# 3 of Figure 2.4) are based on the assumption that the rate of absorption per unit interfacial area, $R_a$, depends only on the absorber hydrodynamics and the reactant concentrations in both phases [18, 36, 54-63]. The $R_a$ values can be determined from laboratory absorbers rather than theory. In doing this, the hydrodynamic parameters in the laboratory absorber must be known precisely and can be matched with those of the full-scale column.

POINT MODEL

The first model is called the Point model [18, 55, 57-59, 61-64]. A schematic representation of the principle of "Point modelling" is shown in Figure 2.14. (Details are
Figure 2.14: Schematic representation of Point model [55].
given by Danckwerts and Alper [55].) The absorption-reaction interactions are measured in a small stirred cell, which is a gas-liquid contactor operating at steady state. There are two stirrers in the cell to keep the bulk gas and liquid concentrations uniform. In order to use this model for simulating absorption, the stirred cell has to be operated in such a way that its $k_G$ and $k_L^0$ values are the same as those in the full-scale absorber. Danckwerts and Alper [55] showed that the desired values of $k_G$ and $k_L^0$, which correspond to purely physical absorption, can be obtained by varying the stirrer speeds. Once these conditions are met, the absorption rate per unit interfacial area in the cell can be measured for various bulk gas and bulk liquid compositions. The resulting $R_a$ values are then substituted into Equation 2.8 to yield the required column height. It is shown that this method eliminates the need for obtaining the reaction kinetics and physico-chemical parameters explicitly.

Danckwerts and Alper [55] tested the Point model by predicting the performance of a CO$_2$ absorber (0.1 m ID) packed with 12.7 mm ceramic Raschig rings to various heights. Aqueous NaOH was used as the absorption medium. Table 2.1 shows that the predicted and actual heights
differed by less than 9% in all cases. Further testing of this model was performed by Laurent [130] with the same system. However, the predicted results were not as good and discrepancies of up to ± 20% occurred. No reason was given for the larger discrepancies in this case.

It should be noted that the Point model is only applicable to systems where the reactions are fast enough to take place in the liquid film near the interface so that there is no reaction in the bulk of the liquid. This limitation arises because the liquid hold up per unit volume of the stirred cell is much larger than that of the packed column.
Table 2.1: Comparison results between actual and predicted height from Point model by Danckwerts and Alper [55].

\[
\text{CBO} = \text{COH}^- (\text{mol l}^{-1}) \quad \text{PCO}_2 \times 10^2 \quad (\text{atm}) \quad \frac{\text{out}}{\text{in}} \quad \frac{d(CBO)h}{\varphi} = \frac{zaZ}{uL} (\text{s cm}^{-1}) \quad \text{Packing height} \quad \text{Predicted height} \quad \text{Difference} \quad \text{Error in material balance} \\
\text{(cm)} \quad \text{(cm)} \quad \% \quad \%
\]

<table>
<thead>
<tr>
<th>Inlet</th>
<th>Outlet</th>
<th>Inlet</th>
<th>Outlet</th>
</tr>
</thead>
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<tr>
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<td>0.29</td>
<td>4.6</td>
<td>3.8</td>
</tr>
<tr>
<td>0.52</td>
<td>0.42</td>
<td>4.1</td>
<td>3.3</td>
</tr>
<tr>
<td>0.58</td>
<td>0.46</td>
<td>4.6</td>
<td>3.6</td>
</tr>
<tr>
<td>0.28</td>
<td>0.10</td>
<td>5.2</td>
<td>3.6</td>
</tr>
<tr>
<td>0.62</td>
<td>0.19</td>
<td>7.6</td>
<td>4.0</td>
</tr>
<tr>
<td>0.60</td>
<td>0.08</td>
<td>10.3</td>
<td>6.2</td>
</tr>
<tr>
<td>0.55</td>
<td>0.19</td>
<td>6.0</td>
<td>3.1</td>
</tr>
<tr>
<td>0.52</td>
<td>0.20</td>
<td>5.0</td>
<td>2.2</td>
</tr>
<tr>
<td>0.55</td>
<td>0.08</td>
<td>10.6</td>
<td>7.0</td>
</tr>
<tr>
<td>0.46</td>
<td>0.10</td>
<td>7.8</td>
<td>5.0</td>
</tr>
<tr>
<td>0.46</td>
<td>0.13</td>
<td>7.8</td>
<td>5.2</td>
</tr>
<tr>
<td>0.58</td>
<td>0.13</td>
<td>10.2</td>
<td>6.7</td>
</tr>
<tr>
<td>0.53</td>
<td>0.26</td>
<td>5.3</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Table 2.2: Comparison results between actual and predicted height from Point model by Laurent [130].

<table>
<thead>
<tr>
<th>$u_O$ (cm s$^{-1}$)</th>
<th>$P_{CO_2} \times 10^2$ (atm)</th>
<th>$u_L$ (cm s$^{-1}$)</th>
<th>$C_{BO} = C_{OH}$ (mol lit$^{-1}$)</th>
<th>$\int_{IN}^{OUT} \frac{dc_{BO}}{\phi_{IN}}$ (s cm$^{-1}$)</th>
<th>$H$ (m)</th>
<th>Predicted height (m)</th>
<th>Difference (%)</th>
<th>Error in material balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>6.2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.60</td>
<td>0.52</td>
<td>654</td>
<td>1.72</td>
<td>10.4</td>
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<td>3.2</td>
<td>0.01</td>
<td>0.5</td>
<td>0.60</td>
<td>0.55</td>
<td>578</td>
<td>1.52</td>
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<tr>
<td>6.9</td>
<td>2.9</td>
<td>0.05</td>
<td>0.23</td>
<td>0.59</td>
<td>0.52</td>
<td>1120</td>
<td>1.84</td>
<td>4.2</td>
</tr>
<tr>
<td>6.9</td>
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<td>0.6</td>
<td>0.23</td>
<td>0.59</td>
<td>0.47</td>
<td>1102</td>
<td>1.81</td>
<td>5.7</td>
</tr>
<tr>
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<td>7.3</td>
<td>0.75</td>
<td>0.23</td>
<td>0.59</td>
<td>0.42</td>
<td>1144</td>
<td>1.88</td>
<td>2.1</td>
</tr>
<tr>
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<td>2.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.30</td>
<td>0.27</td>
<td>673</td>
<td>1.92</td>
<td>7.8</td>
</tr>
<tr>
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<td>0.30</td>
<td>0.24</td>
<td>1096</td>
<td>1.80</td>
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</tr>
<tr>
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<td>0.5</td>
<td>0.23</td>
<td>0.30</td>
<td>0.24</td>
<td>1145</td>
<td>1.88</td>
<td>2.1</td>
</tr>
<tr>
<td>7.5</td>
<td>2.6</td>
<td>0.3</td>
<td>0.5</td>
<td>0.28</td>
<td>0.25</td>
<td>692</td>
<td>1.82</td>
<td>5.2</td>
</tr>
<tr>
<td>7.4</td>
<td>4.2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.28</td>
<td>0.23</td>
<td>722</td>
<td>1.90</td>
<td>1.0</td>
</tr>
</tbody>
</table>
COMPLETE MODEL

The second, previously published method of absorber modelling is based on so-called Complete modelling, which is shown in Figure 2.15. (Full details of Complete modelling using sphere columns are given in References 55 and 60.) The full-scale absorber can be represented by a model column consisting of spheres and a cylindrical shell (see Figure 2.16). The spheres are connected by a rod. On the top of each sphere, there is a liquid pool.

In order to simulate the packed column, the values of $k_G$, $k_L^o$, $(L/G)$, $(a_vZ/L)$ and $(a_v/\gamma)$ in the laboratory absorber must be the same as those in the full-scale column. $\gamma$ represents the hold-up of the absorber. The above conditions can be achieved by selecting the right dimensions for the column (i.e. sphere diameter, pool dimension and shell cylinder diameter). The desired "scaling ratio" ($Z_t/Z_m$) should be about 5-10 (as suggested by Alper and Danckwerts [56, 62]) where the $Z_t$ and $Z_m$ denote the height of the full-scale column and model column, respectively.
Figure 2.15: Schematic representation of Complete modelling [56].
Figure 2.16: Sphere column [56].
This scaling ratio makes the value of the wetting rate \((L_m/a_v,m)\) for the laboratory absorber small since it can be shown that

\[
\frac{Z_t}{Z_m} = \frac{(L/a_v)}{(L_m/a_v,m)} \tag{2.26}
\]

Since \(L/G\) is fixed, the gas flow rate in the model column is also small. If there are reactions in the bulk liquid, the mean residence time of liquid in both columns must be the same. The mean residence time can be written as:

\[
\bar{t} = \gamma \frac{Z_t}{L} = \gamma \frac{Z_m}{L_m} \tag{2.27}
\]

Rearranging Equations 2.26 and 2.27, one obtains

\[
a_v/\gamma = a_{v,m}/\gamma_m \tag{2.28}
\]

This identity of the interfacial area per unit volume of liquid \((a_v/\gamma)\) means that the residence times of the liquid in both columns are the same. This condition must be met in order to provide the same environment for the reactions which occur in the bulk of the liquid. When all of the afore-mentioned parameters are matched, the full-scale column can be simulated by the model column without any
assumption about the transfer mechanism or reaction kinetics. Furthermore, no physico-chemical information is needed.

The procedure for using this model to simulate an industrial packed column is outlined in Figure 2.17 [60]. A good illustration of this technique was presented by Alper and Danckwerts [56] who simulated a 0.1 m ID column packed with 12.7 mm ceramic Raschig rings (0.49 to 1.58 m high) by a string of 10 spheres, 0.49 m in height. The experiments were carried out with various reaction systems where the reactions occurred in the bulk of the liquid phase. In each case, the difference between the predicted and measured total absorption rates was within ± 7%. However, the scale ratio in these experiments was only about 1 to 2. There is no information on using the complete model for higher scale ratios. Another weakness of this model is that the height of the full-scale column is assumed to be known a priori, which is not usually the case in design problems.
Figure 2.17: Procedure for using Complete modelling [60].
2.3.3.1 WEAK POINTS OF LABORATORY MODELS

Although the two models described above have been tested with pilot plant absorbers, they still suffer from some important deficiencies. First, the physical gas absorption properties ($k_G$, $k_L^0$, $a_v$, $\gamma$) of the full-scale absorption column must be precisely known. Second, experiments have to be performed on the laboratory absorbers to obtain the desired values of the physical gas absorption properties, which are identical to those of the full-scale column. Third, in some cases, the desired values of the physical gas absorption properties may not be matched by the laboratory absorbers due to their limited capabilities. An example for the case of Point modelling, the limitation of a stirred cell is its maximum stir speed. If it is operated at a higher speed, the gas-liquid interface area becomes unknown due to ripples at the gas/liquid contacting surface.

It is therefore desirable to develop a new design procedure for full-scale absorbers with chemical reaction which is free of the above restrictions.
CHAPTER 3
THEORY

This chapter presents the theoretical framework for rigorous mathematical modelling and the proposed pilot plant technique for sizing gas absorbers with chemical reaction.

3.1 MATHEMATICAL MODEL

Packed absorber design procedures based on first principles have improved substantially in recent years. Treybal [105] first developed a method for steady state, adiabatic absorption and stripping involving single solute systems. The procedure properly accounts for the heats of absorption, solvent evaporation and condensation as well as heat and mass transfer resistances in both phases. The method was successfully tested by Raal and Khurana [106] using the air-ammonia-water system. Feintuch and Treybal [75] subsequently extended the work to multicomponent systems. Experimental verification was provided by Kelly et al. [106] for the physical absorption of acid gases from coal gas using methanol as the absorbent.

Rigorous theories for absorption with chemical reaction were well documented by Astarita [17] and Danckwersts [18]. The previous efforts were primarily directed towards
developing expressions for the local mass transfer coefficients. By contrast, little emphasis was placed on devising design methods. A new set of design equations for isothermal gas absorption with chemical reaction was recently developed by Joshi et al. [65]. However, assuming adiabatic conditions would have been more realistic because heat losses are generally small in industrial absorbers as suggested by Treybal [104] and Pandya [54].

A rigorous design procedure for adiabatic gas absorbers with chemical reaction was first described by Pandya [54]. The procedure was based on Treybal's concepts [104] for adiabatic, physical gas absorption and Danckwerts' work [18] on isothermal gas absorption with chemical reaction. Pandya's procedure accounted for the heats of absorption and reaction, solvent evaporation and condensation, chemical reactions in the liquid phase as well as heat and mass transfer resistances in both phases. DeLeye and Froment [107] used a similar procedure and presented some numerical results for commercial processes; comparisons with industrial data were however not given. Recently, Sanyal et al. [108] used a similar approach to model Benfield absorbers in which carbon dioxide is removed with hot carbonate solutions. Although good agreement between the predictions and field data was claimed, only two sets of absorber inlet and outlet data were presented.
3.1.1 MODEL FORMULATION

The mathematical model presented here is based on the algorithm proposed by Pandya [54] since it is rigorous and based on the widely accepted concepts proposed by Treybal [104] and Danckwerts [18]. Figures 3.1 and 3.2 are schematic diagrams of an adiabatic, packed absorber and a differential packed section, respectively. A five-component system is considered which is comprised of an inert carrier gas (I), an acid gas (A), an inert liquid solvent (S), a reactant (B) in the liquid and a reaction product (C). The overall chemical reaction in the liquid phase is given by

\[ A + \nu_{AB}B = C \]  \hspace{1cm} (3.1.1)

The major assumptions of the present model are: the reaction is fast and takes place only in the liquid film; heat and mass transfer resistances for the inert solvent (S) in the liquid phase are negligible; the interfacial area is the same for heat and mass transfer; axial dispersion is negligible; the absorber operates adiabatically.
Figure 3.1: Schematic diagram of adiabatic packed absorbers.
Figure 3.2: Differential section of packed absorbers.
Since no reaction occurs in the gas phase, the transfer of both solute A and vapor of solvent S within the gas film can be written as follows:

\[ R_{a,A} \, a_v \, dz = k_{G,A} \, p \, (y_A - y_{A,i}) \, a_v \, dz = G_I \, dY_A \]  

(3.1.2)

\[ R_{a,s} \, a_v \, dz = k_{G,s} \, p \, (y_S - y_{S,i}) \, a_v \, dz = G_I \, dY_S \]  

(3.1.3)

The heat transfer between gas and liquid is given by:

\[ q_{G} a_v \, dz = h_{G} \, (T_G - T_L) \, a_v \, dz \]  

(3.1.4)

Since the reaction is assumed to be fast and taking place only in the liquid film, the concentration of the dissolved gas in the bulk liquid will be nearly that which is at equilibrium within the bulk of the liquid phase. Therefore, the mass transfer of A in the liquid film is:

\[ R_{a,A} \, a_v \, dz = k_{L^0,A} \, I \, (C_{A,i} - C_A^*) \, a_v \, dz \]  

(3.1.5)

where I is the enhancement factor and \( C_A^* \) is the equilibrium concentration of the dissolved gas A in the liquid bulk. As explained in Chapter 2, the enhancement factor is a complex function of hydrodynamic properties, reaction kinetics, and
concentrations of both phases. This function must be
determined for the specific reaction taking place in the
liquid film. For example, for a simple instantaneous second
order irreversible reaction where $C_A^*$ is negligible, the
enhancement factor based on the two-film theory can be
written as [54]:

$$I = \{1 + \left[\frac{(C_B^* D_B)}{(\nu_{AB} C_A i D_A)}\right]\}$$

where $C_B^*$ is a bulk concentration of reactant B. $D_A$ and $D_B$
are the diffusivities of A and B in the liquid film,
respectively. For the case of second-order fast reactions,
the enhancement factor calculations have been explained in
Chapter 2. For other cases, the works by Danckwerts [18]
and Astarita et al. [19] should be consulted.

The change in concentration of reactant (B) and reaction
product (C) can be written as:

$$L \, dC_B = \nu_{AB} R_{a,A} a_v \, dZ \quad \quad (3.1.6)$$

and

$$L \, dC_C = - R_{a,A} a_v \, dZ \quad \quad (3.1.7)$$
Therefore, the overall material balance for a component over the differential height can be obtained by rearranging Equations 3.1.2 and 3.1.6:

\[
G_I \, dY_A = \left( \frac{L}{\nu_{AB}} \right) \, dC_B \tag{3.1.8}
\]

The overall heat balance over \(dZ\) can be written as:

\[
G_I \left( \sum (\gamma_j C_p, j) \right) \, dT_G
\]

(heat change in the gas phase)

\[
= L \, C_p, L \, dT_L
\]

(heat change in the liquid phase)

\[
+ G_I \, H_R \, dY_A
\]

(heats of absorption and reaction)

\[
+ G_I \, H_S \, dY_S
\]

(heats of evaporation)

where \(j\) denotes component \(A, S,\) and \(I\)

Also, the rate of heat transfer between the gas and liquid phases is given by:

\[
G_I \left( \sum (\gamma_j C_p, j) \right) \, dT_G = h_G \, a_v \, (T_G - T_L) \, dZ \tag{3.1.10}
\]

(heat change in the gas phase) (heat transfer between gas and liquid)
The interfacial concentration of the solute gas A is obtained by combining of Equations 3.1.2 and 3.1.5:

\[ Y_{A,i} = Y_A - \frac{R_{a,A}}{P_k^G} \]  \hspace{1cm} (3.1.11)

where

\[ R_a = \frac{[H P (Y_A - C_A^*)]}{[1 + IH(k_{L}^0/k_G)]} \]  \hspace{1cm} (3.1.12)

and \( H \) denotes Henry's constant. Since \( I \) depends on \( C_{A,i} \) and \( Y_{A,i} \), Equations 3.1.11 and 3.1.12 need to be solved simultaneously.

3.1.2 COMPUTATIONAL PROCEDURE

At the start of the calculations, the following parameters are known: the flow rates, temperature and compositions of the inlet gas and liquid phases; the total pressure of the absorber; the type and size of the packing. The concentration of A in the exit gas is typically specified. If the temperature and the concentration of the solvent vapor in the exit gas are known, there is sufficient information to determine packing height by the following computational steps:
1. Assume the temperature of and the solvent vapor concentration \( (Y_s) \) in the outlet gas. These values are subject to later verification. (Good initial approximation of \( T_G \) and \( Y_s \) values at the column top are the equilibrium values with the entering lean solvent.)

2. Compute the liquid temperature and composition of the liquid leaving the absorber by utilizing overall mass and energy balances:

\[
C_{B,\text{out}} = C_{B,\text{in}} - \frac{\{G_i (Y_{A,\text{in}} - Y_{A,\text{out}})}{(L/\nu_{AB})}\] (3.1.13)

The exit temperature of the liquid is given by:

\[
T_{L,\text{out}} = T_{L,\text{in}} + \left[\sum_j G_i (\Sigma j C_{P,j}) \right] (T_{G,\text{in}} - T_{G,\text{out}}) + G_i H_R (Y_{A,\text{in}} - Y_{A,\text{out}}) + G_i H_S (Y_{S,\text{in}} - Y_{S,\text{out}}) / (L \ C_{P,L})\] (3.1.14)

Now, begin the step-by-step computation of heat and mass transfer in a differential height, \( dZ \), starting from the bottom of the column.
3. Obtain all the necessary physical and chemical properties of both phases (i.e. solubility, diffusivity, reaction rate constant etc.).

4. Estimate \( k_{G,A}, k_{L,A}, k_{G,S}, h_G, a_v \) from data bases or correlations.

5. Assume \( y_{A,i} \) and then determine \( C_{A,i} \) which is equal to \( \{H \ P \ y_{A,i}\} \) and the enhancement factor, \( I \). The absorption rate, \( R_a \), is then calculated from Equation 3.1.12.

6. Calculate \( y_{A,i} \) from Equation 3.1.11. Repeat steps 5 and 6 until the values of \( y_{A,i} \) from both steps are approximately equal.

7. Compute the following gradients over the differential height:

\[
\frac{dY_A}{dZ} = \frac{R_{a,A} \ a_v}{G_I} \quad (3.1.15)
\]

\[
\frac{dY_S}{dZ} = \frac{R_{a,S} \ a_v}{G_I} \quad (3.1.16)
\]

\[
\frac{dT_G}{dZ} = \frac{h_G \ a_v \ (T_G-T_L)}{G_I \ \Sigma_j (Y_j C_{P,j})} \quad (3.1.17)
\]

\[
\frac{dT_L}{dZ} = G_I \ \Sigma_j (Y_j C_{P,j}) \ (*) (dT_G/dZ)
\]
\[ \frac{+ G_I H_R(dY_A/dZ)}{+ G_I H_S(dY_S/dZ)}/[L C_{P,L}] \] (3.1.18)

8. Select a reasonably small value of \( \Delta Y_A \), an increment of gas composition, so that the above-mentioned gradients do not change significantly. The level of packing at which the next computation will be made is:

\[
Z_{\text{next}} = Z + \Delta Z
\] (3.1.19)

where \( Z=0 \) for the bottom of the tower and

\[
\Delta Z = \Delta Y_A/(dY_A/dZ)
\] (3.1.20)

9. Compute the compositions and temperatures at \( Z_{\text{next}} \):

\[
Y_{A,\text{next}} = Y_A + \Delta Y_A
\] (3.1.21)

\[
Y_{S,\text{next}} = Y_S + \Delta Z(dY_S/dZ)
\] (3.1.22)

\[
T_{G,\text{next}} = T_G + \Delta Z(dT_G/dZ)
\] (3.1.23)

\[
T_{L,\text{next}} = T_L + \Delta Z(dT_L/dZ)
\] (3.1.24)

\[
C_{B,\text{next}} = C_B + \Delta Z(R_{AB_a, a_v})
\] (3.1.25)

\[
C_{C,\text{next}} = C_C + \Delta Z(R_{a, a_v})
\] (3.1.26)

10. Repeat steps 3 to 9 until the desired \( Y_A \) for the outlet gas is reached.
11. Compare $T_G$ and $Y_S$ values obtained from step 10 with those assumed for step 1. If they do not match, repeat steps 1 to 9 until these two values are approximately equal. However, further iteration may not be needed because the solution is in most cases found to be insensitive to the values of $T_G$ and $Y_S$ as suggested by Pandya [54].

Computer programs written in FORTRAN were developed based on the above computational procedure. A simplified flow chart of these programs is shown in Figure 3.3. The predictive ability of the computer models was tested by comparing their results with the experimental pilot plant data. The comparisons are reported in Chapter 6.
Figure 3.3: Simplified flow chart of the major calculation steps used in the present computer models.
3.2 PROPOSED PILOT PLANT TECHNIQUE FOR DESIGNING GAS ABSORBERS WITH CHEMICAL REACTION

Although there are a few procedures available for designing gas absorbers with chemical reaction, they still suffer from the deficiencies described in Chapter 2. The objective of this section is therefore to develop a new design concept, which involves small-scale laboratory experiments and requires only minimal knowledge of the absorption-reaction system. In particular, it is not necessary to know the chemical reaction mechanism, reaction rate constants, mass transfer coefficients and interfacial area.

3.2.1 THE PILOT PLANT TECHNIQUE*

The proposed procedure, subsequently called the Pilot Plant Technique (PPT), is based on measurements performed on pilot columns and is primarily intended for absorber sizing when basic design data are unavailable. The fundamental idea is to use a small column, subsequently called the "pilot plant model or PPM column", to simulate the full-scale

*Initial work on the PPT has been presented at the Symposium on Scale-up of Industrial Chemical Processes (Toronto, 1988) and has been published in the Canadian Journal of Chemical Engineering, 67(4), 602-607(1989).
(industrial size) absorption tower. The schematic diagram of the proposed procedure is shown in Figure 3.4. An essential condition of the PPT is that the model column must have the same hydrodynamic conditions as the full-scale column.

Consider that steady-state conditions prevail in the packed column and that only one component, A, is absorbed by the liquid. The dominant chemical reaction in the liquid is denoted by:

\[ A + \nu_{AB}B = C \]

At any point in the column, the transfer of A (or the change of B) per unit volume of packing for a differential element \(dZ\) is given by

Overall absorption rate = (A lost by gas phase)

\[ = (A \text{ gained by liquid phase}) \]

\[ + (A \text{ removed by the reaction}) \]

where

(A removed by the reaction)

\[ = \nu_{AB}(B \text{ consumed by the reaction}) \]
Figure 3.4 Schematic of the Pilot Plant Technique.
The overall absorption rate can be expressed as:

\[ R_{v,A} = f\{p_A, C_B, k_G, k_L^0, a_v, \gamma, r_{AB}\} \]

and

\[ R_{v,A} \, dZ = G_t \, dY_A = L \, dC_A + \gamma r_{AB} \, dZ \]  

\[ (3.2.1) \]

\[ (3.2.2) \]

where

\[ r_{AB} = f\{C_A, C_B, T\} \]

and the change of component B is given by:

\[ \nu_{AB} r_{AB} \, dZ = -L \, dC_B \]  

\[ (3.2.3) \]

\( R_{v,A} \) is the overall absorption rate of A per unit volume of packing, \( p_A \) is the partial pressure of A in the bulk gas, \( \gamma \) is the volume of liquid per unit volume of packing, \( C_A \) is the concentration of physically dissolved A, and \( r_{AB} \) is the reaction rate between A and B per volume of liquid and dependent of the reaction kinetics of the reaction between A and B in the liquid phase.

A material balance around the top section of the column can be written as:

\[ G_I [Y_{A, out} - Y_{A, z}] = -L[C_{A, in} - C_{A, z}] + (L/\nu_{AB})[C_{B, in} - C_{B, z}] \]  

\[ (3.2.4) \]

where \( L \) is the superficial liquid flow rate. It should be
noted that there is only one pair of fluid concentrations at
height $Z$ that satisfies Equation 3.2.4 for a given set of
top and bottom conditions.

For some gas treating processes, especially amine
processes, the liquid composition is usually expressed in
terms of the liquid loading, $a$, which is defined as moles
of soluble gas (physically and chemically absorbed) per mole
of total reactant in the liquid.

\[ C_{A,t} = C_A + C_{A,\text{c}} \]  \hspace{2cm} (3.2.5)

where $C_{A,t}$ is the total concentration of A physically and
chemically absorbed in the liquid phase and $C_{A,\text{c}}$ denotes the
concentration of the chemical sink for the component $A$. The
loading of component $A$ in the liquid is given by:

\[ a_A = C_{A,t}/C_{B,t} = (C_A + C_{A,\text{c}})/C_{B,t} \]  \hspace{2cm} (3.2.6)

where

\[ C_{A,\text{c}} = (1/\nu_{AB})(C_{B,t} - C_B) \]  \hspace{2cm} (3.2.7)

Therefore,

\[ da_A = \left(1/C_{B,t}\right) (dC_A + dC_{A,\text{c}}) \]  \hspace{2cm} (3.2.8)

and

\[ dC_{A,\text{c}} = -(1/\nu_{AB})dC_B \]  \hspace{2cm} (3.2.9)
The mass balance over the top part of the column can be written in terms of loading as:

\[ G_I[Y_{A,\text{out}} - Y_{A,z}] = L C_{B,t} [a_{A,\text{in}} - a_{A,z}] \]  \hspace{1cm} (3.2.10)

The above equations can be rearranged and integrated to obtain the total height, \( Z_t \), of the column:

\[ Y_{A,\text{in}} \]
\[ Z_t = G_I \int \frac{dy_A}{R_{V,A}} \left( 1 - y_A \right)^2 \]  \hspace{1cm} (3.2.11)

\[ Y_{A,\text{out}} \]

(from Equation 3.2.1)

or

\[ C_{A,\text{out}} \]
\[ C_{B,\text{out}} \]
\[ Z_t = L \int \frac{dC_A}{R_{V,A}} - L \int \frac{dC_B}{\nu_{AB} R_{V,A}} \]  \hspace{1cm} (3.2.12)

\[ C_{A,\text{in}} \]
\[ C_{B,\text{in}} \]

(from Equations 3.2.1 and 3.2.3)

or

\[ a_{A,\text{in}} \]
\[ a_{A,\text{out}} \]
\[ Z_t = L C_{B,t} \int \frac{da_A}{R_{V,A}} \]  \hspace{1cm} (3.2.13)

\[ a_{A,\text{out}} \]

(from Equations 3.2.2, 3.2.3, 3.2.8 and 3.2.9)
In order to evaluate the integral, \(R_{\text{fA}}\) must be known as a function of gas and liquid compositions. For any height \(Z\), these concentrations can be obtained from mass balance equations, provided the corresponding values at the top (or the bottom) of the column are given, as is usually the case.

Although there are a few methods to determine \(R_{\text{fA}}\) values, they cannot be applied to the systems where fundamental design data are not known. The weaknesses of the aforementioned methods have been described in Chapter 2. By using the PPT, the \(R_{\text{fA}}\) values along the full scale column can be measured directly from a model column if both columns have the same hydrodynamic conditions which include mass transfer coefficients, interfacial area and liquid hold-up. Similar hydrodynamics can be achieved by packing the PPM column with the same type and size of packings as the full-scale column. The PPM column must also be operated at the same superficial gas and liquid velocities as those of the full-scale column. This means that the PPM column can be much smaller than the full-scale column in both diameter and height as long as the gas and liquid flow rate per unit cross-sectional area of the PPM column are the same as those in the full-scale column. Under these conditions, the flow behavior of gas and liquid in both columns should be similar. Therefore, the physical gas absorption data for both columns should be identical provided wall effects are
negligible. The specific absorption rate per unit volume of packing, which now depends only on the bulk concentrations of reactants in the gas and liquid phases, can be measured for various gas and liquid compositions.

Once the bulk compositions and temperature of the gas and liquid phases at level $Z_m$ in the PPM column are arranged to be the same as those at level $Z$ in the full-scale column, then $R_{v,A}$ (at $Z$ and $Z_m$) must be similar in the PPM and full-scale columns. Hence $R_{v,A}$ can be determined experimentally as a function of the fluid concentrations by using the PPM column. The height of the full-scale absorption tower is then readily found by numerical integration of Equations 3.2.11, 3.2.12 or 3.2.13. (Alternatively, if the full-scale tower height is given, its absorption capacity can be predicted.)

It is clear that the PPT does not require knowledge of the hydrodynamic and physico-chemical parameters. Consequently, the weak points of the previous models are overcome (see Route # 4 in Figure 3.5). Since experimental values are obtained for $R_{v,A}$ from the PPM column which has the same hydrodynamic characteristics as the full-scale tower, the PPT procedure is applicable to all cases regardless of whether the overall rate of absorption is
DEFINITION OF PROCESS CONDITIONS
- Total flow rates of gas and liquid
- Inlet and outlet conditions

SPECIFY GAS-LIQUID CONTACTING SYSTEM
- Type and details of packings

OBTAIN PHYSICAL INFORMATION
- Densities and viscosities
- Gas-liquid equilibrium data

DETERMINATION OF SUPERFICIAL VELOCITIES
- Liquid side
- Gas side

OBTAIN PHYSICAL GAS ABSORPTION PARAMETERS
- Mass transfer coefficients
- Interfacial area
- Liquid hold-up

OBTAIN ADDITIONAL INFORMATION
- Diffusivities
- Solubilities
- Reaction kinetics

DETERMINATION OF ENHANCEMENT FACTOR

DETERMINATION OF \((K_{Gva})_{ave}\)

DETERMINATION OF ABSORPTION RATE

DETERMINATION OF COLUMN HEIGHT

Figure 3.5: Main design procedures for gas absorbers with chemical reaction
primarily determined by the reaction in the liquid film, in
the bulk or in both. This implies that the PPT may be
applied to systems with all reaction regimes ranging from
instantaneous to slow reaction (also see Section 2.1 and
Figure 2.2) provided that the wall and end effects are
negligible.

The model column may have wall and end effects which
are different (typically greater) than those of the full-
scale column. Fortunately, these effects may be minimized
by proper design of the packed column. In general, such a
design can be achieved if the following criteria are
satisfied:

1. Good initial and intermediate fluid
distribution in the packed bed. According to
Fair[85], the number of liquid streams per unit
cross sectional area of the column should be at
least 340 per m^3. As was suggested by Treybal
[86], the good liquid distribution can be
maintained by having a redistribution plate inside
the column every 6 to 10 column diameters or every
6 to 7 m of packing height.

2. Large ratio of column diameter to packing
size. According to Fair [134], the ratio of the
column ID to packing size must be at least 8 for conventional packings in order to minimize wall flow (wall effect). However, this ratio may be reduced to 6 for high efficiency random packings as reported by Billet [132]. For structured packings, the column diameter may be as small as 0.03 m without any significant wall effects [133].

More details on the proper column design criteria are presented in Chapter 5.

**DETERMINATION OF R\(_{V,A}\)**

To obtain the specific absorption rate from PPM column tests, the concentration profile in the column is measured and \( R_{V,A} \) is calculated from the slope of the profiles, i.e.

\[
R_{V,A} = G_I \frac{dY_A}{dZ} \quad (3.2.14)
\]

where the mole ratio, \( Y_A \), is given by

\[
Y_A = \frac{y_A}{1 - y_A - y_S} \quad (3.2.15)
\]

The specific absorption rate can also be obtained from the profile of the liquid composition, i.e.

\[
R_{V,A} = L \frac{dC_A}{dZ} - \left( \frac{L}{v_{AB}} \right) \frac{dC_B}{dZ} \quad (3.2.16)
\]
or

\[ R_{V,A} = L C_{B,t} \frac{da_A}{dZ} \]  \hspace{1cm} (3.2.17)

Since the \( R_{V,A} \) values are determined from the slope of the concentration profiles, there is no need to assume that the overall mass transfer coefficients are constant as implied by the empirical design method (see section 2.3.1).

The experimental procedures of obtaining the \( R_{V,A} \) values will be described in Sections 5.5 and 7.1.

3.2.2 A SHORT-CUT PROCEDURE FOR PPT

If the concentration of the liquid reactant and the degree of conversion are high, the liquid temperature may rise significantly due to the heats of absorption and reaction. Once the operation becomes non-isothermal, the temperature along the column changes appreciably and, since the chemical reaction rates, solubility and diffusivity all depend on temperature, \( R_{V,A} \) may be affected. To apply the PPT to non-isothermal situations, \( R_{V,A} \) values have to be determined as functions of gas and liquid concentrations as well as temperature. The total height (or absorption capacity) of the column can still be found by using Equation
3.2.11. It is convenient, and in most cases valid, to assume that the temperature of the gas and liquid at any point of the column are approximately the same since the heat capacity of the liquid phase is much larger than that of the gas phase.

To reduce the experimental work inherent in the PPT, it is not necessary to determine the specific absorption rate for the entire range of gas and liquid compositions. To simulate absorption-reaction behavior in the full-scale column for a given set of operating conditions, only $R_{v,A}$ values that correspond to the concentrations along the column are really needed; a time-saving procedure therefore suggests itself. The full-scale column is notionally divided into m sections (see Figure 3.6). The model column (equipped with n sampling points) is used to simulate the full-scale column section by section, starting from section 1 at the top. The liquid feed composition $\{C_B(1,1)\}$ is known and the treated gas composition $\{y_A(1,1)\}$, which is specified, can be obtained by varying the gas composition $\{y_A(1,n)\}$ entering the base of the PPM column. In the case of non-isothermal operation, the inlet temperature of the liquid of the model column is also adjusted to be the same as that of the full-scale column. Since the heat capacity of the gas phase is much smaller than that of the liquid, the
Figure 3.6 Schematic representation to simulate industrial absorbers using the PPT short-cut procedure.
temperature of gas entering the model column may be adjusted to be the same as that of the liquid. When these conditions are met, the model column behaves like section 1 of the full-scale column; consequently the outlet concentration of the liquid \( C_B(1,n) \) and the temperature at the model column bottom can be measured. Then, the concentration profiles along the model column {e.g. \( C_B(1,1) \) to \( C_B(1,n) \) and \( y_A(1,1) \) to \( y_A(1,n) \)} can be measured and \( R_{V,A} \) values can be determined.

For section 2, its top concentrations \( C_B(2,1) \) and \( y_A(2,1) \) are made equal to the concentrations at the bottom of the section 1 {\( C_B(1,n) \) and \( y_A(1,n) \), respectively}. If it is necessary for the temperature to be matched for the case of non-isothermal operation, the temperature of the liquid entering the model column is also set to be the same as that of the exit stream leaving section 1. The model column can then be used to simulate this section in the same way as the section 1.

The procedure is repeated until the bottom conditions of the full-scale column are reached. \( R_{V,A} \) values along the full-scale column can thus be obtained. The number of experiments required to simulate the full-scale column is of the order of \( m \). When \( R_{V,A} \) does not change rapidly, this number can be further reduced by performing experiments only
on some selected sections (e.g. section 1, 3, 5,... or 1, 4, 8,...)

3.2.3 VERIFICATION OF PPT

Although the PPT concept developed in this thesis is believed to have general validity, its feasibility and usefulness were tested with full-length absorption towers in which carbon dioxide is absorbed from air by aqueous solutions of sodium hydroxide and 2-amino-2-methyl-1-propanol (AMP) which is a sterically hindered amine. The verification will be presented in Chapter 7.

The carbon dioxide - sodium hydroxide system was chosen because it has been studied extensively previously, is relatively easy to examine experimentally and permits evaluation of absorber performances based on first principles. By contrast, the carbon dioxide - AMP system was chosen because it is a relatively new system, having been introduced to industry in the early 1980's and very little information on this system is currently available. Consequently, prediction of column performance for this system based on first principles is not possible.
CHAPTER 4

SOLUBILITY OF CO₂ IN 2-AMINO-2-METHYL-1-PROpanol SOLUTIONS*

Very little information on the CO₂-AMP system has been reported in the open literature and even the solubility characteristics are missing. This chapter, which is self contained, is therefore presented to provide comprehensive solubility data on the CO₂ - AMP system.

4.1 BACKGROUND INFORMATION

Sterically hindered amines have been introduced recently and are claimed to excel over conventional amines in terms of CO₂ absorption capacity, degradation resistance and selectivity [71, 100]. Very little information has been reported in the open literature even for 2-amino-2-methyl-1-propanol, or "AMP", which is one of the more widely used sterically hindered amines. The structural formula of AMP is:

* This chapter has been published in the Journal of Chemical and Engineering Data, 36(1), 130-133 (1991).
Sartori and Savage [71] reported the CO₂ solubility in 3 M AMP solutions at 40 and 120 °C. Roberts and Mather [95] provided CO₂ and H₂S solubility data for 2 M AMP solutions at 40 and 100 °C and, more recently, Teng and Mather [96] have examined the dissolution of the same gases in 3.43 M AMP solutions at 50 °C.

The principal objective of this chapter is to acquire solubility data for CO₂ in 2 and 3 M AMP solutions at temperatures ranging from 20 to 80 °C since these values cover the typical operating ranges of absorbers and have not been reported. The present and previous data are subsequently interpreted with a modified Kent-Eisenberg model [97]. The performance of AMP is also compared with that of monoethanolamine.
4.2 EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus and procedures used in this study were similar to those described by Muhlbauer and Monaghan [98]. Gas mixtures of the desired concentration were formed by metering streams of pure CO₂ and N₂ through precision rotameters. The mixture was then bubbled (at a flow rate of approximately 500 mL/min) through a gas disperser into a vessel filled with 50 mL of a NaCl solution, which had a water vapor pressure identical to that of the AMP solution under examination. The gas mixture was then dispersed into an equilibrium vessel containing 50 mL of aqueous AMP solution. Both vessels were placed in a constant temperature bath controlled to within ±0.5 °C. The CO₂ dissolution was followed by taking small samples of the AMP solution periodically; 4 to 8 hours were usually required to reach equilibrium. Three AMP samples were then taken and analyzed for their amine concentration and CO₂ loading using the methods described in section 5.6.

4.3 PREDICTIVE MODEL FOR CO₂ SOLUBILITY IN AMP SOLUTIONS

A model of the type proposed by Kent and Eisenberg [97] was chosen because it is based on the fundamental theory of Danckwerts and McNeil [99] and because it had given good
performance for predicting acid gas solubilities in alkanolamine solutions [101,118].

The chemical equilibrium in systems comprised of CO₂, primary amines and water is governed by the following equations:

\[
\begin{align*}
\text{RNH}_3^+ & = \text{H}^+ + \text{RNH}_2 & \text{4.1} \\
\text{RNHCOO}^- + \text{H}_2\text{O} & = \text{RNH}_2 + \text{HCO}_3^- & \text{4.2} \\
\text{H}_2\text{O} + \text{CO}_2 & = \text{H}^+ + \text{HCO}_3^- & \text{4.3} \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^- & \text{4.4} \\
\text{HCO}_3^- & = \text{H}^+ + \text{CO}_3^{2-} & \text{4.5}
\end{align*}
\]

Equations 4.1 and 4.2 represent the amine protonation and the amine carbamate hydrolysis, respectively [100]. Equations 4.3 to 4.5 are the typical ionization reactions for aqueous systems containing CO₂.

Since AMP has a tertiary carbon atom attached to the amino group, its carbamate ion is highly unstable and easily reverts to amine and bicarbonate; this was first discovered by Sartori and Savage [71]. Chakraborty et al. [72] recently reported that carbamate ions could not be detected in CO₂ bearing AMP solutions and they concluded that the bicarbonate and carbonate ions are the only major chemical sinks for CO₂.
The equilibrium constants representing the important reactions in the \( \text{CO}_2\)-AMP-H\(_2\)O system, in which water is present in excess, are given by:

\[
\begin{align*}
K_1 &= \frac{[\text{H}^+][\text{RNH}_2]}{[\text{RNH}_3^+]} & 4.6 \\
K_3 &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} & 4.7 \\
K_4 &= [\text{H}^+][\text{OH}^-] & 4.8 \\
K_5 &= [\text{H}^+][\text{CO}_3^=]/[\text{HCO}_3^-] & 4.9
\end{align*}
\]

Although some values of \( K_1 \) (or \( pK_1 \) where \( pK_1 = -\log K_1 \)) have been reported, they usually only apply to infinitely dilute solutions at 25 and 40 °C. Detailed information on \( pK_1 \) as a function of solution concentration and temperature is still lacking.

In addition to the above equilibrium equations, overall material and charge balances must also be satisfied:

\[
\begin{align*}
[\text{AMP}] &= [\text{RNH}_2] + [\text{RNH}_3^+] & 4.10 \\
\alpha[\text{AMP}] &= [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^=] & 4.11 \\
[\text{RNH}_3^+] + [\text{H}^+] &= [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^=] & 4.12
\end{align*}
\]

where \([\text{AMP}]\) and \( \alpha \) denote the total AMP concentration and the \( \text{CO}_2 \) loading of the AMP solution, respectively.
The physical solubility of CO\textsubscript{2} in the liquid phase is governed by Henry's law:

\[ P_{\text{CO}_2} = H_{\text{CO}_2} [\text{CO}_2] \]  \hspace{1cm} 4.13

where \( P_{\text{CO}_2} \) and \( H_{\text{CO}_2} \) denote the partial pressure of carbon dioxide in the gas phase and Henry's constant, respectively.

Equations 4.6 to 4.13 may be used to find the concentrations of seven species (i.e. \([\text{RNH}_2] \), \([\text{H}^+] \), \([\text{RNH}_3^+] \), \([\text{HCO}_3^-] \), \([\text{CO}_2] \), \([\text{OH}^-] \), \([\text{CO}_3^{2-}] \)) and \( K_1 \) provided \([\text{AMP}] \), \( a \), \( P_{\text{CO}_2} \), \( H_{\text{CO}_2} \), \( K_3 \), \( K_4 \) and \( K_5 \) are given. The first three parameters may be measured experimentally. The latter four parameters may be taken from the correlations derived by Kent and Eisenberg [97] since they were successful in representing CO\textsubscript{2} equilibria in aqueous solutions of conventional amines [102,103]. These correlations were later converted into SI units by Chakma and Meisen [118]:

\[ K_3 = \exp\{-241.818 + 298.253 \times 10^3 T^{-1} - 148.528 \times 10^6 T^{-2} \]
\[ + 332.648 \times 10^8 T^{-3} - 282.394 \times 10^1 T^{-4}\} \] \hspace{1cm} (4.14)

\[ K_4 = \exp\{39.5554 - 987.9 \times 10^2 T^{-1} + 568.828 \times 10^5 T^{-2} \]
\[ - 146.451 \times 10^8 T^{-3} + 136.146 \times 10^1 T^{-4}\} \] \hspace{1cm} (4.15)
\[ K_5 = \exp\{-294.74 + 364.385 \times 10^3 T^{-1} - 184.158 \times 10^6 T^{-2} \\
+ 415.793 \times 10^8 T^{-3} - 354.291 \times 10^1 T^{-4}\} \] (4.16)

\[ \text{HCO}_2 = \exp\{22.2819 - 138.306 \times 10^2 T^{-1} + 691.346 \times 10^4 T^{-2} \\
- 155.895 \times 10^7 T^{-3} + 120.037 \times 10^9 T^{-4}\}/7.50061 \] (4.17)

A nonlinear equation solver called NDINVT, which is based on the generalized secant method and which is available from The University of British Columbia Computing Centre, was used to solve the equations numerically. Initial estimates of the concentrations and \( K_1 \) had to be provided for the iterative calculations. These initial values could be obtained from the approximate equilibrium reaction equation of the \( \text{CO}_2 \)-AMP system suggested by Chakraborty et al.[72]:

\[ \text{CO}_2 + \text{RNH}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{RNH}_3^+ \]

The free amine, [\( \text{RNH}_2 \)], is approximately equal to \( \text{[AMP]}(1 - a) \) and the chemical sink \( \text{CO}_2, a[\text{AMP}], \) is approximately equal to \( \text{[HCO}_3^-] \) and \( \text{[RNH}_3^+] \). Since the pH of the solution is usually in the order of 9 to 11 and the value of \( K_5 \) is normally in the order of \( 10^{-10} \) kmol-ions/m\(^3\), the values of \( [\text{H}^+] \) and \( [\text{CO}_3^-] \) were assigned to be \( 10^{-10} \) and \( 10^{-8} \), respectively. The initial values are summarized below:
\[
[\text{RNH}_2] = [\text{AMP}]^{(1.0-a)} \quad [\text{H}^+] = 10^{-10} \quad [\text{RNH}_3^+] = a[\text{AMP}]
\]
\[
[\text{HCO}_3^-] = a[\text{AMP}] \quad [\text{CO}_2] = P_{\text{CO}_2}/[\text{HCO}_2] \quad [\text{OH}^-] = K_4/[\text{H}^+]
\]
\[
[\text{CO}_3^{2-}] = 10^{-8} \quad K_1 = 10^{-8}.
\]

Since the values of the unknown parameters range over several orders of magnitude, false convergence may occur. To ensure this does not happen, back calculations were performed by using a different nonlinear routine called QNEWT which is based on a quasi-Newton method. By taking the \(K_1\) values computed with NDINVT, \(P_{\text{CO}_2}\) or \(a\) values were recalculated and compared with the experimental results. The comparisons were always excellent and proved that false convergence had not arisen.

4.4 RESULTS AND DISCUSSION

The \(\text{CO}_2\) solubility data and the \(pK_1\) values are summarized in Tables 4.1 and 4.2. To assess the validity of the results, the \(\text{CO}_2\) solubilities in 2 and 3 M AMP solutions at 40 \(^\circ\)C were compared with those reported previously [71, 96]. As shown by Figures 4.1 and 4.2, the agreement is very good thereby validating the present experimental procedure.
Table 4.1: Experimental Solubility of CO$_2$ in 2 M AMP Solution.

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>CO$_2$ Partial Pressure, kPa</th>
<th>CO$_2$ Solubility mol CO$_2$/mol AMP</th>
<th>pK$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>98.93</td>
<td>0.960</td>
<td>9.343</td>
</tr>
<tr>
<td>293</td>
<td>49.88</td>
<td>0.900</td>
<td>9.316</td>
</tr>
<tr>
<td>293</td>
<td>19.28</td>
<td>0.880</td>
<td>9.704</td>
</tr>
<tr>
<td>293</td>
<td>8.39</td>
<td>0.815</td>
<td>9.842</td>
</tr>
<tr>
<td>293</td>
<td>3.23</td>
<td>0.781</td>
<td>10.242</td>
</tr>
<tr>
<td>313</td>
<td>94.00</td>
<td>0.940</td>
<td>9.339</td>
</tr>
<tr>
<td>313</td>
<td>47.05</td>
<td>0.841</td>
<td>9.167</td>
</tr>
<tr>
<td>313</td>
<td>18.01</td>
<td>0.768</td>
<td>9.373</td>
</tr>
<tr>
<td>313</td>
<td>7.94</td>
<td>0.704</td>
<td>9.576</td>
</tr>
<tr>
<td>313</td>
<td>2.70</td>
<td>0.620</td>
<td>9.864</td>
</tr>
<tr>
<td>333</td>
<td>82.66</td>
<td>0.830</td>
<td>8.994</td>
</tr>
<tr>
<td>333</td>
<td>41.14</td>
<td>0.735</td>
<td>9.015</td>
</tr>
<tr>
<td>333</td>
<td>16.46</td>
<td>0.600</td>
<td>9.066</td>
</tr>
<tr>
<td>333</td>
<td>8.00</td>
<td>0.476</td>
<td>9.059</td>
</tr>
<tr>
<td>333</td>
<td>1.90</td>
<td>0.375</td>
<td>9.410</td>
</tr>
<tr>
<td>353</td>
<td>53.33</td>
<td>0.618</td>
<td>8.720</td>
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<tr>
<td>353</td>
<td>25.84</td>
<td>0.463</td>
<td>8.638</td>
</tr>
<tr>
<td>353</td>
<td>10.40</td>
<td>0.291</td>
<td>8.507</td>
</tr>
<tr>
<td>353</td>
<td>4.99</td>
<td>0.212</td>
<td>8.504</td>
</tr>
<tr>
<td>353</td>
<td>1.59</td>
<td>0.154</td>
<td>8.692</td>
</tr>
</tbody>
</table>
Table 4.2: Experimental Solubility of CO$_2$ in 3 M AMP Solution.

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>CO$_2$ Partial Pressure, kPa</th>
<th>CO$_2$ Solubility .mol CO$_2$/mol AMP</th>
<th>pK$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>98.93</td>
<td>0.898</td>
<td>9.161</td>
</tr>
<tr>
<td>293</td>
<td>49.88</td>
<td>0.846</td>
<td>9.272</td>
</tr>
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<td>293</td>
<td>19.28</td>
<td>0.830</td>
<td>9.680</td>
</tr>
<tr>
<td>293</td>
<td>8.39</td>
<td>0.763</td>
<td>9.854</td>
</tr>
<tr>
<td>293</td>
<td>3.23</td>
<td>0.747</td>
<td>10.342</td>
</tr>
<tr>
<td>313</td>
<td>94.00</td>
<td>0.875</td>
<td>9.170</td>
</tr>
<tr>
<td>313</td>
<td>47.05</td>
<td>0.815</td>
<td>9.267</td>
</tr>
<tr>
<td>313</td>
<td>18.01</td>
<td>0.714</td>
<td>9.399</td>
</tr>
<tr>
<td>313</td>
<td>7.94</td>
<td>0.643</td>
<td>9.589</td>
</tr>
<tr>
<td>313</td>
<td>2.70</td>
<td>0.582</td>
<td>9.949</td>
</tr>
<tr>
<td>333</td>
<td>82.66</td>
<td>0.809</td>
<td>9.116</td>
</tr>
<tr>
<td>333</td>
<td>41.14</td>
<td>0.683</td>
<td>9.056</td>
</tr>
<tr>
<td>333</td>
<td>16.46</td>
<td>0.546</td>
<td>9.107</td>
</tr>
<tr>
<td>333</td>
<td>8.00</td>
<td>0.427</td>
<td>9.104</td>
</tr>
<tr>
<td>333</td>
<td>1.90</td>
<td>0.321</td>
<td>9.405</td>
</tr>
<tr>
<td>353</td>
<td>53.33</td>
<td>0.524</td>
<td>8.658</td>
</tr>
<tr>
<td>353</td>
<td>25.84</td>
<td>0.394</td>
<td>8.621</td>
</tr>
<tr>
<td>353</td>
<td>10.40</td>
<td>0.247</td>
<td>8.514</td>
</tr>
<tr>
<td>353</td>
<td>4.99</td>
<td>0.169</td>
<td>8.458</td>
</tr>
<tr>
<td>353</td>
<td>1.59</td>
<td>0.126</td>
<td>8.673</td>
</tr>
</tbody>
</table>
Figure 4.1: Solubility of CO₂ in a 2 M AMP solution at 40 °C. (Solid circles – present experimental data; open circles – Roberts and Mather [95]; solid lines – present model.)
Figure 4.2: Solubility of CO$_2$ in a 3 M AMP solution at 40 °C. (Solid circles – present experimental data; open circles – Roberts and Mather [95]; squares – Sartori and Savage [71]; solid lines – present model.)
The values of $K_1$ reported here are apparent equilibrium constants since the effects of system nonidealities were not explicitly accounted for in the model, but lumped into the $K_1$ values. The latter were therefore expressed as a function of $T$, $[CO_2]$ and $[AMP]$. Using $[CO_2]$ is preferable to $a$ since the former can be calculated directly from $PCO_2$ and $HCO_2$ as suggested by Chakma and Meisen [118]. The following correlation was found to be optimal:

$$pK_1 = 2309.1 + 0.49828 T - 70850.1/T$$
$$- 388.03 \ln T - 6.3899 [CO_2]$$
$$- 0.095221 \ln[CO_2] + 0.038508 [AMP] \quad (4.18)$$

Table 4.3 provides a comparison between the $pK_1$ values found in this work and those reported earlier. The results predicted by Equation 4.18 agree well with the data reported by Sartori and Savage [71] and Teng and Mather [96], but they are somewhat higher than those of Chakraborty et al. [72].

When Equation 4.18 is used to find $K_1$, then Equations 4.6 to 4.13 may be evaluated to obtain the concentrations of all species for a given set of $T$, $[CO_2]$ and $[AMP]$. As a result, the total $CO_2$ solubility, $a$, may be determined.
Table 4.3: Comparison of present and previously reported pK₈ values.

<table>
<thead>
<tr>
<th>Source</th>
<th>Temp. (°C)</th>
<th>AMP Conc. (M)</th>
<th>CO₂ Partial Pres., (kPa)</th>
<th>pK₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sartori and Savage [71]</td>
<td>40</td>
<td>3</td>
<td>0.7-305</td>
<td>9.70</td>
</tr>
<tr>
<td>Chakraborty et al. [72]</td>
<td>40</td>
<td>1-3</td>
<td>10.0</td>
<td>8.50</td>
</tr>
<tr>
<td>This work (Eq. 4.18)</td>
<td>40</td>
<td>3</td>
<td></td>
<td>9.67</td>
</tr>
<tr>
<td>Teng and Mather [96]</td>
<td>50</td>
<td>3.43</td>
<td>4-5650</td>
<td>9.11</td>
</tr>
<tr>
<td>This work (Eq. 4.18)</td>
<td>50</td>
<td>3.43</td>
<td>100</td>
<td>9.16</td>
</tr>
</tbody>
</table>
The QNEWT routine was employed for this purpose with the initial estimates of \( \alpha \) falling into the range of 0.5 to 1.0 mol CO\(_2\)/mol AMP. As can be seen from Figures 4.1 to 4.4, good agreement was found between the predicted and measured results; the mean square deviation was 6.0 % for the present experimental results. It should be noted that the solubility of CO\(_2\) in AMP solution is a fairly weak function of temperature between 20 and 40 °C, but it becomes a strong function in the range of 60 to 80 °C.

The CO\(_2\) solubilities in 2.5 M AMP and MEA solutions are shown in Figure 4.5. It is interesting to note that the solubilities in AMP solutions are higher than those in MEA solutions at 40 °C. At 80 °C the opposite is true and a cross-over is seen at 60 °C. From the point of solubility, AMP solutions are therefore superior to MEA solutions for the regenerative separation of CO\(_2\) since absorbers operate at low temperatures where \( \alpha \) is large and regenerators operate at elevated temperatures where \( \alpha \) is low. However, there are indications that the reaction and mass transfer rates are lower for the CO\(_2\)-AMP system than the CO\(_2\)-MEA system [103]. Further research is therefore warranted on AMP reaction kinetics, mass transfer rates and stability. Some of the pilot plant absorption data of these two systems will also be compared and discussed in Chapter 7.
Figure 4.3: Solubility of CO₂ in a 2 M AMP solution at various temperatures. (Open circles - 20 °C; solid circles - 40 °C; squares - 60 °C; triangles - 80 °C; solid lines - present model.)
Figure 4.4: Solubility of CO$_2$ in a 3 M AMP solution at various temperatures. (Open circles - 20 °C; solid circles - 40 °C; squares - 60 °C; triangles - 80 °C; solid lines - present model.)
Figure 4.5: Solubility of CO₂ in 2.5 M AMP and MEA solutions at various temperatures. (Dotted, dashed and chain dotted lines are the model predictions for the CO₂-AMP system at 40, 60 and 80 °C, respectively. Solid lines are from the Kent-Eisenberg model [97] for the CO₂-MEA system.)
CHAPTER 5
PILOT PLANT AND EXPERIMENTAL PROCEDURE

The pilot plant shown in Figure 5.1 was used to perform the present absorption studies. Figure 5.2 shows the way in which the pilot plant fitted into the existing laboratory of the Chemical Engineering Department, UBC. The equipment details are described in the following sections.

5.1 THE FULL-LENGTH ABSORPTION COLUMN

The full-length absorption column (7.2 m high, 0.1 m ID) was made of acrylic plastic and was packed with 12.7 mm (1/2") ceramic Berl Saddles (provided by Koch Engineering Co. of Calgary, Alberta). These dimensions were selected since they could be readily accommodated in the existing laboratory and provided realistic experimental data. Figure 5.3 shows the detailed dimensions of the absorber.

The full-length column was comprised of six sections (each 1.2 m high) with redistributors inserted between sections. The drawings of the column section and redistributors are shown in Figures 5.4 and 5.5, respectively. Figure 5.6 also shows how two sections are joined together.
Figure 5.1: Schematic of the pilot plant
Figure 5.2: Picture showing how the pilot plant equipment fitted into the Chemical Engineering Building
Figure 5.3: Schematic of the absorption column
Figure 5.4: Drawing of a column section.
Figure 5.5: Schematic of the redistributors
Figure 5.6: Drawing of the joint between two sections
The dimensions selected for this absorber were carefully checked by comparing them with the "proper" design criteria suggested previously. The comparisons are shown in Table 5.1.

To pack a column section, approximately 500 mL of packing elements were dumped into the empty section and planed. (This way of packing is commonly used in industry [38, 137].) The process was repeated until a packing height of approximately 1.1 m was reached.

In order to vary the effective packing height over which absorption occurred in the full-length column, the gas could be introduced at different positions between sections as shown in Figure 5.7.

The gas and liquid phases could be sampled at each section inlet and outlet to determine their composition. To measure the column temperature profile, a thermocouple (J type, Omega Engineering) was inserted just below the redistributor of each section. The diagram of the sampling system is shown in Figure 5.8. The fluid sampling probes consisted of 100 mm long, 18-gauge needles fitted with specially made 9 mm O.D. and 9 mm high Teflon cups at their tips. To sample the gas phase, the cups were positioned in such a way that their open ends faced into the direction of
the gas flow. The needle outlets were connected to an infrared gas analyzer by nylon tubes. The gas sampling rate was controlled by polycarbonate clamps (Canlab, Vancouver, B.C.). For liquid sampling, the open ends of the cups pointed into the direction of the liquid flow and the needles were connected to 50 mL syringes. The positions of both cups can be changed along the column radius. A picture of the sampling system is shown in Figure 5.7.
Table 5.1: "Proper" Design Criteria of Packed Columns.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Present column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column ID $\geq 0.10$ m</td>
<td>0.10 m</td>
</tr>
<tr>
<td>(Fair [134], Rase [33])</td>
<td></td>
</tr>
<tr>
<td>Packing size $\geq 12.7$ mm</td>
<td>12.7 mm</td>
</tr>
<tr>
<td>(Fair [134], Rase [33])</td>
<td></td>
</tr>
<tr>
<td>Column ID to packing size ratio $\geq 6$ to 8</td>
<td>8</td>
</tr>
<tr>
<td>(Billet et al. [132], Fair [134])</td>
<td></td>
</tr>
<tr>
<td>Liquid distribution:</td>
<td></td>
</tr>
<tr>
<td>No. of stream $\geq 340$ per m$^2$</td>
<td>2546 per m$^2$</td>
</tr>
<tr>
<td>(Fair [85])</td>
<td></td>
</tr>
<tr>
<td>Redistribution:</td>
<td></td>
</tr>
<tr>
<td>every 6 to 10 column ID's</td>
<td>every 1.10 m</td>
</tr>
<tr>
<td>or 6 to 7 m</td>
<td></td>
</tr>
<tr>
<td>(Treybal [86])</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.7: Picture of the sampling system and the joint between two sections
Figure 5.8: Schematic of the sampling system
5.2 PILOT PLANT MODEL (PPM) COLUMN

For the sake of convenience, the top section of the full-length absorber was used as the PPM column (see Figure 5.3). The drawing of this section is shown in Figure 5.9. In order to evaluate the $R_{v,A}$ values, the gas or liquid concentration profile is needed (see Equations 3.2.14 to 3.2.17). The liquid compositions may be measured using on-line instruments such as pH meters or ionic specific electrodes. However, they are not very reliable unless they are properly calibrated.

In the present study, it was decided to measure the CO$_2$ concentration profile in the gas phase using infrared spectroscopy, which is reliable, readily available and easy to use. The details of the gas composition analyzer will be given in Section 5.6. The PPM column was designed in such a way that the gas phase could be sampled every 0.1 m along the section. This was achieved by carefully placing gas sampling probes within the packing along the column. Figure 5.10 shows the position of the gas sampling probes inside the column. The pictures of the PPM column is shown in Figures 5.11 and 5.12.
Figure 5.9: Drawing of the PPM column
Figure 5.10: Diagram showing the gas sampling position
Figure 5.11: Picture of the PPM column
Figure 5.12: Picture of sampling probes along the PPM column
5.3 REGENERATION COLUMN

In the case of amine solutions, the CO₂-rich solution was regenerated in a separate unit. The diagram of the regenerator is shown in Figure 5.13. The column had a diameter of 0.1 m ID, was made of QVF glass and packed with 12.7 mm ceramic Raschig rings to a height of 1.4 m. The reboiler was made from a stainless steel drum (0.7 m ID x 0.7 m high). A steam coil (15.88 mm OD x 12 m) with 1.93 m² heating area was used as the heating element. The condenser at the regenerator top was a stainless steel double tube jacket. A water cooling coil (9.53 mm OD x 6 m long) was also fitted inside the condenser. The total cooling surface is about 0.325 m².

Figures 5.14 to 5.16 show the pictures of the regenerator.
Figure 5.13: Schematic of the regenerator
Figure 5.14: Picture of the regenerator
Figure 5.15: Picture of the top part of the regenerator
Figure 5.16: Picture of the bottom part of the regenerator
5.4 AUXILIARY EQUIPMENT

This section describes the detailed specifications of the auxiliary equipment used in the absorption studies (also see Figure 5.1).

The liquid feed and storage tanks were made of 45 gallon polyethylene drums. The capacity of each tank was about 0.2 m³ and permitted experimental runs lasting at least 90 minutes.

The constant temperature bath was used to control the fluid temperatures. It was made of a 45 gallon stainless steel drum equipped with a 6 kW immersion heater (Model MT 360, Chromalox Canada). Water, which was agitated by a stirrer in order to keep the bath temperature uniform, was used as the heating medium. The bath temperature was controlled (within ±1 °C) by a proportional controller (Model 49, Omega Engineering Inc., Stamford, CT).

A magnetic drive pump made of polypropylene and powered by a 1/3 Hp motor (Fabco, Model MDR-60t-t03) was used to feed the solution to the column. The maximum operating pressure and flow rate were 190 kPa and 3.8 m³/hr, respectively. A stainless steel gear pump (Arco Instrument Co., Model 211-513) was used to pump the CO₂ rich solution.
back to the feed tank or to the regenerator. Its maximum operating pressure and flow rate were 1374.0 kPa and 0.34 m$^3$/hr, respectively.

A calibrated rotameter from Omega Engineering Inc. (Model FL-73C) was used to measure the air flow rate. Its operating range was 0 to 255 (std) L/min. Since the physical properties of solutions change with concentration and solvent type, the liquid rotameter (Model FL-73M, Omega Engineering Inc.) was calibrated before each run using a precision measuring cylinder and stop watch. The maximum measurable flow rate of the liquid rotameter was about 4.0 L/min. The rotameter for measuring CO$_2$ flow rates was obtained from Brooks Instrument, Markham, Ontario (Model R-8M-25-2[tube] and 8-RV-8[float]). Its maximum measurable flow rate is about 91 (std) L/min.
5.5 PROCEDURE FOR ABSORPTION EXPERIMENTS USING THE FULL-LENGTH AND PPM COLUMNS

The feed solutions were prepared in advance with the desired compositions. (The exact compositions of the solutions were determined by methods described in Section 5.6.) All solution chemicals were of commercial grade provided by Van Water and Rogers Co., Vancouver, BC.

For the full-length column experiments, the liquid, air and CO₂ flow rates were measured by the rotameters. The air and CO₂ were then premixed and flowed in the same gas line. All fluids were preheated in the constant temperature bath. After the flow rate and concentration of the feed gas were set to the desired values, the gas mixture was introduced into the column and flowed upwards and counter-currently to the liquid solution which was introduced into the top of the tower. The exit gas left at the top of the absorber. The CO₂ rich solution leaving the absorber bottom was collected in the storage tanks.

Steady state was usually reached within 15 to 20 minutes for the PPM column runs and 30 to 40 minutes for the full-length column runs. Steady state was indicated by constant temperature readings along the column and constant concentration of the exit gas. After reaching steady state,
the gas concentration and temperature profiles along the column were measured and recorded. The gas sampling rate was about 20 mL/min. Approximately 40 mL of liquid sample were also withdrawn at each sampling location during the run using the sampling syringe. The compositions of the liquid samples were determined upon completion of a run and using methods described in the next section.

For experimental runs conducted with the PPM column, the gas mixture was fed into the column just below the redistribution plate of the top section. The experimental procedure was then the same as that of the full-length column.

The systems and operating conditions used in these studies are summarized in Tables 5.2 and 5.3
Table 5.2: Systems studied and number of experimental runs.

<table>
<thead>
<tr>
<th>System</th>
<th>Absorbent</th>
<th>No. of Runs</th>
<th>Purpose</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-NaOH</td>
<td>1.2</td>
<td>6</td>
<td>17</td>
<td>to verify well PPT and known system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>to test theoretical model</td>
</tr>
<tr>
<td>CO₂-MEA</td>
<td>up to 3.8</td>
<td>10</td>
<td>-</td>
<td>to test moderately well known system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>theoretical model</td>
</tr>
<tr>
<td>CO₂-NaOH</td>
<td>up to 2.5</td>
<td>6</td>
<td>24</td>
<td>to verify well PPT and known system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>to test theoretical model</td>
</tr>
<tr>
<td>CO₂-AMP</td>
<td>2.0</td>
<td>8</td>
<td>24</td>
<td>to verify new system</td>
</tr>
</tbody>
</table>

|                | no. of runs | 30 + 65 = 95 (total) |

Table 5.3: Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate</td>
<td>11.1 to 14.8 mol/m³ hr</td>
</tr>
<tr>
<td>CO₂ concentration</td>
<td>up to 20 %</td>
</tr>
<tr>
<td>Liquid flow rate</td>
<td>9.5 to 13.5 m³/m² hr</td>
</tr>
<tr>
<td>Total absorbent concentration</td>
<td>1.2 to 3.8 kmol/m³</td>
</tr>
<tr>
<td>Column temperature</td>
<td>14 to 57 °C</td>
</tr>
<tr>
<td>Column pressure</td>
<td>101 kPa</td>
</tr>
<tr>
<td>Flooding condition</td>
<td>30 to 70 %</td>
</tr>
<tr>
<td>Packing height</td>
<td>3.25 to 6.55 m</td>
</tr>
</tbody>
</table>
5.6 ANALYSIS OF SAMPLES

The concentration of CO$_2$ in the gas phase was measured by an infrared gas analyzer (Model 300D, Nova Analytical Systems, Hamilton, Ontario). The reading range was 0.0 to 20.0 % of CO$_2$ by volume. Before each run, the analyzer was calibrated with standard gas mixtures of CO$_2$ in nitrogen provided by Matheson, Vancouver, BC. The accuracy of the analyzer was within $\pm 2$ % of the full scale reading. No interference of water vapor on the measurements was found.

In the case of the NaOH solutions, the standard method described by Basset et al. [73] was used to determine their compositions. The total alkali content (carbonate and hydroxide) was found by titration with standard 1.0 N HCl solutions using methyl orange as the indicator. To determine the hydroxide content, the carbonate ions were first precipitated by adding excess barium chloride solution. The solution was then titrated with 1 N HCl using phenolphthalein as the indicator. The latter titration gave the sodium hydroxide content; the sodium carbonate content was then obtained by difference.

In the case of the amine solutions, the total amine concentration was determined by titration with standard 1 N HCl solutions to the methyl orange end point. The CO$_2$
content in the liquid sample was determined by the standard method given by the Association of Official Analytical Chemists (AOAC) [115]. The latter involved acidifying a precisely measured quantity of the sample by adding excess 2 N HCl solution. The CO₂ gas was released and then collected in a precision gas burette and used to calculate the CO₂ loading in the solution. The details of the gas apparatus and the procedure are given in Appendix A.

Sample calculations of the liquid composition analyses are found in Appendix A.
5.7 COLUMN TESTING

According to Fair [95], there are three major considerations in testing packed columns:

1) Capacity or flood point
2) Pressure drop
3) Mass transfer

In order to ensure that the packed column used in this research work was properly installed, the afore-mentioned considerations were applied. The results of flooding and pressure drop measurements are reported in this section. The mass transfer evaluation is provided in Chapter 6.

A tower containing a given type and size of packing and being fed with a given descending liquid flow exhibits an upper limit of the gas flow rate at which flooding occurs. If the gas flow is increased beyond the flooding velocity, the liquid ceases to descend and the column become inoperable. The flooding point can be found from the pressure drop and the gas flow rate relationship

To determine the flooding velocity of the absorber, each section was equipped with a water-filled manometer to measure the pressure difference between the inlet and
outlet. Water and air were used as the liquid and gas phase, respectively. The water flow rate was set to a predetermined value and the gas was then adjusted to the desired flow rate. The pressure drop of each section was then measured after steady state was reached (approximately 10 to 15 minutes after the gas flow rate was set). The pressure drops were found to be virtually the same for each section which indicating uniform packing, liquid and gas flow rates.

The average pressure drops from 6 sections were plotted against the gas and liquid flow rates as shown in Figure 5.17. To determine the gas velocity at flooding for a given liquid flow rate, the criterion suggested by Fair [95] was used, i.e. flooding occurred when the pressure drop reached 2.04 kPa/m of packing (2.5" of water/ft). The results are shown in Table 5.4

To predict pressure drop and flooding, the generalized correlation of Figure 5.18 suggested by Treybal [86] was used. The abscissa is the dimensionless flow parameter, FP, defined as

\[
FP = \left(\frac{L'}{G'}\right) \left(\frac{\rho_G}{\rho_L}\right)^{0.5}
\]

(5.1)

where \(L'\) and \(G'\) are the superficial mass flow rates.

The ordinate is the capacity parameter:
CP = \left( G'^2C_f\mu_L 0.1J \right) / (\rho_G (\rho_L - \rho_G) \gamma C) \quad (5.2)

To use Figure 5.18, the values of FP and CP are calculated from Equations 5.1 and 5.2 and the pressure drop is read from the graph.

In order to use this correlation, the packing factor, \( C_f \), must be supplied. Unfortunately, investigators have reported wide discrepancies in \( C_f \) values. Lobo et al. [92], Clay et al. [93], and Eckert [94] reported the \( C_f \) values of 12.7 mm (1/2") Berl Saddles as 450, 380 and 240, respectively. This discrepancy was also mentioned by Treybal [86]. According to the experimental results obtained in the present study, a \( C_f \) value of 380 gave the best predictions for flooding (see Table 5.4). When this number was used to calculate the pressure drops, accurate predictions were also obtained as shown in Figure 5.19.
Figure 5.17: Pressure drops as functions of gas and liquid flow rate. (Liquid flow rate (kg/m² s): solid squares - 2.802; open squares - 4.160; open circles - 6.740; solid circles - 8.112)
Table 5.4: Gas and liquid flow rates at flooding point

<table>
<thead>
<tr>
<th>Experimental L. flow rate kg/m² s</th>
<th>Experimental Gas flow rate kg/m² s</th>
<th>Predicted Gas flow rate kg/m² s (Cf=240)</th>
<th>Predicted Gas flow rate kg/m² s (Cf=380)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.808</td>
<td>1.02</td>
<td>1.35</td>
<td>1.08</td>
</tr>
<tr>
<td>4.160</td>
<td>0.89</td>
<td>1.16</td>
<td>0.93</td>
</tr>
<tr>
<td>6.740</td>
<td>0.75</td>
<td>0.98</td>
<td>0.79</td>
</tr>
<tr>
<td>8.112</td>
<td>0.64</td>
<td>0.86</td>
<td>0.67</td>
</tr>
</tbody>
</table>
$G' = \text{gas mass velocity, kg/m}^2\cdot\text{s}$

$L' = \text{liquid mass velocity, kg/m}^2\cdot\text{s}$

$C_f = \text{packing factor}$

$\mu_L = \text{liquid viscosity, mPa (centipoises)}$

$\rho_G = \text{gas density, kg/m}^3$

$\rho_L = \text{Liquid density, kg/m}^3$

$q_c = 1.0$

$J = 1.0$

Figure 5.18: Generalized correlation for pressure drop and flooding calculations suggested by Treybal [86].
Figure 5.19: Measured and predicted pressure drops.
CHAPTER 6

RESULTS AND DISCUSSION: COMPARISON BETWEEN
FULL-LENGTH ABSORBER PERFORMANCE AND THEORETICAL PREDICTIONS

The primary objective of this chapter is to provide comprehensive experimental data (i.e. gas and liquid concentrations and temperature profiles along the column) for CO₂ absorption into aqueous sodium hydroxide (NaOH) and monoethanolamine (MEA) solutions. As mentioned in Chapter 2, no comprehensive comparisons between experimental results and theoretical predictions have been reported in the open literature. The second objective of this chapter is therefore to provide comparisons of these experimental results with the predictions from the mathematical model described in Section 3.1. At the present time, only the CO₂-NaOH and CO₂-MEA systems could be modelled exactly since the necessary fundamental data are available in the open literature. Rigorous modelling of the CO₂-AMP system was not possible since insufficient fundamental data have been reported.
6.1 FULL-LENGTH ABSORBER PERFORMANCE

To emphasize the importance of detailed full-length column performance with concentration and temperature profiles, a statement in the paper by Krishnamurthy and Taylor [140], asking for comprehensive and detailed experimental data in order to verify their nonequilibrium stage model, is quoted as follows: "....For this (testing the model), we need data, preferably taken on industrial scale columns. Composition and temperature profiles (along the tower) are highly desirable. Details of the equipment used are also necessary. ......The authors would greatly appreciate correspondence with any of our readers who have information of this kind. ...."

In the present absorption studies, the results from 22 experimental runs are summarized in Tables 6.1 and 6.2. They include 378 measured data points: 131 points of CO₂ concentration; 116 points of liquid composition; 131 points of temperature. The column was operated at 30 to 75 % flooding velocities which is typical for gas absorber operations. The following ranges of operating conditions were used: superficial gas flow rate 11.1 to 14.8 mol/m³s; superficial liquid flow rate 9.5 to 13.5 m³/m²h; feed CO₂ concentration 11.5 to 19.8 %; total absorbent concentration 1.2 to 3.8 kmol/m³; CO₂ loading in the liquid feed 0.00 to
0.237 mol CO₂/mol absorbent; liquid feed temperature 14 to 20 °C; total pressure 103.15 kPa.

The data in Tables 6.1 to 6.2 are significantly different from the measurements reported by other researchers because the latter generally used shorter columns (typically 1 to 2 m high) and recorded only inlet and outlet conditions. By contrast, the data in Tables 6.1 and 6.2 were obtained from fairly tall columns (up to 6.55 m of packing height) and provide extensive concentration and temperature measurements along the column. The present data are therefore well suited to test the performance of theoretical models. The present overall concentration and temperature changes are also considerable. The CO₂ concentration in the gas phase ranged from 19.1 to 0.0 %, the CO₂ loading in the liquid varies from 0.0 to 0.583 moles of CO₂/mole of absorbent and temperature changed from 15 to 48 °C.
Table 6.1: Experimental results for the CO$_2$-NaOH system.

<table>
<thead>
<tr>
<th>Run (#)</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
<th>T5</th>
<th>T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Flow Rate (mol/m$^2$ s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>Liquid Flow Rate (m$^3$/m$^2$ h)</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Absorbent Feed Conc. (kmol/m$^3$)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Gas CO$_2$ Conc. (%) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>2.3</td>
<td>4.4</td>
<td>7.7</td>
<td>1.0</td>
<td>2.9</td>
<td>1.9</td>
</tr>
<tr>
<td>1.05 m</td>
<td>4.0</td>
<td>7.8</td>
<td>12.3</td>
<td>2.2</td>
<td>5.3</td>
<td>3.7</td>
</tr>
<tr>
<td>2.15 m</td>
<td>6.3</td>
<td>11.8</td>
<td>16.5</td>
<td>4.2</td>
<td>8.5</td>
<td>6.7</td>
</tr>
<tr>
<td>3.25 m</td>
<td>8.9</td>
<td>14.6</td>
<td>18.2</td>
<td>6.8</td>
<td>11.2</td>
<td>10.1</td>
</tr>
<tr>
<td>4.35 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>9.1</td>
<td>12.3</td>
<td>12.5</td>
</tr>
<tr>
<td>5.45 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6.55 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CO$_2$ removal (%)</td>
<td>75.6</td>
<td>73.1</td>
<td>62.2</td>
<td>89.4</td>
<td>78.4</td>
<td>86.8</td>
</tr>
<tr>
<td>OH$^-\text{ Conc.}$ (kmol/m$^3$) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>0.750</td>
<td>1.000</td>
<td>1.020</td>
<td>0.800</td>
<td>0.860</td>
<td>1.030</td>
</tr>
<tr>
<td>1.05 m</td>
<td>0.610</td>
<td>0.690</td>
<td>0.590</td>
<td>0.710</td>
<td>0.660</td>
<td>0.880</td>
</tr>
<tr>
<td>2.15 m</td>
<td>0.420</td>
<td>0.310</td>
<td>0.190</td>
<td>0.550</td>
<td>0.390</td>
<td>0.620</td>
</tr>
<tr>
<td>3.25 m</td>
<td>0.180</td>
<td>0.050</td>
<td>0.010</td>
<td>0.320</td>
<td>0.130</td>
<td>0.300</td>
</tr>
<tr>
<td>4.35 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.100</td>
<td>0.010</td>
<td>0.070</td>
</tr>
<tr>
<td>5.45 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6.55 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Mass Bal. Error (%)</td>
<td>+1.54</td>
<td>-0.37</td>
<td>+1.91</td>
<td>+3.06</td>
<td>-1.24</td>
<td>-3.76</td>
</tr>
<tr>
<td>Liq. Temp (°C) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>15.0</td>
<td>16.0</td>
<td>16.0</td>
<td>18.0</td>
<td>16.5</td>
<td>16.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>17.0</td>
<td>20.0</td>
<td>21.5</td>
<td>19.0</td>
<td>19.0</td>
<td>18.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>20.0</td>
<td>25.0</td>
<td>26.5</td>
<td>20.5</td>
<td>23.0</td>
<td>21.0</td>
</tr>
<tr>
<td>3.25 m</td>
<td>23.0</td>
<td>29.0</td>
<td>29.0</td>
<td>24.0</td>
<td>26.5</td>
<td>26.0</td>
</tr>
<tr>
<td>4.35 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>26.0</td>
<td>27.0</td>
<td>27.5</td>
</tr>
<tr>
<td>5.45 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6.55 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Note: For run T1 to T6, the column was not insulated.
Table 6.1 (con't): Experimental results for the CO2-NaOH system.

<table>
<thead>
<tr>
<th>Run (#)</th>
<th>T7</th>
<th>T8</th>
<th>T9</th>
<th>T10</th>
<th>T11</th>
<th>T12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Flow Rate (mol/m² s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>Liquid Flow Rate (m³/m² h)</td>
<td>9.5</td>
<td>9.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Absorbent Feed Conc. (kmol/m³)</td>
<td>2.0</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Gas CO₂ Conc. (%) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>1.25</td>
<td>1.70</td>
<td>1.00</td>
<td>1.75</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>2.95</td>
<td>3.50</td>
<td>2.65</td>
<td>3.60</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>6.15</td>
<td>7.05</td>
<td>5.80</td>
<td>6.65</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>3.25 m</td>
<td>11.20</td>
<td>12.85</td>
<td>11.55</td>
<td>10.90</td>
<td>3.1</td>
<td>1.4</td>
</tr>
<tr>
<td>4.35 m</td>
<td>15.45</td>
<td>18.60</td>
<td>18.45</td>
<td>15.20</td>
<td>7.0</td>
<td>3.7</td>
</tr>
<tr>
<td>5.45 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>12.0</td>
<td>8.2</td>
</tr>
<tr>
<td>6.55 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>15.5</td>
<td>15.4</td>
</tr>
<tr>
<td>CO₂ removal (%)</td>
<td>93.0</td>
<td>92.5</td>
<td>95.5</td>
<td>90.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>OH⁻ Conc. (kmol/m³) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>2.000</td>
<td>2.500</td>
<td>2.000</td>
<td>1.500</td>
<td>1.530</td>
<td>1.900</td>
</tr>
<tr>
<td>1.05 m</td>
<td>1.800</td>
<td>2.275</td>
<td>1.900</td>
<td>1.350</td>
<td>(1.480)</td>
<td>1.900</td>
</tr>
<tr>
<td>2.15 m</td>
<td>1.425</td>
<td>1.800</td>
<td>1.625</td>
<td>1.060</td>
<td>1.475</td>
<td>1.900</td>
</tr>
<tr>
<td>3.25 m</td>
<td>0.720</td>
<td>0.950</td>
<td>1.075</td>
<td>0.625</td>
<td>(1.270)</td>
<td>1.750</td>
</tr>
<tr>
<td>4.35 m</td>
<td>0.137</td>
<td>0.180</td>
<td>0.370</td>
<td>0.243</td>
<td>0.930</td>
<td>1.600</td>
</tr>
<tr>
<td>5.45 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.470</td>
<td>1.150</td>
</tr>
<tr>
<td>6.55 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.080</td>
<td>0.480</td>
</tr>
<tr>
<td>Mass Bal. Error (%)</td>
<td>-1.78</td>
<td>-2.23</td>
<td>-5.69</td>
<td>+1.50</td>
<td>+1.20</td>
<td>+1.42</td>
</tr>
<tr>
<td>Liq. Temp (°C) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>14.5</td>
<td>14.0</td>
<td>15.0</td>
<td>15.0</td>
<td>20.0</td>
<td>21.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>17.0</td>
<td>17.0</td>
<td>17.0</td>
<td>17.0</td>
<td>20.0</td>
<td>21.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>23.0</td>
<td>23.5</td>
<td>22.0</td>
<td>20.0</td>
<td>21.0</td>
<td>22.0</td>
</tr>
<tr>
<td>3.25 m</td>
<td>35.0</td>
<td>39.0</td>
<td>29.0</td>
<td>26.0</td>
<td>23.5</td>
<td>23.0</td>
</tr>
<tr>
<td>4.35 m</td>
<td>37.0</td>
<td>42.0</td>
<td>35.0</td>
<td>30.0</td>
<td>28.0</td>
<td>26.0</td>
</tr>
<tr>
<td>5.45 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>35.0</td>
<td>33.0</td>
</tr>
<tr>
<td>6.55 m</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>37.5</td>
<td>39.0</td>
</tr>
</tbody>
</table>

Note: The values in ( ) are calculated from mass balance.
Table 6.2: Experimental results for the CO₂-MEA system.

<table>
<thead>
<tr>
<th>Run (＃)</th>
<th>T13</th>
<th>T14</th>
<th>T15</th>
<th>T16</th>
<th>T17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Flow Rate (mol/m² s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>Liquid Flow Rate (m³/m² h)</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>9.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Absorbent Feed Conc. (kmol/m³)</td>
<td>2.00</td>
<td>2.00</td>
<td>2.03</td>
<td>2.08</td>
<td>3.8</td>
</tr>
<tr>
<td>Gas CO₂ Conc. (%) @height from top:</td>
<td>0.00 m</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1.05 m</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>2.15 m</td>
<td>0.4</td>
<td>1.4</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>3.25 m</td>
<td>1.0</td>
<td>4.0</td>
<td>2.1</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>4.35 m</td>
<td>3.3</td>
<td>8.4</td>
<td>6.6</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>5.45 m</td>
<td>8.3</td>
<td>12.8</td>
<td>13.6</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>6.55 m</td>
<td>15.3</td>
<td>15.6</td>
<td>19.5</td>
<td>15.5</td>
</tr>
</tbody>
</table>

CO₂ removal (%) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

CO₂ loading (mol CO₂/mol MEA) @height from top:

| | 0.00 m | 0.000 | 0.118 | 0.000 | 0.000 | 0.237 |
| | 1.05 m | (0.000) | (0.125) | (0.000) | (0.000) | (0.237) |
| | 2.15 m | (0.012) | 0.140 | 0.013 | 0.038 | 0.243 |
| | 3.25 m | 0.025 | (0.198) | (0.040) | 0.090 | 0.255 |
| | 4.35 m | 0.078 | 0.295 | 0.140 | 0.255 | 0.296 |
| | 5.45 m | 0.200 | 0.400 | 0.302 | 0.425 | 0.350 |
| | 6.55 m | 0.362 | 0.480 | 0.475 | 0.500 | 0.428 |

Mass Bal. Error (%) | +2.36 | +0.09 | -0.34 | -2.31 | +0.89 |

Liq. Temp (°C) @height from top:

| | 0.00 m | 19.0 | 19.0 | 19.0 | 19.0 | 20.0 |
| | 1.05 m | 19.0 | 20.0 | 19.0 | 19.0 | 20.0 |
| | 2.15 m | 19.5 | 21.0 | 19.0 | 20.0 | 21.0 |
| | 3.25 m | 20.0 | 22.0 | 21.0 | 26.0 | 22.0 |
| | 4.35 m | 23.0 | 28.0 | 25.0 | 33.0 | 26.0 |
| | 5.45 m | 29.0 | 33.0 | 35.0 | 41.0 | 32.0 |
| | 6.55 m | 34.0 | 34.0 | 37.5 | 39.0 | 36.0 |

Note: The values in ( ) are calculated from mass balance.
### Table 6.2 (con't):
Experimental results for the CO2-MEA system.

<table>
<thead>
<tr>
<th>Run (#)</th>
<th>T18</th>
<th>T19</th>
<th>T20</th>
<th>T21</th>
<th>T22</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air Flow Rate</strong> (mol/m² s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>11.1</td>
<td>14.8</td>
</tr>
<tr>
<td><strong>Liquid Flow Rate</strong> (m³/m² h)</td>
<td>9.5</td>
<td>13.5</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
</tr>
<tr>
<td><strong>Absorbent Feed Conc. (kmol/m³)</strong></td>
<td>2.00</td>
<td>2.00</td>
<td>2.55</td>
<td>2.00</td>
<td>3.00</td>
</tr>
<tr>
<td><strong>Gas CO₂ Conc. (%)</strong> @ height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>3.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>7.9</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>14.0</td>
<td>0.1</td>
<td>2.8</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>3.25 m</td>
<td>17.2</td>
<td>0.2</td>
<td>7.7</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>4.35 m</td>
<td>18.4</td>
<td>1.4</td>
<td>14.2</td>
<td>6.0</td>
<td>5.3</td>
</tr>
<tr>
<td>5.45 m</td>
<td>18.8</td>
<td>4.8</td>
<td>17.7</td>
<td>13.2</td>
<td>12.8</td>
</tr>
<tr>
<td>6.55 m</td>
<td>19.1</td>
<td>11.5</td>
<td>19.2</td>
<td>11.1</td>
<td>19.1</td>
</tr>
<tr>
<td><strong>CO₂ removal (%)</strong></td>
<td>85.4</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td><strong>CO₂ loading (mol CO₂/mol MEA)</strong> @ height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1.05 m</td>
<td>0.150 (0.000)</td>
<td>0.010 (0.000)</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>2.15 m</td>
<td>0.362 (0.002)</td>
<td>0.070</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>3.25 m</td>
<td>0.482</td>
<td>0.005</td>
<td>0.190</td>
<td>0.030</td>
<td>0.033</td>
</tr>
<tr>
<td>4.35 m</td>
<td>(0.530)</td>
<td>0.032 (0.366)</td>
<td>0.142</td>
<td>0.125</td>
<td></td>
</tr>
<tr>
<td>5.45 m</td>
<td>0.538</td>
<td>0.108</td>
<td>0.474</td>
<td>0.325</td>
<td>0.292</td>
</tr>
<tr>
<td>6.55 m</td>
<td>0.558</td>
<td>0.265</td>
<td>0.514</td>
<td>0.488</td>
<td>0.443</td>
</tr>
<tr>
<td><strong>Mass Bal. Error (%)</strong></td>
<td>-0.94</td>
<td>+4.58</td>
<td>-3.14</td>
<td>-1.19</td>
<td>+0.92</td>
</tr>
<tr>
<td><strong>Liq. Temp (°C)</strong> @ height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>20.0</td>
<td>19.0</td>
<td>19.0</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>27.0</td>
<td>19.0</td>
<td>20.0</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>36.0</td>
<td>19.0</td>
<td>22.0</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>3.25 m</td>
<td>43.0</td>
<td>19.0</td>
<td>32.0</td>
<td>21.0</td>
<td>21.0</td>
</tr>
<tr>
<td>4.35 m</td>
<td>42.0</td>
<td>20.0</td>
<td>47.0</td>
<td>26.0</td>
<td>29.0</td>
</tr>
<tr>
<td>5.45 m</td>
<td>41.0</td>
<td>24.0</td>
<td>57.0</td>
<td>33.5</td>
<td>45.0</td>
</tr>
<tr>
<td>6.55 m</td>
<td>36.0</td>
<td>30.0</td>
<td>48.0</td>
<td>37.5</td>
<td>47.0</td>
</tr>
</tbody>
</table>

Note: The values in ( ) are calculated from mass balance.
6.1.1 EFFECT OF OPERATING CONDITIONS

To show the effect of various operating variables on column performance, the CO₂ concentration profiles are plotted against the column height in Figures 6.1 to 6.6. The effect of CO₂ loading on the profile is shown in Figure 6.1 (Run T13 vs T14). When the loading is increased from 0.0 to 0.118 while keeping all other conditions approximately the same, the packing height required for nearly complete removal increased from about 5.45 to 6.55 m. This increase is, of course, due to the reduced availability of free absorbent for reacting with the absorbed carbon dioxide.

Figure 6.2 (Run T16 vs T18) shows the effect of CO₂ concentration in the inlet gas. The removal of CO₂ falls from approximately 100% to 81% when the CO₂ inlet concentration is raised from about 15% to 19%. The effect of liquid flow rate is shown in Figure 6.3 (Run T15 vs T18). When the liquid flow rate is increased, the absorption rate and capacity of the column are increased due to: (i) higher \( k_L^o \) and \( a_V \) values and (ii) higher concentrations of free absorbent. The increase in free absorbent also enhances the effective mass transfer coefficient of the liquid phase.
For absorbers using physical solvents (absorption *without* chemical reaction), the primary way to increase the absorption capacity is to increase the solution flow rate. By contrast, for gas absorption with chemical reaction, the capacity can be enhanced by just increasing the absorbent concentration as shown by Figure 6.4 (Run T18 vs T20). As expected, reducing the gas feed rate increases the degree of removal (see Figure 6.5 - Run T18 vs T21).

The effect of solvent type on the absorption rate is demonstrated by Figure 6.6. There is almost no difference in the column performance when using NaOH or MEA under the conditions of Runs T11 and T14 (see Figure 6.6). It may be inferred that there is no significant difference in absorption capacity when either one of these solvents is used under the present operating conditions.
Figure 6.1: Effect of CO₂ loading. The inlet CO₂ loading was increased from 0.0 (Run T13 - solid circles) to 0.118 (Run T14 - open squares) mol CO₂ per mol MEA. Operating conditions: gas flow rate = 14.8 mol/m² s; liquid flow rate = 13.5 m³/m² h; total MEA concentration = 2.0 kmol/m³; inlet gas CO₂ concentration = 15.5%. 
Figure 6.2: Effect of gas CO$_2$ concentration. The inlet CO$_2$ concentration was increased from 15.6 % (Run T16 - open squares) to 19.1 % (Run T18 - solid circles). Operating conditions: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ h; total MEA concentration = 2.0 kmol/m$^3$; inlet CO$_2$ loading = 0.0 mol CO$_2$ / mol MEA.
Figure 6.3: Effect of liquid flow rate. The liquid flow rate was increased from 9.5 (Run T18 - solid circles) to 13.5 (Run T15 - open squares) m³/m² s.
Operating conditions: gas flow rate = 14.8 mol/m² s; total MEA concentration = 2.0 kmol/m³; inlet CO₂ loading = 0.0 mol CO₂ / mol MEA; inlet gas CO₂ concentration = 19.5%.
Figure 6.4: Effect of absorbent concentration. The total MEA concentration was increased from 2.0 (Run T18 - solid circles) to 2.55 (Run T20 - open squares) kmol/m³. Operating conditions: gas flow rate = 14.8 mol/m² s; liquid flow rate = 9.5 m³/m² h; inlet CO₂ loading = 0.0 mol CO₂ / mol MEA; inlet gas CO₂ concentration = 19.1%.
Figure 6.5: Effect of gas flow rate. The gas flow rate was increased from 11.1 (Run T21 - open squares) to 14.8 (Run T18 - solid circles) mol/m² s.
Operating conditions: liquid flow rate = 9.5 m³/m² h; inlet CO₂ loading = 0.0 mol CO₂ / mol MEA; inlet gas CO₂ concentration = 19.1%; total MEA concentration = 2.0 kmol/m³.
Figure 6.6: Effect of absorbent type. The solvent type was changed from NaOH (Run T11 - solid circles) to MEA (Run T14 - open squares). Operating conditions: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 13.5 m$^3$/m$^2$ h; total absorbent concentration = 2.0 kmol/m$^3$; inlet gas CO2 concentration = 15.5%.
6.2 COMPARISON BETWEEN FULL-LENGTH ABSORBER PERFORMANCE AND THEORETICAL PREDICTIONS*

Computer programs, which were developed based on the algorithm and computation procedures described in Section 3.2, were used to predict the full-length absorber performance for the CO$_2$-NaOH and CO$_2$-MEA systems.

6.2.1 SOURCES OF BASIC INFORMATION

Before the model equations can be evaluated, various parameters (e.g. mass transfer coefficients, solubility, reaction rate constant, etc.) are needed. These parameters may be obtained from experimental measurements or correlations. Great caution has to be exercised because there are considerable discrepancies between the previously recorded data as reported by Kelly et al.[106] and Raal and Khurana, [105] and these discrepancies can strongly affect the prediction results.

* Some exploratory results on the comparison between absorber performance and theoretical predictions were presented at 38th Canadian Chemical Engineering Conference (Edmonton, Oct. 2-5, 1988) and were published in "Gas Separation Technology" edited by Vansant and Dewolfs, Elsevier, p. 38-90, 1990.
Some typical values of these basic parameters used in the computer models are listed in Table 6.3 for CO$_2$-NaOH system (Run T9) and Table 6.4 for CO$_2$-MEA system (Run T22).

Although several correlations are available for estimating $k_G$ and $a_v$, the expressions proposed by Onda et al. [35] were chosen because they were found to be satisfactory for conventional packings by Kelly et al. [106] and Sanyal et al. [108]. A new set of data for the liquid mass transfer in Berl Saddles packing recently reported by Cho [110] was used in this model. The heat transfer coefficient was calculated by using the correlation suggested by Pandya [54]. The values for the total heat of absorption, which is the sum of the heat of solution and the heat of reaction, were taken from Danckwerts [18] and Kohl and Riesenfeld [5] for the CO$_2$-NaOH and CO$_2$-MEA systems, respectively.

One of the most important parts of gas absorption with chemical reaction modelling is the enhancement factor calculation. Unlike physical gas absorption, the $k_L$ and $I$ values in the chemical absorbers change significantly from the bottom to the top due to the effect of the chemical reaction as previously mentioned in Section 2.3.2. This effect will also be demonstrated in the following section.
Table 6.3: List of operating conditions and parameters for Run T9 (CO₂-NaOH system).

<table>
<thead>
<tr>
<th>Property</th>
<th>Column top</th>
<th>Column bottom</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (m³/m² h)</td>
<td>13.5</td>
<td>13.5</td>
<td>Experiment</td>
</tr>
<tr>
<td>C_B (kmol/m³)</td>
<td>2.0</td>
<td>0.413</td>
<td>&quot;</td>
</tr>
<tr>
<td>G_I (mol/m² s)</td>
<td>14.8</td>
<td>14.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>Y_CO2</td>
<td>0.1</td>
<td>0.185</td>
<td>&quot;</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>15.0</td>
<td>35.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>D_A (m²/s)</td>
<td>1.518x10⁻⁹</td>
<td>1.803x10⁻⁹</td>
<td>Danckwerts and Sharma [1]</td>
</tr>
<tr>
<td>D_B (m²/s)</td>
<td>0.893x10⁻⁹</td>
<td>1.060x10⁻⁹</td>
<td>Danckwerts and Alper [5]</td>
</tr>
<tr>
<td>k_G (kmol/m² s kPa)</td>
<td>3.168x10⁻⁶</td>
<td>3.168x10⁻⁶</td>
<td>Onda et al. [35]</td>
</tr>
<tr>
<td>k_L (m/s)</td>
<td>6.283x10⁻⁵</td>
<td>6.846x10⁻⁵</td>
<td>Cho [110]</td>
</tr>
<tr>
<td>a_V (m²/m³)</td>
<td>150.</td>
<td>150.</td>
<td>Onda et al. [35]</td>
</tr>
<tr>
<td>H (kmol/m³ kPa)</td>
<td>2.274x10⁻⁴</td>
<td>1.076x10⁻⁴</td>
<td>Pohorecki and Monuik [111]</td>
</tr>
<tr>
<td>h_G (kJ/s m² °K)</td>
<td>0.099</td>
<td>0.099</td>
<td>Pandya [54]</td>
</tr>
<tr>
<td>k_2 (m³/kmol s)</td>
<td>1.025x10⁺⁴</td>
<td>4.574x10⁺⁴</td>
<td>Pohorecki and Monuik [111]</td>
</tr>
<tr>
<td>H_R (kJ/kmol)</td>
<td>1.021x10⁺⁵</td>
<td>1.021x10⁺⁵</td>
<td>Danckwerts[18]</td>
</tr>
<tr>
<td>I</td>
<td>90.6</td>
<td>48.7</td>
<td>Welleck et al. [89]</td>
</tr>
</tbody>
</table>
Table 6.4: List of operating conditions and parameters for Run T22 (CO$_2$-MEA system).

<table>
<thead>
<tr>
<th>Property</th>
<th>Column top</th>
<th>Column bottom</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (m$^3$/m$^2$ h)</td>
<td>9.5</td>
<td>9.5</td>
<td>Experiment</td>
</tr>
<tr>
<td>Total MEA (kmol/m$^3$)</td>
<td>3.0</td>
<td>3.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>Loading (mol CO$_2$/mol MEA)</td>
<td>0.0</td>
<td>0.443</td>
<td>&quot;</td>
</tr>
<tr>
<td>G$_I$ (mol/m$^2$ s)</td>
<td>14.8</td>
<td>14.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>Y$_{CO2}$</td>
<td>0.0</td>
<td>0.191</td>
<td>&quot;</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>19.0</td>
<td>47.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>D$_A$ (m$^2$/s)</td>
<td>1.209x10$^{-9}$</td>
<td>1.558x10$^{-9}$</td>
<td>Thomas and Furzer [112]</td>
</tr>
<tr>
<td>D$_B$ (m$^2$/s)</td>
<td>0.756x10$^{-9}$</td>
<td>0.974x10$^{-9}$</td>
<td>Thomas and Furzer [112]</td>
</tr>
<tr>
<td>k$_G$ (kmol/m$^2$ s kPa)</td>
<td>3.168x10$^{-6}$</td>
<td>3.168x10$^{-6}$</td>
<td>Onda et al. [35]</td>
</tr>
<tr>
<td>k$_L^o$ (m/s)</td>
<td>5.387x10$^{-5}$</td>
<td>6.115x10$^{-5}$</td>
<td>Cho [110]</td>
</tr>
<tr>
<td>a$_v$ (m$^2$/m$^3$)</td>
<td>135.</td>
<td>135.</td>
<td>Onda et al. [35]</td>
</tr>
<tr>
<td>H (kmol/m$^3$ kPa)</td>
<td>6.220x10$^{-4}$</td>
<td>2.049x10$^{-4}$</td>
<td>Pohorecki and Monuik [111]</td>
</tr>
<tr>
<td>h$_G$ (kJ/s m$^2$ °K)</td>
<td>0.099</td>
<td>0.099</td>
<td>Pandya [54]</td>
</tr>
<tr>
<td>k$_2$ (m$^3$/kmol s)</td>
<td>0.401x10$^{+4}$</td>
<td>1.854x10$^{+4}$</td>
<td>Blauwhoff et al. [43]</td>
</tr>
<tr>
<td>H$_R$ (kJ/kmol)</td>
<td>0.937x10$^{+5}$</td>
<td>0.937x10$^{+5}$</td>
<td>Danckwerts[18]</td>
</tr>
<tr>
<td>I</td>
<td>70.9</td>
<td>24.13</td>
<td>Welleck et al. [89]</td>
</tr>
</tbody>
</table>
For the reaction of CO$_2$-NaOH and CO$_2$-MEA systems, the second-order reaction can be assumed [1, 17, 18, 54]. To avoid complex numerical calculation, there are a few equations available for the approximate solutions (see Section 2.3.2). The explicit equation presented by Welleck et al. [89] was used (see Equation 2.25). However, the information regarding the rate constant and physico-chemical properties of the system must be known before the enhancement factor can be evaluated.

The rate constant of CO$_2$-NaOH reaction, in the temperature range and at the ionic strength of practical interest, has been recently correlated by Pohorecki and Moniuk [111] as

$$\log k_{2,\text{NaOH}} = 11.895 - \frac{2382}{T} + 0.221 I_C - 0.016 (I_C)^2 \quad (6.1)$$

where $I_C$ is the ionic strength of the solution.

For CO$_2$-MEA system, Blauwhoff et al. [43] correlated its second-order rate constant as

$$\log k_{2,\text{MEA}} = 10.99 - \frac{2152}{T} \quad (6.2)$$
The Henry's constant for CO₂ solubility in NaOH solution is estimated using the following expression:

\[ \log(H/H_w) = -K_S I_C \]  \hspace{1cm} (6.3)

where \( K_S \) is the sum of the contributions due to ions in the liquid phase and reported by Danckwerts [18]. \( H_w \) denotes the Henry's constant of CO₂ in water:

\[ \log(H_w) = 9.1229 - 5.9044 \times 10^{-2} T + 7.8857 \times 10^{-5} T^2 \]  \hspace{1cm} (6.4)

This correlation was taken from Pohorecki and Moniuk [111].

For the CO₂-MEA system, Hikita et al. [49] found a salting-in effect correlated by

\[ \log(H/H_w) = 0.3[\text{MEA}]/(1 - \kappa[\text{MEA}]) - K_S I_C \]  \hspace{1cm} (6.5)

where \( \kappa = 1/(1.2850 - 0.001(T - 314.5513)^2) \)

The diffusivity data for CO₂-NaOH and CO₂-MEA systems were reported by Danckwerts and Sharma [1] and Thomas and Furzer [112]. The effect of temperature on diffusivity is calculated using an equation suggested by Reid et al.[113]:

\[ D_{ab}(T_2)/D_{ab}(T_1) = ((T_c-T_1)/(T_c-T_2))^n \]  \hspace{1cm} (6.6)
where $T_c$ is the critical temperature of the solvent. The index $n$ is related to the heat of vaporization of the solvent. In our case, $n$ is equal to 3.

The data for other parameters such as density, viscosity, specific heat, etc. were taken from Perry's Handbook, Gas Purification by Kohl and Riesenfeld [15], and Gas Conditioning Fact Book by Dow Chemical Company [74].

It should be noted that the information on some parameters have been reported quite recently even though the $CO_2$-NaOH and $CO_2$-MEA systems have been studied for a long period of time. This shows that acquiring the fundamental data for designing gas absorbers with chemical reaction is very difficult and time-consuming.
6.2.2 COMPARISON OF RESULTS

The computer models predictions were first tested against some calculated results reported previously to ensure that the programs worked properly. As can be seen in Table 6.5, the predictions and previous results are virtually identical thereby confirming the validity of the present programs.

Typical plots of experimental (points) and predicted (solid lines) gas concentrations, liquid compositions and temperatures along the column are shown in Figures 6.7 (Run T9) and 6.8 (Run T22) for the CO$_2$-NaOH and CO$_2$-MEA systems, respectively. The lists of basic parameters and operating conditions for Run T9 and Run T22 are given in Tables 6.3 and 6.4, respectively. The agreement between the results is generally very good thereby again confirming the validity of the mathematical model. Additional evidence for the good agreement is provided by Figures 6.10 to 6.13.

As seen from Figures 6.7a and 6.8a, the gas and liquid temperature profiles differ significantly near the column bottom where the entering gas is rapidly heated by the
Table 6.5: Comparison between the calculation results from previous reports and from this work.

<table>
<thead>
<tr>
<th>Source and Conditions</th>
<th>Computed Height</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pandya [54]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$-MEA system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Column: 0.1m ID, 12.7mm Raschig rings</td>
<td>0.84 m</td>
<td>0.84 m</td>
</tr>
<tr>
<td>Operating Conditions:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas rate = 1573 kg/m$^2$.h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid rate = 13.68 m$^3$/m$^2$.s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total MEA conc. = 2.5 kmol/m$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>loading = 0.15 (top) and 0.4 (bottom)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$_{CO2}$ = 0.0176(top) and 0.176 (bottom)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Column temp. = 46 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Column Pressure = 2020 kPa.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| **Danckwerts and Sharma [1]**          | 1.42 m          | 1.51 m    |
| CO$_2$-MEA system                       |                 |           |
| Column: 2.27m, 38.1mm Raschig rings    |                 |           |
| Operating Conditions:                  |                 |           |
| gas rate = 2628 kg/m$^2$.h             |                 |           |
| liquid rate = 60.84 m$^3$/m$^2$.s      |                 |           |
| Total MEA conc. = 2.5 kmol/m$^3$       |                 |           |
| loading = 0.15 (top) and 0.4 (bottom)  |                 |           |
| Y$_{CO2}$ = 0.025(top) and 0.25 (bottom) |             |           |
| Column temp. = 30 °C                   |                 |           |
| Column Pressure = 2020 kPa.            |                 |           |

| **Alper [56]**                         | 1.54 m          | 1.48 m    |
| CO$_2$-NaOH system                     |                 |           |
| Column: 0.1m ID, 12.7mm Raschig rings  |                 |           |
| Operating Conditions:                  |                 |           |
| gas rate = 1831 kg/m$^2$.h             |                 |           |
| liquid rate = 10.08 m$^3$/m$^2$.s      |                 |           |
| $[Na^+]$ conc. = 1.2 kmol/m$^3$         |                 |           |
| $[OH^-]$ = 0.6(top) and 0.08(bottom) kmol/m$^3$ |             |           |
| Y$_{CO2}$ = 0.066(top) and 0.115 (bottom) |             |           |
| Column temp. = 25 °C                   |                 |           |
| Column Pressure = 101 kPa.             |                 |           |
Figure 6.7: Predicted (lines) and experimental (points) results for the CO$_2$ – NaOH system (Run T9): [a] Temperature profiles for the liquid (solid line) and gas phases (dotted line), Open squares are the experimental measurements of the liquid temperature; [b] concentration profiles of CO$_2$ (open circle) and NaOH (solid circle); [c] Enhancement factor.
Figure 6.8: Predicted (lines) and experimental (points) results for the CO$_2$ - MEA system (Run T22): [a] Temperature profiles for the liquid (solid line) and gas phases (dotted line), Open squares are the experimental measurements of the liquid temperature; [b] concentration profiles of CO$_2$ (open circle) and loading (solid circle); [c] Enhancement factor.
descending liquid. Higher up in the column, the gas and liquid temperatures reach a maximum and then become very similar resulting from the facts that the heat capacity and the mass flow rate of the liquid are higher than those of the gas phase. This evidence also confirms the assumption stated in Section 3.2.2 that the temperatures of the gas and liquid phases along the column are approximately the same.

Figures 6.7b-c and 6.8b-c show relatively steeper gradients of gas and liquid composition profiles at the bottom part of the column. These are due to higher driving force between the phases resulting in higher absorption rate. Since the enhancement factor depends strongly on the concentration of both gas and liquid, it varies considerably along the column with the greater changes occurring in the lower section as shown in Figures 6.7c and 6.8c. The assumption of a constant enhancement is therefore not generally justifiable. For instance, in the case of Run T9 (see Figure 6.7), the enhancement factor increases from about 48 at the column bottom to about 90 at the column top. This means that the absorption rate with chemical reaction is 48 to 90 times higher than without chemical reaction.

Near the top of the column, the reactant concentration is relatively high and, therefore, most of CO$_2$ is consumed right after being dissolved at the interface. As a result,
the reaction zone is located close to the gas-liquid interface resulting in higher values of the enhancement factor. On the other hand, near the bottom of the column, the concentration of the liquid reactant is much lower but the CO2 concentration at the interface is considerably higher by comparison with that at the top of the column. The CO2 can then diffuse deeply into the liquid film before reacting with the liquid reactant. As a result, the reaction zone is located further away from the interface resulting in reduced enhancement factors.

Since the enhancement factor is a complex function of the hydrodynamic conditions of the absorber as well as the physico-chemical properties of the system, it is difficult to make direct comparisons between the results from this and other studies. To our knowledge, only 2 sets of experimental values of the enhancement factor for CO2-NaOH absorption in packed columns have been explicitly reported by Merchuk et al.[142] and Onda et al.[143]. As can be seen from Table 6.6, the enhancement factors obtained in this study are of the same order as those reported by the afore-mentioned authors.
Table 6.6: Comparison of enhancement factor values obtained from Merchuk et al.[142], Onda et al.[143] and Run T9.

<table>
<thead>
<tr>
<th>Source</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merchuk et al. [142]</td>
<td>6 to 60</td>
</tr>
<tr>
<td>Column: 0.25m ID, 0.335m high</td>
<td></td>
</tr>
<tr>
<td>25.4mm carbon Raschig rings</td>
<td></td>
</tr>
<tr>
<td>Conditions:</td>
<td></td>
</tr>
<tr>
<td>gas rate = 2800 to 3000 kg/m² h</td>
<td></td>
</tr>
<tr>
<td>liquid rate = 3.0 to 10.0 m³/m² h</td>
<td></td>
</tr>
<tr>
<td>NaOH conc. = 0.5 to 1.0 kmol/m³</td>
<td></td>
</tr>
<tr>
<td>CO₂ conc. = 8.0 to 90.0 %</td>
<td></td>
</tr>
<tr>
<td>Column temperature = 29.0 to 32 °C</td>
<td></td>
</tr>
</tbody>
</table>

| Onda et al. [143]                | 10 to 150          |
| Column: 0.076m ID, 0.4m high     |                    |
| 6.0mm ceramic Raschig rings      |                    |
| Conditions:                      |                    |
| liquid rate = 6.37 to 39.25 m³/m² h|                    |
| NaOH conc. = 0.5 to 3.0 kmol/m³  |                    |
| CO₂ conc. = 100 %                |                    |
| Column temperature = 15 to 45 °C |                    |

This work - Run T9

| Column: 0.10m ID, 4.35m high     | 48 to 90            |
| 12.7mm ceramic Berl saddles      |                    |
| Conditions:                      |                    |
| gas rate = 1545 kg/m² h          |                    |
| liquid rate = 13.5 m³/m² h       |                    |
| NaOH conc. = 0.413 to 2.0 kmol/m³|                    |
| CO₂ conc. = 1.0 to 18.45 %       |                    |
| Column temperature = 15.0 to 35.0 °C|                    |
COMPARISON AT HIGH LOADING

When the CO₂ loading at the column bottom reached 0.5 moles of CO₂ per mole of amine for the CO₂-MEA system, the difference between the results and prediction are significant as shown by Figure 6.9 (Run T16). If only terminal conditions are considered, good agreement would be deduced. Nevertheless, the discrepancy between the two profiles is large (see solid line and points). This shows that a comparison of model predictions and experimental results at the absorber inlet and outlet are insufficient to validate models.

One reason for the discrepancy in this case may be due to bicarbonate formation, which becomes important as the CO₂ loading approaches 0.5 moles of CO₂ per mole of MEA; the bicarbonate formation was not taken into account in the present model. Another reason may be because the reaction rate is affected by the ionic concentration which was not included in the rate constant (Equation 6.2). The loading increases with the ionic strength but there is no information on variation in rate constant for CO₂-MEA reaction with ionic strength. The effect of the ionic strength on the rate constant is well known and has been studied extensively for the CO₂-NaOH system. For example, Pohorecki and Moniuk [111] reported that the value of
Figure 6.9: Concentration of CO$_2$ in the gas phase for Run T16. Open circles represent experimental measurements; the solid line and dotted lines denote the predicted values using a column comprised of six and five sections, respectively. (Operating conditions: gas flow rate = 14.8 m$^3$/m$^2$ h; liquid flow rate = 9.5 m$^3$/m$^2$ h; inlet CO$_2$ loading = 0.0 mol CO$_2$ / mol MEA; inlet gas CO$_2$ concentration = 15.5%; total MEA concentration = 2.0 kmol/m$^3$.)
$k_{2, NaOH}$ increases by more than 4 times when the ionic strength was increased from 0.0 to 3.8 kmol/m$^3$. This effect should be further studied for CO$_2$-amine systems.

Since both the reaction mechanism and the rate constant influence the enhancement factor, it is not surprising that good agreement was not obtained at the high CO$_2$ loadings. To confirm this, the calculations were repeated for just the top five sections of the absorber and using the experimentally determined compositions of the liquid and gas phases leaving and entering the bottom of the lowest section, respectively. Under these conditions, the solution loading ranged from 0.00 to 0.425 moles CO$_2$ per mole of MEA. As shown by the dotted line in Figure 6.9, the agreement between the predicted and experimental values becomes once again very good.
OVERALL COMPARISON

Due to the large amount of experimental data, it is difficult to illustrate the comparison in tabular form. Therefore, the comparisons between results and predictions of CO₂ concentration, NaOH concentration, CO₂ loading and liquid temperature for all runs are shown in Figures 6.10, 6.11, 6.12 and 6.13, respectively. Since the predictions when CO₂ loading approaches 0.5 moles of CO₂ per mole of amine for the CO₂-MEA system are not accurate, the results of the bottom sections of runs T15, T16, T18, T20 and T21 are not included in the comparisons. As can be seen from those figures, good agreements between experimental results and predictions are obtained. The discrepancies between the two are, on the average, about 12%.

It was also found that the model appears to be quite sensitive to the mass balance. In some cases, deviations of a few percent in the input data (concentrations) can result in large differences in the predicted height. Some sample calculations are shown in Table 6.7 (Run T9). If the liquid concentration at the column bottom is reduced by 0.2 kmol/m³ (10% of the total concentration), the height prediction deviates by 13.9%. However, if the concentration is further reduced by 15%, the deviation is exponentially increased to about 26%. The effect of concentration on the absorber
height prediction is even larger when saturation is approached. This is not surprising since the enhancement factor and the specific absorption rate are strongly dependent on the fluid concentrations. Therefore, obtaining good experimental data for verifying mathematical models should be as important as developing more rigorous theoretical models.
Figure 6.10: Cross plot of predicted and measured CO₂ concentrations in the gas phase.
Figure 6.11: Cross plot of predicted and measured NaOH concentrations in the liquid phase.
Figure 6.12: Cross plot of predicted and measured CO$_2$ loading in the MEA solution.
Figure 6.13: Cross plot of predicted and measured temperatures in the liquid phase.
Table 6.7: Effect of mass balance on the height prediction for Run T9 (NaOH-CO₂ system). Operating Conditions: gas rate = 1545 kg/m² h; liquid rate = 13.5 m³/m² h; NaOH conc. = 0.413 to 2.0 kmol/m³; CO₂ conc. = 1.0 to 18.45%; Column temperature = 15.0 to 35.0 °C

<table>
<thead>
<tr>
<th>Mass balance at Column bottom</th>
<th>Predicted height</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_B - 0% of 2.0 kmol/m³ (at 0.37 kmol/m³)</td>
<td>4.40 m</td>
<td>0.0%</td>
</tr>
<tr>
<td>C_B - 10% of 2.0 kmol/m³ (at 0.17 kmol/m³)</td>
<td>5.01 m</td>
<td>13.9%</td>
</tr>
<tr>
<td>C_B - 15% of 2.0 kmol/m³ (at 0.07 kmol/m³)</td>
<td>5.56 m</td>
<td>26.4%</td>
</tr>
</tbody>
</table>
EFFECT OF BASIC PARAMETERS

Since the uncertainties associated with the data or correlations available in the open literature are high, it is useful to know the degree of importance of these parameters on the predicted results. The conditions of Run-T9 are used to illustrate the deviation in the predicted results when values of $k_G$, $k_L^0$, $a_v$, $H$, and $I$ in the computer model are forced to increase or decrease by 20%; these are typical ranges of uncertainty associated for these parameters. The calculated results are summarized in Table 6.8. As can be seen, the impact of the interfacial area and the enhancement factor are as high as 26.1% and 20.4%, respectively. On the other hand, the impact of the physical mass transfer coefficients is rather small while that of Henry's constant, $H$, is moderate.

To identify whether reaction in the liquid phase is fast or slow, Levenspiel [30, 141] suggested that a measurement of the so-called film conversion parameter be used:

\[
M = \frac{\text{maximum possible conversion in liquid film}}{\text{maximum diffusion transport through the film}}
\]

\[
= \frac{(k_2 C_{A,i} C^*_B \delta)/(D_A/\delta) C_{A,i}}{k_2 C^*_B D_A/(k_L^0)^2}
\]
If the value of $M$ is much greater than 1, all reaction occurs in the liquid film, and effective contacting area is the controlling rate. On the other hand, no reaction takes place in the film, and bulk volume of the liquid phase becomes the controlling factor when $M \ll 1$. In the case of Run T9 as well as other runs, the values of $M$ along the column are well over 100. It is not surprising that the effects of the interfacial area and the enhancement factor on the height prediction are therefore very high.
Table 6.8: Effects of major parameters on the height prediction for Run T9 (NaOH-CO₂). Operating Conditions: gas rate = 1545 kg/m² h; liquid rate = 13.5 m³/m² h; NaOH conc. = 0.413 to 2.0 kmol/m³; CO₂ conc. = 1.0 to 18.45 %; Column temperature = 15.0 to 35.0 °C

The normal predicted height = 4.40 m

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Predicted height</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_G + 20%</td>
<td>4.28 m</td>
<td>2.7 %</td>
</tr>
<tr>
<td>- 20%</td>
<td>4.69 m</td>
<td>6.4 %</td>
</tr>
<tr>
<td>k_L° + 20%</td>
<td>4.36 m</td>
<td>0.9 %</td>
</tr>
<tr>
<td>- 20%</td>
<td>4.56 m</td>
<td>3.6 %</td>
</tr>
<tr>
<td>a_V + 20%</td>
<td>3.70 m</td>
<td>15.9 %</td>
</tr>
<tr>
<td>- 20%</td>
<td>5.55 m</td>
<td>26.1 %</td>
</tr>
<tr>
<td>H + 20%</td>
<td>3.94 m</td>
<td>10.4 %</td>
</tr>
<tr>
<td>- 20%</td>
<td>5.19 m</td>
<td>17.9 %</td>
</tr>
<tr>
<td>I + 20%</td>
<td>3.86 m</td>
<td>12.3 %</td>
</tr>
<tr>
<td>- 20%</td>
<td>5.30 m</td>
<td>20.4 %</td>
</tr>
</tbody>
</table>
CHAPTER 7

RESULTS AND DISCUSSIONS: COMPARISON BETWEEN FULL-LENGTH ABSORBER PERFORMANCE AND PREDICTIONS BASED ON PPT

The objective of this chapter is to test and verify the results of the PPT design procedure proposed in Chapter 3. The validation is based on using $R_V$-concentration diagrams and a PPT short-cut procedure.

7.1 VERIFICATION USING $R_V$-CONCENTRATION DIAGRAM

The absorption of CO$_2$ into NaOH solutions was used to demonstrate the performance of PPT. The temperature changes in the PPM and full-length columns were within ±3 and ±8 °C, respectively. These changes are sufficiently small to assume that both columns operated isothermally.

Figure 7.1 shows a typical plot of $Y_{CO2}$ vs $Z$. The data points vary systematically and do not fall on a straight line even for this short PPM column. This implies that the overall mass transfer coefficient was not constant and demonstrates the importance of measuring the concentration profiles rather than just the terminal conditions. As discussed in Section 6.2.2, the value of the enhancement
Figure 7.1: A typical plot of CO$_2$ mole ratio in the gas phase as a function of height in the PPM column, Run S5. Points denote experimental data and the solid line indicates the best fit using a third order polynomial equation. (Experimental conditions: Liquid flow rate = 13.5 m$^3$/m$^2$ hr; air flow rate = 14.8 mol/m$^2$ s; temperature = 293 K; total pressure = 101.3 kPa; [Na$^+$] = 1.20 kmol/m$^3$; [OH$^-$] = 0.75 to 0.56 kmol/m$^3$; CO$_2$ concentration = 4.1 to 2.0%).
factor can change by as much as a factor of 2 over the column height.

For each experimental run with the PPM column, the concentration measurements were fitted by means of a third order polynomial equation. The correlation coefficients for the fits generally exceeded 0.99. The polynomials were then differentiated analytically. The values of \( R_v \) were obtained from the product of the differentiated results and \( G_I \) (also see Equation 3.2.14).

In the case of the CO\(_2\)-NaOH system, all fundamental parameters are known and \( R_v \), which is the product of \( R_a \) and \( a_v \), could also be calculated based on first principles as described previously in Chapter 2. The deviations between the experimental and calculated \( R_v \) values were, on the average, 5.5\% (maximum 12\%) and due to experimental and numerical uncertainties. The fundamental parameters required in these calculations are taken from the same sources as the computer model (also see Section 6.2.1). The quality of the agreement is good as shown by Figure 7.2 because: (i) the CO\(_2\)-NaOH system has been studied extensively and its kinetics model is well understood, (ii) the reaction is simple and irreversible, which improves the accuracy of the
Figure 7.2: Comparison of $R_v$ values obtained experimentally from model column tests and from first principles. (Experimental conditions: Liquid flow rate = 13.5 m$^3$/m$^2$ hr; air flow rate = 14.8 mol/m$^2$ s; temperature = 293 K; total pressure = 101.3 kPa; [Na$^+$] = 1.20 kmol/m$^3$.)
enhancement factor calculation, and (iii) almost all $k_L^0$, $k_G$ and $a_v$ values, which are reported in the literature, have been derived for the CO$_2$-NaOH system.

The $R_v$-concentration diagram is presented in Figure 7.3. The diagram shows the relationship between the specific absorption rate and the fluid compositions. The continuous lines show the calculated values of $R_v$ for different fluid compositions. As can be seen, the computed $R_v$ values agree very well with the experimental results, showing that it is possible to design packed absorbers with chemical reaction based on first principles provided that the fundamental data (mass transfer coefficients, physico-chemical properties, etc.) are reliably known.

The $R_v$ values obtained from model column tests can then be used to evaluate the integral in Equation 3.2.11 using either graphical or numerical methods. In order to perform this integration, the $R_v$ must be available as a function of fluid compositions or in the from of $R_v$-concentration diagrams such as shown in Figure 7.3. In the present case, 56 data points from 14 PPM column runs were entered into a data base. The $R_v$ values corresponding to any desired pair of gas and liquid concentrations were retrieved from the
Figure 7.3: Specific absorption rate ($R_v$) as a function of CO$_2$ concentration in the gas phase and OH$^-$ concentration. The points and solid lines are obtained from experiments and theoretical calculations, respectively. The dotted line denotes typical $R_v$ values along the column for Run T2. (Experimental conditions: Liquid flow rate $= 13.5$ m$^3$/m$^2$/hr; air flow rate $= 14.8$ mol/m$^2$/s; temperature $= 293$ K; total pressure $= 101.3$ kPa; [Na$^+$] $= 1.20$ kmol/m$^3$.)
data base by using an interpolation package called DFIN3D, which is based on a weighted least squares interpolation method and which is available from the University of British Columbia Computing Centre.

The dotted line in Figure 7.3 shows typical $R_v$ values along the full-length column for Run T2. As can be seen, the specific absorption rate changes significantly along the absorber due to the variations of the fluid concentrations.

The results of six experimental runs conducted with the full-length column for a variety of CO$_2$ and hydroxide concentrations are shown in Table 7.1. The difference between the actual and predicted heights is always less than 8% thereby providing strong support for the validity of the PPT. The good agreement could be expected because: (i) the hydrodynamics of the full-length and model columns were the same and (ii) the effect of concentration on the specific absorption rate and enhancement factor was fully taken into account. Figure 7.4 also shows excellent agreement between predicted (solid lines which are from the integration of Equation 3.2.11) and experimental values (points) when the model results are used to predict the concentration profiles in the full-length column.
Table 7.1: Actual and predicted heights for the absorption tower removing CO₂ from air by contact with an aqueous NaOH solution.

(Experimental conditions: Liquid flow rate = 13.5 m³/m² hr; air flow rate = 14.8 mol/m² s; temperature = 293 K; total pressure = 101.3 kPa; [Na⁺] = 1.20 kmol/m³.)

<table>
<thead>
<tr>
<th>Run</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH⁻] Conc.</td>
</tr>
<tr>
<td>#</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>T1</td>
</tr>
<tr>
<td>T2</td>
</tr>
<tr>
<td>T3</td>
</tr>
<tr>
<td>T4</td>
</tr>
<tr>
<td>T5</td>
</tr>
<tr>
<td>T6</td>
</tr>
</tbody>
</table>

For the details of the full-length column profiles, see Table 6.1.
Figure 7.4: Actual (points) and predicted (solid lines) of CO$_2$ and NaOH concentrations in the full-scale absorber for Run T2. (Experimental conditions: Liquid flow rate = 13.5 m$^3$/m$^2$ hr; air flow rate = 14.8 mol/m$^2$ s; temperature = 293 K; total pressure = 101.3 kPa; [Na$^+$] = 1.20 kmol/m$^3$.)
7.2 VERIFICATION USING THE PPT SHORT-CUT PROCEDURE

As can be seen from Figure 7.3, only the $R_v$ values that correspond to the concentrations along the column for a given set of operating conditions are really needed. When the gas and liquid flow rates are changed, the $R_v$-concentration diagram must be constructed as a function of the fluid flow rate as well. In doing this, it is necessary to perform a large number of experiments with the PPM column. Therefore, using the PPT short-cut procedure as explained in Section 3.2.2 would be practical under such circumstances. The approximation of adiabatic operation would also be more realistic since there is very little heat exchange between the column and surroundings [54, 105]. To ensure adiabatic condition, the column was insulated with 3/4" fiber glass. The $R_v$ values thus depend on the fluid concentrations and the temperature. The verification was performed using NaOH-CO$_2$ and AMP-CO$_2$ systems operated under a variety of fluid concentrations.

7.2.1 NaOH-CO$_2$ SYSTEM

Originally it had been intended to use the CO$_2$-MEA system for the short-cut verification. However, the absorption of CO$_2$ into highly concentrated (2.0 - 2.5 M)
NaOH solutions was selected instead, since exploratory experiments showed that both have similar absorption-reaction characteristics (see Chapter 6 and Figure 6.6). The reasons for favoring the CO₂-NaOH system were that it takes less time and resources to run experiments and the analysis of the liquid sample is more direct and reliable.

The results of 4 sets of experiments (4 full-length runs and 16 section runs using the model column) are shown in Table 7.2. Due to the fact that highly concentrated NaOH solutions were used and high conversion (up to more than 90%) occurred, the temperature increases in the full-length absorber ranged from 14 up to 42 °C. To verify the ability of the PPT to design full-length absorbers operating under non-isothermal conditions, experiments were performed with the PPM column by matching the fluid concentrations as well as temperatures section by section starting from the top of the absorber (also see section 3.2.2). As can be noted from Table 7.2, the differences between the actual and predicted heights are always less than 7%. Figures 7.5 to 7.8 also show good agreement between experimental measurements and PPT predicted results for the concentration profile along the full-length columns.
Table 7.2: Verification results for the PPT short-cut procedure using the NaOH-CO₂ system.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T7</th>
<th>T8</th>
<th>T9</th>
<th>T10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid flow rate (m³/m² h)</td>
<td>9.5</td>
<td>9.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Gas flow rate (mol/m² s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>[Na⁺] total conc. (kmol/m³)</td>
<td>2.0</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>[OH⁻] conc.</td>
<td>in 2.00</td>
<td>2.50</td>
<td>2.00</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>out 0.09</td>
<td>0.18</td>
<td>0.37</td>
<td>0.24</td>
</tr>
<tr>
<td>CO₂ conc. (%)</td>
<td>in 15.45</td>
<td>18.60</td>
<td>18.45</td>
<td>15.20</td>
</tr>
<tr>
<td></td>
<td>out 1.25</td>
<td>1.70</td>
<td>1.00</td>
<td>1.75</td>
</tr>
<tr>
<td>Liquid temp. (°C)</td>
<td>in 14.5</td>
<td>14.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>out 37.0</td>
<td>42.0</td>
<td>35.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Mass Balance Error (%)</td>
<td>-1.79</td>
<td>-2.23</td>
<td>-5.69</td>
<td>+1.51</td>
</tr>
<tr>
<td>Actual height (m)</td>
<td>4.35</td>
<td>4.35</td>
<td>4.35</td>
<td>4.35</td>
</tr>
<tr>
<td>PPT predicted height (m)</td>
<td>4.40</td>
<td>4.53</td>
<td>4.65</td>
<td>4.62</td>
</tr>
<tr>
<td>Error (%)</td>
<td>1.2</td>
<td>4.1</td>
<td>6.9</td>
<td>6.2</td>
</tr>
</tbody>
</table>

For details of the column profiles, see Table 6.1.
However, the temperature measurements predicted by the short-cut procedure using the model column were a little lower (2 to 5 °C) than the actual measurements as shown by Figures 7.9 to 7.12. The reason for this may be that unsaturated air was used as the inert gas. As a result, water vaporization occurred and consumed some heat which caused the temperature measured by the PPT short-cut procedure to be lower than the actual values. Since the reaction rate is an increasing function of temperature, the reduced temperatures resulted in lower enhancement factors and specific absorption rates. To confirm the effect of temperature, the computer model described in Chapter 6 was forced to lower the liquid temperature by 3 °C. The predicted absorber height was found to be 4.52 m compared with 4.39 m under the normal condition. The difference between the two is approximately 3%. For this reason, the PPT predicted heights shown in Table 7.2 are up to about 7% greater than the actual heights. Deviations of 7% in the prediction of column heights are however very small compared with industrial design approaches that utilize safety factor of 1.5 to 2.5 (50% to 150%).
Figure 7.5: Actual (points) and PPT predicted values of CO$_2$ (solid line) and NaOH (dotted line) concentrations in the full-scale absorber for Run T7. Operating conditions: air flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; CO$_2$ concentration = 1.25%(top) and 15.45%(bottom); [OH$^-$] = 2.0(top) and 0.14(bottom) kmol/m$^3$. 
Figure 7.6: Actual (points) and PPT predicted values of CO$_2$ (solid line) and NaOH (dotted line) concentrations in the full-scale absorber for Run T8. Operating conditions: air flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; CO$_2$ concentration = 1.7% (top) and 18.6% (bottom); [OH$^-$] = 2.5 (top) and 0.18 (bottom) kmol/m$^3$. 
Figure 7.7: Actual (points) and PPT predicted values of CO$_2$ (solid line) and NaOH (dotted line) concentrations in the full-scale absorber for Run T9. Operating conditions: air flow rate = 14.8 mol/m$^2$s; liquid flow rate = 13.5 m$^3$/m$^2$ hr; CO$_2$ concentration = 1.0% (top) and 18.45% (bottom); [OH$^-$] = 2.0 (top) and 0.37 (bottom) kmol/m$^3$. 
Figure 7.8: Actual (points) and PPT predicted values of CO$_2$ (solid line) and NaOH (dotted line) concentrations in the full-scale absorber for Run T10. Operating conditions: air flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 13.5 m$^3$/m$^2$ hr; CO$_2$ concentration = 1.75% (top) and 15.2% (bottom); [OH$^-$] = 1.5 (top) and 0.24 (bottom) kmol/m$^3$. 
Figure 7.9: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T7. Operating conditions: air flow rate = 14.8 mol/m²s; liquid flow rate = 9.5 m³/m² hr; CO₂ concentration = 1.25% (top) and 15.45% (bottom); [OH⁻] = 2.0 (top) and 0.14 (bottom) kmol/m³.
Figure 7.10: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T8. Operating conditions: air flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; CO$_2$ concentration = 1.7% (top) and 18.6% (bottom); [OH$^-$] = 2.5 (top) and 0.18 (bottom) kmol/m$^3$. 
Figure 7.11: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T9. Operating conditions: air flow rate = 14.8 mol/m² s; liquid flow rate = 13.5 m³/m² hr; CO₂ concentration = 1.0%(top) and 18.45%(bottom); [OH⁻] = 2.0(top) and 0.37(bottom) kmol/m³.
Figure 7.12: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T10. Operating conditions: air flow rate = 14.8 mol/m² s; liquid flow rate = 13.5 m³/m² hr; CO₂ concentration = 1.75% (top) and 15.2% (bottom); [OH⁻] = 1.5 (top) and 0.24 (bottom) kmol/m³.
7.2.2 CO₂-AMP SYSTEM

Further verification of the PPT is performed using the absorption of CO₂ by 2 M AMP solutions. The verification procedure for this system is the same as that used for the NaOH-CO₂ system described in the previous section. However, before dealing with the verification it is necessary to make some general observations.

GENERAL OBSERVATIONS

Since no comprehensive experimental data have been reported regarding columns using the CO₂-AMP system, the temperature and composition profiles along the full-length absorber are presented, for the first time, in Table 7.3. Since the experimental data for CO₂ absorption into the solution of MEA in the same packed column are available, the column performance is therefore compared by plotting the CO₂ concentration profile along the column height as shown in Figures 7.13 and 7.14. It is interesting to see that the absorption rate using MEA is much higher than for AMP when the loading is below approximately 0.5 moles of CO₂ per mole of amine as shown in Figure 7.13 (Runs T21 and T27). This may be due largely to the fact that the reaction rate of CO₂-AMP system is slower than that of CO₂-MEA [72, 145].
Table 7.3:
Experimental results for the CO$_2$-AMP system.

<table>
<thead>
<tr>
<th>Run (#)</th>
<th>T23</th>
<th>T24</th>
<th>T25</th>
<th>T26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Flow Rate (mol/m$^2$ s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>Liquid Flow Rate (m$^3$/m$^2$ h)</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Absorbent Feed Conc. (kmol/m$^3$)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Gas CO$_2$ Conc. (%) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>6.80</td>
<td>8.90</td>
<td>10.10</td>
<td>7.70</td>
</tr>
<tr>
<td>1.05 m</td>
<td>8.60</td>
<td>10.50</td>
<td>11.80</td>
<td>9.55</td>
</tr>
<tr>
<td>2.15 m</td>
<td>10.70</td>
<td>12.20</td>
<td>13.40</td>
<td>11.55</td>
</tr>
<tr>
<td>3.25 m</td>
<td>13.30</td>
<td>13.85</td>
<td>15.15</td>
<td>13.70</td>
</tr>
<tr>
<td>4.35 m</td>
<td>15.25</td>
<td>15.45</td>
<td>16.70</td>
<td>15.70</td>
</tr>
<tr>
<td>5.45 m</td>
<td>-.-</td>
<td>-.-</td>
<td>17.80</td>
<td>17.35</td>
</tr>
<tr>
<td>6.55 m</td>
<td>-.-</td>
<td>-.-</td>
<td>18.90</td>
<td>18.65</td>
</tr>
<tr>
<td>CO$_2$ removal (%)</td>
<td>60.4</td>
<td>46.6</td>
<td>51.8</td>
<td>63.6</td>
</tr>
<tr>
<td>CO$_2$ loading (mol CO$_2$/mol AMP) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>0.000</td>
<td>0.147</td>
<td>0.152</td>
<td>0.022</td>
</tr>
<tr>
<td>1.05 m</td>
<td>0.058</td>
<td>0.202</td>
<td>0.215</td>
<td>0.083</td>
</tr>
<tr>
<td>2.15 m</td>
<td>0.131</td>
<td>0.258</td>
<td>0.277</td>
<td>0.149</td>
</tr>
<tr>
<td>3.25 m</td>
<td>0.212</td>
<td>0.317</td>
<td>0.341</td>
<td>0.223</td>
</tr>
<tr>
<td>4.35 m</td>
<td>0.285</td>
<td>0.387</td>
<td>0.396</td>
<td>0.303</td>
</tr>
<tr>
<td>5.45 m</td>
<td>-.-</td>
<td>-.-</td>
<td>0.442</td>
<td>0.358</td>
</tr>
<tr>
<td>6.55 m</td>
<td>-.-</td>
<td>-.-</td>
<td>0.464</td>
<td>0.411</td>
</tr>
<tr>
<td>Mass balance error (%)</td>
<td>-4.24</td>
<td>+1.52</td>
<td>-7.53</td>
<td>-4.31</td>
</tr>
<tr>
<td>Liq. Temp (°C) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>16.0</td>
<td>17.0</td>
<td>17.0</td>
<td>17.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>17.0</td>
<td>19.0</td>
<td>18.0</td>
<td>20.0</td>
</tr>
<tr>
<td>3.25 m</td>
<td>19.0</td>
<td>21.0</td>
<td>21.0</td>
<td>23.0</td>
</tr>
<tr>
<td>4.35 m</td>
<td>23.0</td>
<td>21.0</td>
<td>23.0</td>
<td>26.5</td>
</tr>
<tr>
<td>5.45 m</td>
<td>-.-</td>
<td>-.-</td>
<td>24.5</td>
<td>28.0</td>
</tr>
<tr>
<td>6.55 m</td>
<td>-.-</td>
<td>-.-</td>
<td>24.5</td>
<td>29.0</td>
</tr>
</tbody>
</table>

Note: The values in ( ) are calculated from mass balance.
Table 7.3 (cont): Experimental results for the CO2-AMP system.

<table>
<thead>
<tr>
<th>Run (#)</th>
<th>T27</th>
<th>T28</th>
<th>T29</th>
<th>T30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Flow Rate ( \text{mol/m}^2 \text{s} )</td>
<td>11.1</td>
<td>14.8</td>
<td>14.8</td>
<td>11.1</td>
</tr>
<tr>
<td>Liquid Flow Rate ( \text{m}^3/\text{m}^2 \text{h} )</td>
<td>9.5</td>
<td>9.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Absorbent Feed Conc. ( \text{kmol/m}^3 )</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Gas CO\textsubscript{2} Conc. (%) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>4.25</td>
<td>13.25</td>
<td>5.95</td>
<td>2.65</td>
</tr>
<tr>
<td>1.05 m</td>
<td>6.15</td>
<td>14.55</td>
<td>7.65</td>
<td>4.00</td>
</tr>
<tr>
<td>2.15 m</td>
<td>8.40</td>
<td>15.65</td>
<td>9.50</td>
<td>6.00</td>
</tr>
<tr>
<td>3.25 m</td>
<td>11.20</td>
<td>16.75</td>
<td>11.70</td>
<td>8.70</td>
</tr>
<tr>
<td>4.35 m</td>
<td>14.15</td>
<td>17.75</td>
<td>14.70</td>
<td>12.25</td>
</tr>
<tr>
<td>5.45 m</td>
<td>16.95</td>
<td>18.40</td>
<td>17.05</td>
<td>15.85</td>
</tr>
<tr>
<td>6.55 m</td>
<td>19.00</td>
<td>19.15</td>
<td>19.00</td>
<td>19.00</td>
</tr>
<tr>
<td>CO\textsubscript{2} removal (%)</td>
<td>81.1</td>
<td>35.5</td>
<td>73.0</td>
<td>88.4</td>
</tr>
<tr>
<td>CO\textsubscript{2} loading ( \text{mol CO}_2/\text{mol AMP} ) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>0.021</td>
<td>0.371</td>
<td>0.038</td>
<td>0.029</td>
</tr>
<tr>
<td>1.05 m</td>
<td>0.058</td>
<td>0.417</td>
<td>(0.079)</td>
<td>0.045</td>
</tr>
<tr>
<td>2.15 m</td>
<td>0.113</td>
<td>0.449</td>
<td>(0.119)</td>
<td>0.078</td>
</tr>
<tr>
<td>3.25 m</td>
<td>0.174</td>
<td>0.484</td>
<td>(0.173)</td>
<td>0.122</td>
</tr>
<tr>
<td>4.35 m</td>
<td>0.254</td>
<td>0.536</td>
<td>(0.251)</td>
<td>0.182</td>
</tr>
<tr>
<td>5.45 m</td>
<td>0.323</td>
<td>0.550</td>
<td>(0.316)</td>
<td>0.233</td>
</tr>
<tr>
<td>6.55 m</td>
<td>0.383</td>
<td>0.583</td>
<td>0.385</td>
<td>0.300</td>
</tr>
<tr>
<td>Mass balance error (%)</td>
<td>-9.31</td>
<td>-9.67</td>
<td>+3.61</td>
<td>-11.60</td>
</tr>
<tr>
<td>Lig. Temp ( ^\circ \text{C} ) @height from top:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00 m</td>
<td>15.0</td>
<td>15.0</td>
<td>14.0</td>
<td>15.0</td>
</tr>
<tr>
<td>1.05 m</td>
<td>16.5</td>
<td>16.0</td>
<td>16.0</td>
<td>16.0</td>
</tr>
<tr>
<td>2.15 m</td>
<td>19.0</td>
<td>18.0</td>
<td>18.0</td>
<td>17.0</td>
</tr>
<tr>
<td>3.25 m</td>
<td>21.0</td>
<td>19.0</td>
<td>20.0</td>
<td>19.0</td>
</tr>
<tr>
<td>4.35 m</td>
<td>24.5</td>
<td>20.0</td>
<td>22.5</td>
<td>21.0</td>
</tr>
<tr>
<td>5.45 m</td>
<td>26.0</td>
<td>21.0</td>
<td>24.0</td>
<td>23.0</td>
</tr>
<tr>
<td>6.55 m</td>
<td>28.0</td>
<td>21.0</td>
<td>26.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Note: The values in ( ) are calculated from mass balance.
Figure 7.13: Column performance at low loading. MEA (Run T21 - open squares) vs AMP (Run T27 - solid circles). Operating conditions: gas flow rate = 11.1 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total amine concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.0%; inlet CO₂ loading = 0.02 moles of CO₂ / mole of amine.
Figure 7.14: Column performance at high loading. AMP (Run T28 - solid circles) vs MEA (Run T18 - open squares). Operating conditions: gas flow rate = 14.8 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total amine concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.15%; outlet CO₂ loading = 0.583 moles of CO₂ / mole of amine. The lines represent smoothed experimental values.
On the other hand, the opposite is true and a cross-over can be seen when the loading exceeds 0.5 moles of CO$_2$ per mole of amine as shown in Figure 7.14 (Run T18 vs T28). The reason for this is that when the loading is larger than 0.5 moles of CO$_2$ per mole of amine, the free amine concentration in MEA solutions is virtually nil. By contrast, the free amine concentration in AMP solutions for the same situation is approximately half of the total amine concentration due to the hindered effect which causes instability for the AMP carbamate. As a result, the carbamate is easily reversed to free AMP (also see Sections 2.2 and 4.3). It should be noted that the solid lines in Figures 7.13 and 7.14 are drawn from smoothed values of the corresponding data.

After the AMP solution had been used for approximately 8 runs, a tendency to flood did occur due to foaming problems although the absorber was designed and operated below the flooding velocity. The problem is believed to be caused by the foaming nature of the solution, which was further aggravated by fine particulate matter from the packing and the air. It was also noticed that flooding was more serious in the absorber than in the regenerator. The problem was reduced completely by addition of a few ppm of the antifoaming agent, Antifoam B (trade name) manufactured by Dow Corning Corp. and marketed in Canada by BDH Inc. of Toronto, Ont. In spite of the addition of the antifoaming
agent, the problem would reappear after solution regeneration. The flooding reappearance may be due to the evaporation and/or degradation of the antifoaming agent caused by the high temperature in the reboiler. 5 to 10 ppm of the antifoaming agent were therefore typically added to the solution after each regeneration run. To ensure that there is no significant effect of the antifoam on the overall absorption, comparison runs were performed as shown in Figure 7.15. The solution used for run S70 contained no antifoam agent. On the other hand, run S94 was conducted with antifoam added and had been used for more than 40 absorption and regeneration experiments. Both runs, S70 and S94, were performed under the same conditions. Figure 7.15 shows that the CO$_2$ concentration profile from both runs are virtually identical.

**Comparison Results**

The results of 6 experimental runs predicted by the short-cut procedure using 24 PPM column runs are summarized in Table 7.4. As can be seen from Table 7.4, good agreement was obtained. The difference between the actual and PPT predicted results was always less than 12%. Slightly less accurate results were obtained with the CO$_2$-AMP system than
Figure 7.15: CO$_2$ concentration profile of Run #S70 \textit{without} antifoaming agent (open circles) and Run #S94 \textit{with} antifoaming agent (stars). Operating conditions: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; total amine concentration = 2.0 kmol/m$^2$. 
Table 7.4: Verification results for the PPT short-cut procedure using the AMP-CO$_2$ system.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T23</th>
<th>T24</th>
<th>T25</th>
<th>T26</th>
<th>T27</th>
<th>T30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid flow rate (m$^3$/m$^2$ h)</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Gas flow rate (mol/m$^2$ s)</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>11.1</td>
<td>11.1</td>
</tr>
<tr>
<td>Total conc. of AMP (kmol/m$^3$)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>CO$_2$ loading in (mol CO$_2$/mol CO$_2$)</td>
<td>0.000</td>
<td>0.147</td>
<td>0.152</td>
<td>0.022</td>
<td>0.021</td>
<td>0.29</td>
</tr>
<tr>
<td>CO$_2$ loading out (mol CO$_2$/mol CO$_2$)</td>
<td>0.285</td>
<td>0.387</td>
<td>0.464</td>
<td>0.411</td>
<td>0.383</td>
<td>0.300</td>
</tr>
<tr>
<td>CO$_2$ conc. in (%)</td>
<td>15.25</td>
<td>15.45</td>
<td>18.90</td>
<td>18.65</td>
<td>19.00</td>
<td>19.00</td>
</tr>
<tr>
<td>CO$_2$ conc. out (%)</td>
<td>6.80</td>
<td>8.90</td>
<td>10.10</td>
<td>7.70</td>
<td>4.25</td>
<td>2.65</td>
</tr>
<tr>
<td>Liquid temp. in (°C)</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Liquid temp. out (°C)</td>
<td>23.0</td>
<td>21.0</td>
<td>24.0</td>
<td>29.0</td>
<td>28.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Mass Balance Error (%)</td>
<td>-4.24</td>
<td>+1.52</td>
<td>-7.53</td>
<td>-4.31</td>
<td>-9.31</td>
<td>-11.6</td>
</tr>
<tr>
<td>Actual height (m)</td>
<td>4.35</td>
<td>4.35</td>
<td>6.55</td>
<td>6.55</td>
<td>6.55</td>
<td>6.55</td>
</tr>
<tr>
<td>PPT predicted height (m)</td>
<td>4.85</td>
<td>4.75</td>
<td>6.37</td>
<td>6.15</td>
<td>6.68</td>
<td>6.88</td>
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<tr>
<td>Error (%)</td>
<td>11.5</td>
<td>9.0</td>
<td>2.7</td>
<td>6.1</td>
<td>2.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

For more details on the column profiles, see Table 7.3.
the CO$_2$-NaOH system. The reason for this may be due to the fact that the analysis of liquid samples for the former system is indirect and therefore less precise than that for the latter. For a given sample size and concentration, the accuracy of composition analysis of Na$^+$ and OH$^-$ is within $\pm$ 2 % as compared with $\pm$ 3.3 % for the CO$_2$ loading in the AMP solution (also see Appendix A). Since the values of $R_v$ could be affected by the fluid composition, the uncertainty involved in predicting the column height in this case is larger than that for the CO$_2$-NaOH system. By comparison with industrial design practice which typically allows for safety factors of 1.5 to 2.5 (50 to 150%), the 12 % accuracy for the PPT predictions is very good.

Figures 7.16 to 7.27 also show good agreement between the experimental and PPT results for the column profiles. It should be noted that the precise prediction of the overall absorption rate in, or the performance of, the column using the AMP-CO$_2$ system based on first principles is practically impossible because the reaction mechanism involved is not well understood and insufficient fundamental data regarding its physico-chemical properties have been reported.
Figure 7.16: Actual (points) and predicted values of CO₂ (solid line) and liquid loading (dotted line) in the full-scale absorber for Run T23. Operating conditions: gas flow rate = 14.8 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 15.5%; inlet liquid loading = 0 mol CO₂/mol AMP.
Figure 7.17: Actual (points) and predicted values of CO₂ (solid line) and liquid loading (dotted line) in the full-scale absorber for Run T24. Operating conditions: gas flow rate $= 14.8$ mol/m² s; liquid flow rate $= 9.5$ m³/m² hr; total AMP concentration $= 2.0$ kmol/m²; inlet gas CO₂ concentration $= 15.5\%$; inlet liquid loading $= 0.147$ mol CO₂/mol AMP.
Figure 7.18: Actual (points) and predicted values of CO\textsubscript{2} (solid line) and liquid loading (dotted line) in the full-scale absorber for Run T25. Operating conditions: gas flow rate = 14.8 mol/m\textsuperscript{2} s; liquid flow rate = 9.5 m\textsuperscript{3}/m\textsuperscript{2} hr; total AMP concentration = 2.0 kmol/m\textsuperscript{2}; inlet-gas CO\textsubscript{2} concentration = 18.9%; inlet liquid loading = 0.152 mol CO\textsubscript{2}/mol AMP.
Figure 7.19: Actual (points) and predicted values of CO$_2$ (solid line) and liquid loading (dotted line) in the full-scale absorber for Run T26. Operating conditions: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; total AMP concentration = 2.0 kmol/m$^2$; inlet gas CO$_2$ concentration = 18.65%; inlet liquid loading = 0.022 mol CO$_2$/mol AMP.
Figure 7.20: Actual (points) and predicted values of CO$_2$ (solid line) and liquid loading (dotted line) in the full-scale absorber for Run T27. Operating conditions: gas flow rate = 11.1 mol/m$^2$/s; liquid flow rate = 9.5 m$^3$/m$^2$/hr; total AMP concentration = 2.0 kmol/m$^2$; inlet gas CO$_2$ concentration = 19.0%; inlet liquid loading = 0.021 mol CO$_2$/mol AMP.
Figure 7.21: Actual (points) and predicted values of CO₂ (solid line) and liquid loading (dotted line) in the full-scale absorber for Run T30. Operating conditions: gas flow rate = 11.1 mol/m² s; liquid flow rate = 13.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.0%; inlet liquid loading = 0.29 mol CO₂/mol AMP.
Figure 7.22: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T23. Operating conditions: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; total AMP concentration = 2.0 kmol/m$^2$; inlet gas CO$_2$ concentration = 15.5%; inlet liquid loading = 0 mol CO$_2$/mol AMP.
Figure 7.23: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T24. Operating conditions: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate = 9.5 m$^3$/m$^2$ hr; total AMP concentration = 2.0 kmol/m$^2$; inlet gas CO$_2$ concentration = 15.5%; inlet liquid loading = 0.147 mol CO$_2$/mol AMP.
Figure 7.24: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T25. Operating conditions: gas flow rate = 14.8 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 18.9%; inlet liquid loading = 0.152 mol CO₂/mol AMP.
Figure 7.25: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T26. Operating conditions: gas flow rate = 14.8 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 18.65%; inlet liquid loading = 0.022 mol CO₂/mol AMP.
Figure 7.26: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T27. Operating conditions: gas flow rate = 11.1 mol/m² s; liquid flow rate = 9.5 m³/m² hr; total AMP concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.0%; inlet liquid loading = 0.021 mol CO₂/mol AMP.
Figure 7.27: Column temperature measured from the full-length column (solid circles) and PPM column (open squares) for Run T30. Operating conditions: gas flow rate = 11.1 mol/m$^2$ s; liquid flow rate = 13.5 m$^3$/m$^2$ hr; total AMP concentration = 2.0 kmol/m$^2$; inlet gas CO$_2$ concentration = 19.0%; inlet liquid loading = 0.29 mol CO$_2$/mol AMP.
7.3 DISCUSSION OF THE VERIFICATION RESULTS

The validity of the PPT design procedure has been tested under a variety of operating conditions with two distinct systems: the CO₂-NaOH system which is well known and the CO₂-AMP system which is new. As can be seen from Tables 7.1-7.2 and 7.4, the maximum difference between the actual and predicted heights is always less than ±12% for both systems. From these results, it can be concluded that the PPT design procedure proposed in Chapter 3 is sound. It must be noted that no assumption has been made regarding the reaction kinetics and mechanism. Therefore, the PPT can be applied to all reaction regimes shown in Figure 2.2 which were suggested by Levenspiel [30, 31]. Furthermore, no assumptions were made regarding the gas-liquid mass transfer mechanism and fluid flow in packings. This means that the influence of the hydrodynamics on the specific absorption rate is fully taken into account in the PPT procedure.

Very recently (May 1990), Bosch et al. [120] have reported a study on the reaction kinetics of CO₂ in aqueous AMP solution. They have suggested that the overall reaction consists of two parallel and highly reversible reactions:

\[ \text{CO}_2 + 2 \text{RNH}_2 = \text{RNHCOO}^- + \text{RNH}_3^+ \quad \text{(g)} \]

and
The hydroxyl ion is derived from AMP:

\[
\text{RNH}_2 + \text{H}_2\text{O} = \text{RNH}_3^+ + \text{OH}^-
\] (i)

If this hypothesis is indeed correct, the evaluation of the enhancement factor would be very complicated. First of all, finding solutions of partial differential equations which represent simultaneous diffusional mass transfer and chemical reaction in the liquid phase is unavoidable. Secondly, the equilibrium and reaction rate constants of both reactions as well as all other physico-chemical parameters must be precisely known. It should be kept in mind that these parameters normally could not be measured directly. Indirect methods, which are usually applied, would increase the uncertainty in parameter estimation.

By applying the PPT method for column design using this system or similar systems, the above-mentioned problems would be eliminated.

To evaluate the uncertainties (errors) associated with \(R_v\) determination based on the theoretical calculations,
laboratory models and the Pilot Plant Technique, an error analysis of the type suggested by Mickly et al.[144] was made. The details of this error analysis are given in Appendix B and the results are summarized in Table B.2.

As can be seen from Appendix B, the potential errors associated with the \( R_v \) determination based on theoretical calculations, laboratory models and the Pilot Plant Technique are in the order of 95%, 40% and 20%, respectively. The uncertainty associated with \( R_v \) values obtained from the theoretical calculation is the largest since they are a function of many parameters including the mass transfer coefficients, interfacial area and the enhancement factor. As mentioned in Chapter 2, the uncertainties associated with their estimation are, in general, in the order of \( \pm 25\% \). By contrast, the accuracy of \( R_v \) determined by the PPT depends only on the measurements of the fluid flow rate and composition profiles. The precise measurement of these two quantities could be achieved with minimum uncertainty using the currently available instruments.

If we use the operating conditions of Run T9 to illustrate the effect of uncertainty associated with \( R_v \) values on the height prediction, the results can be seen in
Table 7.5. The predicted height is varied from 4.65 to 2.32 m when the error related to $R_v$ is increased to about 100%.

Table 7.5 also shows the ratio of the height predicted with a given uncertainty to that under normal conditions. This ratio can be considered as a minimum safety factor, $F_s$, required in order to ensure that the designed absorber performs as expected or to avoid the chance of failure. As can be seen, the design based on the PPT approach needs only a factor of 1.2 by comparison with 1.4 for the laboratory models and about 2.0 for the theoretical design approach.

It is thus not surprising that a safety factor of 1.5 to 2.5 is commonly applied in industrial design practice for gas absorbers with chemical reaction. It is also interesting to know that a safety factor of about 1.7 is usually needed for sizing packed distillation towers and physical gas absorbers according to Bolles and Fair [146]. It should be noted that these two are just diffusional mass transfer operations without chemical reaction. When reactions take place in the fluid, the situation becomes more complex and the uncertainty increases considerably. As a result, the required safety factor is higher for the case of gas absorption with chemical reaction.
Table 7.5: Effect of uncertainty associated with $R_v$ on the predicted height using operating conditions of Run T9 (NaOH-CO$_2$). Operating condition: gas flow rate = 14.8 mol/m$^2$ s; liquid flow rate= 9.5 m$^3$/m$^2$ hr; inlet CO$_2$ concentration = 18.4%; inlet [OH$^-$] =2.0 kmol/m$^3$.

<table>
<thead>
<tr>
<th>Uncertainty</th>
<th>Predicted Height</th>
<th>$F_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_v + 0%$</td>
<td>4.65 m</td>
<td>1.0</td>
</tr>
<tr>
<td>$R_v + 20%$</td>
<td>3.87 m</td>
<td>1.2</td>
</tr>
<tr>
<td>$R_v + 40%$</td>
<td>3.32 m</td>
<td>1.4</td>
</tr>
<tr>
<td>$R_v + 80%$</td>
<td>2.58 m</td>
<td>1.8</td>
</tr>
<tr>
<td>$R_v + 100%$</td>
<td>2.32 m</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$F_s$ is defined as the ratio of the height predicted with uncertainty to that at the normal condition. For example, if a given uncertainty associated with $R_v$ is 100% for the case, $F_s$ would be equal to 2.0 (4.65/2.32).
7.4 LIMITATIONS OF PPT

There are practical and fundamental limitations of the PPT. Both types of limitations relate to the ability of measuring the specific absorption rate, $R_v$.

Practical Limitations:

* The PPM column must be constructed of materials compatible with the absorption system and its operating conditions (particularly temperature and pressure).

* The diameter of the PPM column cannot be smaller than 6 to 10 times the diameter of the random packing to ensure that the wall effect is negligible.

* On-line and/or off-line sensors must be available to measure the concentrations in the liquid and gas phases reliably.

* An adequate supply of chemical absorbent and gas mixture must be available; when expensive chemicals are involved, a regenerator may be required.
Fundamental Limitations:

* For the PPM column to represent the conditions in section of the full-scale column, the bulk of the liquid and gas phases must be well mixed. (This condition may not be met for highly viscous liquids).

* For multicomponent systems the number of concentration measurements may become prohibitively large and the interaction between the absorption rates may not be easily determined.

* For multicomponent systems, the inlet and outlet conditions for full-scale industrial columns are not usually given and it is therefore difficult to specify the terminal conditions for the PPM column as well. Iterative procedures may be required to overcome this problem.

* If the axial dispersion in the full-length column is significant, the PPM column has to be designed in such a way that similar dispersion occurs.
The following section discusses various ways in which the PPT concept may be applied in industrial situations.

In general, the size of absorbers used in industry is in the order of a few meters in diameter and several meters in height. The packing size is usually about 37.5 to 62.5 mm (1.5" to 2.5") for random packing. For a specific example, the size of a chemical gas absorber removing CO$_2$ from natural gas at the Rayong Natural Gas Separation Plant (Petroleum Authority of Thailand) is 3.75 m O.D. x 14.0 m in height. The absorber is packed with 50.0 mm Pall rings. If we want to simulate the absorption rate occurring in this column using the Pilot Plant Technique, a PPM column of 0.5 m ID x 1.0 - 2.0 m high could be used. The column of this size is small enough to be handled in laboratory environment and the column is still able to duplicate the hydrodynamic properties of the industrial column. The $R_v$ values would then be measured as functions of the fluid concentrations and used to construct the $R_v$ - concentration diagram like the one in Figure 7.3 for the desired ranges of operating conditions. This diagram could then be employed to predict the absorption capacity of the industrial column by applying the proposed Pilot Plant Technique. Alternatively, the model column can be used to simulate this industrial size column.
section by section using the PPT short-cut procedure. As can be seen from this example, the scaling factor for this case would be in the order of one hundred.

If structured packings are used in industrial absorbers, the PPM column diameter could be reduced to the 0.03 to 0.10 m range and therefore the scaling factor would increase considerably.

The above suggestion can also be used for designing new absorbers. The design steps up to the determination of absorber diameter are already given in Section 2.3. At this point, the following items are selected or determined: packing type and size; column diameter; fluid superficial velocities. The dimensions of the PPM column can then be sized based on proper design criterion given in Table 5.1. This PPM column is then used to obtain the values of $R_v$ for the desired range of fluid compositions, in order to predict the full-scale absorber height.

As discussed previously, the Pilot Plant Technique does not require knowledge of the hydrodynamic and physico-chemical parameters. The PPT method would be suitable for helping design engineers to design new chemical absorbers or process engineers to retrofit the existing columns. This technique should be very useful when it is applied to
systems that use high-efficiency packings and solvents which are favoured by industry. Some of these packings were already shown in Figures 2.11 and 2.12. Some of the high-capacity solvents are listed in Table 7.6. To design and simulate these systems based on first principles would be either too complicated - if indeed possible - or would lead to large errors due to the uncertainty in parameter estimations.

Table 7.6: Some of high-capacity solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sterically hindered amines</td>
<td>[71, 101]</td>
</tr>
<tr>
<td>High concentration alkanolamines</td>
<td>[10, 11]</td>
</tr>
<tr>
<td>Alkanolamines in nonaqueous solvents</td>
<td>[116, 117]</td>
</tr>
<tr>
<td>Alkanolamines in a mixture of nonaqueous and aqueous solvents</td>
<td>[10, 11]</td>
</tr>
<tr>
<td>Mixture of amines</td>
<td>[10, 11]</td>
</tr>
</tbody>
</table>

In some industrial situations, the presence of impurities are unavoidable and can be a major problem. To
quote from Bisio [80], ".... One of the most serious and frustrating problems that can be encountered in a commercial operation is the presence of impurities that were not considered or studied in the smaller scale laboratory or pilot plant studies. ....... Moreover, once a commercial installation has been built without giving adequate consideration to the removal of impurities from process streams, modification can be made only with great difficulty and at significant expense. .... " In gas treating with chemical solvents, a good example is the accumulation of the degradation products in the solution when it has been used for an extended period of time. Recently, Kennard and Meisen [117] and Chakma and Meisen [118] have reported that these degradation compounds could significantly affect both absorption rate and capacity of the solution. To integrate these factors into the procedures for designing new absorbers or simulating existing units based only on first principles would be very complicated, if it is indeed feasible. The PPT method would provide a more realistic way to deal with the above-mentioned problems. By applying the PPT method to these situations, the PPM column must be operated with the solutions containing the same or similar compositions as those in the industrial plants. The effective values of $R_v$ obtained this way can then be used to predict the capacity or height of absorber using such solutions. This is an application of the PPT method that awaits further research.
CHAPTER 8
SUMMARY OF RESULTS AND CONCLUSIONS

The results and principal conclusions drawn from the research studies may be summarized as follows:

**SOLUBILITY OF CO\textsubscript{2} IN AMP SOLUTIONS**

* Significantly extended results from the previous works are reported. These solubility data cover the typical operating ranges of absorbers.

* The modified Kent-Eisenberg model represents the experimental data quite accurately and is well suited for use in the design of regenerative AMP separation processes.

* The solubility of CO\textsubscript{2} in AMP solution was found, by comparison with that of CO\textsubscript{2} in MEA solution, to be higher at low temperatures ( < 60 °C ) and lower at high temperatures ( >60 °C ).
EXPERIMENTAL AND SIMULATION RESULTS OF FULL SCALE ABSORBERS

* Comprehensive pilot plant data including gas and liquid concentrations and temperature profiles along the pilot plant absorber for the CO₂ absorption into NaOH and MEA solutions were reported.

* Good agreement was found between the experimental measurements and model predictions for the CO₂-NaOH and CO₂-MEA systems except at loadings approaching 0.5 moles of CO₂ per mole of MEA.

* Theoretical model verification should be based on concentration and temperature profiles and not just on the conditions at the absorber top and bottom.

* The enhancement factor varies significantly along the absorption column and must be accurately known for reliable modelling.

THE PILOT PLANT TECHNIQUE (PPT)

* A new method, called the "Pilot Plant Technique" has been proposed for sizing gas-absorption towers with chemical reaction. This new design technique does not
require explicit knowledge of hydrodynamics and physico-chemical parameters.

* The results obtained with the CO$_2$-NaOH and CO$_2$-AMP systems show that the PPT can be used for precise sizing of absorbers; the accuracy falls typically within ± 12%.

* Since the accuracy of $R_v$ values obtained from the PPT depends only on the measurements of the fluid flow rates and compositions, the uncertainty associated with its determination is relatively low compared with that obtained from first principles and laboratory models.

* Potentially, the PPT may be applied to other continuous contacting operations involving mass transfer with chemical reaction (e.g. packed bed reactors, extraction columns, reactive distillation columns).

* The primary drawback of the PPT is that the values of $R_v$ must be obtained experimentally in the PPM column which has to be specially constructed and operated.

* The PPT may not be practical for multicomponent systems.
CHAPTER 9
RECOMMENDATIONS FOR FURTHER WORK

SOLUBILITY STUDIES

Considerable work has been done on the CO\textsubscript{2} solubility in aqueous solutions of single amines. However, no substantial work has been reported on CO\textsubscript{2} solubility in mixtures of amines. It would therefore be worthwhile to conduct such experiments since there are some suggestions in the literature that these solutions may have higher absorption capacity as well as mass transfer rate.

COMPUTER MODELLING

As discussed in Chapter 6, the prediction of absorber performance is still not accurate when the liquid loading approaches 0.5 moles of CO\textsubscript{2} per mole of amine. Further experimental and modelling work should be conducted to study these aspects. The physico-chemical properties and reaction kinetics of partially loaded solutions should be further investigated, especially at high loadings (i.e. at 0.4 to 1.0 moles of CO\textsubscript{2} / mole of amine).
THE PILOT PLANT TECHNIQUE

In this thesis, the PPT design approach has been successfully tested with two different systems under a variety of conditions. It would therefore be worthwhile to conduct further tests on the PPT with industrial absorbers and under plant conditions. The ideal situation is to obtain a complete data set of an existing industrial absorber which include the temperature and composition profiles as well as the details of the absorber. The PPT can then be used to predict the tower height or its absorption capacity.

It would also be worthwhile to conduct further tests on the PPT in other industrial situations such as simultaneous absorption of more than one gas species and tray absorption towers.

As discussed earlier, the $R_v$ values can be computed from first principles for well-known systems such as CO$_2$-NaOH. However, for new systems like CO$_2$-AMP, the $R_v$ values can only be obtained experimentally. Fundamentally, experimental values of $R_v$ obtained in the model column could be used for back-calculations in order to estimate the hydrodynamics and physico-chemical parameters, provided the kinetic model of the system is known. Results from some exploratory works have suggested that such parameter
estimation may be feasible [150]. Theoretically, optimization techniques could be employed to determine the set of unknown parameters which would give the minimum error between the computed and experimental absorption rates. In many cases when the rate constant and/or mass transfer coefficients are not known, this technique can be applied to extract the unknown parameters. The parameter estimation approach suggested here may be used for gas absorption with chemical reaction systems involving new packings and/or high-efficiency absorbents.
NOMENCLATURE

\( a_v \)  interfacial area per unit volume of packing, \( m^2/m^3 \)

\( C_f \)  packing factor

\( C_j \)  concentration of component \( j \) in the liquid, \( kmol/m^3 \)

\( C_{P,j} \)  heat capacity of component \( j \) in the gas, \( kJ/kmol \cdot ^\circ K \)

\( C_{P,L} \)  heat capacity of solution, \( kJ/m^3 \cdot ^\circ K \)

\( D_j \)  diffusivity of component \( j \), \( m^2/s \)

\( F_S \)  safety factor (see Table 7.5)

\( G' \)  gas mass velocity, \( kg/m^2.s \)

\( G_I \)  molar gas flow rate of component \( I \), \( kmol/m^2.s \)

\( H \)  Henry's law constant, \( kmol/m^3.kPa \)

\( h_G \)  heat transfer coefficient, \( kJ/s.m^2.\cdot ^\circ K \)

\( H_R \)  heat of absorption and reaction, \( kJ/kmol \)

\( H_S \)  heat of vaporization of solvent \( S \), \( kJ/kmol \)

\( I \)  enhancement factor

\( I_C \)  ionic strength, \( kmol/m^3 \)

\( K \)  equilibrium constant

\( K_G \)  overall gas mass transfer coefficient, \( kmol/m^2.s.kPa \)

\( k_2 \)  reaction rate constant, \( m^3/kmol.s \)

\( k_G \)  physical gas mass transfer coefficient, \( kmol/m^2.s.kPa \)

\( k_L \)  physical liquid mass transfer coefficient, \( m/s \)

\( L \)  liquid flow rate, \( m^3/m^2.s \)

\( L' \)  liquid mass velocity, \( kg/m^2.s \)

\( M \)  film conversion parameter

\( N_j \)  mass transfer flux of component \( j \), \( kmol/m^2.s \)
P  total pressure, kPa
Rₐ  specific rate of absorption per unit interfacial area of packing, kmol/m² s
Rᵥ  specific rate of absorption per unit volume of packing, kmol/m² s
r  rate of reaction in the liquid phase, kmol/m³ s
T  temperature, °K
t  time, s
Yⱼ  mole ratio of component j, kmol j/kmol I
yⱼ  mole fraction of component j, kmol j/mol
Z  packing height, m

Superscripts
*  equilibrium

Subscripts
A  absorbed compound
B  reagent in liquid
G  gas
I  inert carrier gas
i  interface
j  generalized component j
L  liquid
m  model
S  inert liquid solvent
t  total
w  water

**Greek Letters**

\( \nu \)  stoichiometric coefficient

\( \rho \)  density, kg/m\(^3\)

\( \gamma \)  liquid hold-up, m\(^3\) of liquid/m\(^3\) of packing

\( \delta \)  liquid film thickness, mm

\( \mu \)  viscosity, mPa s (centipoise)
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A.1 COMPOSITION DETERMINATION OF CAUSTIC SOLUTION

The following procedure is obtained from Reference [73]. The first titration is to determine the total alkali (carbonate + hydroxide) by titration with standard 1 N HCl, using methyl orange as indicator. In a second sample of the solution, the carbonate is precipitated with a slight excess of barium chloride solution:

\[ \text{Na}_2\text{CO}_3 + \text{BaCl}_2 = \text{BaCO}_3 \text{ (insoluble)} + 2\text{NaCl} \]

The solution is then titrated with standard 1 N HCl using phenolphthalein as indicator. The latter titration gives the hydroxide content, and by subtracting this from the first titration, the volume of acid required for the carbonate is obtained.

Sample Calculation

If the sample size = 5.0 ml and the acid required for the first and second titrations are 10.0 and 5.0 ml, respectively.
Therefore,

\[ [\text{Na}^+] = \text{total alkali} = (10.0/5.0) \times 1.0 = 2.0 \text{ N} \]

\[ [\text{OH}^-] = \text{hydroxide content} = (5./5.) \times 1.0 = 1.0 \text{ N} \]

\[ [\text{CO}_3^{2-}] = \text{carbonate content} = (10.-5.)/(5.x2.) = 0.5 \text{ N} \]

The major contribution to the error is the volume measurement of HCl which is accurate within ± 0.1 ml. Therefore, the uncertainty associated with the determination of \([\text{Na}^+]\) and \([\text{OH}^-]\) is within ± 1.0×10^-4 moles per 5 ml sample (5.0×10^-3 moles). For the above sample calculation, the error in obtaining \([\text{OH}^-]\) is 2.0 %. 
A.2 DETERMINATION OF CARBON DIOXIDE LIQUID LOADING

The following details are taken from Reference [114].

Gas measuring apparatus. Figure A.1. Connect decomposition flask, A, by glass T-tube, B, provided with stopcock, C, to graduated gas-measuring tube, D, connected in turn with leveling bulb, E. For flask A, use 250 ml Pyrex flask fitted with 2-hole rubber stopper, through one hole of which passes extended tip of 25 ml buret, F, and through other, the glass tube of same diameter as connecting T-tube. Use buret graduated in ml, numbered at 1 ml intervals, and fitted with extra-long tip bent to pass through rubber stopper. Connect glass tube leading from decomposition flask to T-tube with rubber tubing to permit rotation of flask. Use gas-measuring tube graduated in ml with 0 mark at point 25 ml below top marking to allow for graduating upward from 0 to 25 ml and downward from 0 to 200 ml. Connect gas-measuring tube to 300 ml leveling bulb, E, with long rubber tube.

Displacement solution. Dissolve 100 g NaCl in 350 ml of distilled water. Add 1 g of NaHCO₃ and 2 ml Methyl orange to make just acid (decided pink). Stir until all CO₂ is removed. This solution is used in gas measuring tube and leveling bulb.
Figure A.1: Gas measuring apparatus [114].
Determination. Pipette 5 ml of liquid sample into flask A, and connect flask with apparatus, see Figure A.1. Open stopcock C, and using leveling bulb E, bring displacement solution to 10 ml graduation above 0 mark. (This 10 ml is practically equal to volume of acid to be used in decomposition.) Let apparatus stand 1 to 2 minute for temperature and pressure within apparatus to come to room conditions.

Close stopcock, lower leveling bulb somewhat to reduce pressure within apparatus, and slowly add 10 ml of 2 M HCl to decompose the sample in the flask A from buret F. To prevent escape of liberated CO₂ through acid buret into air, at all times during decomposition keep displacement solution at level lower in leveling bulb than that in gas-measuring tube. Rotate and then vigorously agitate flask to mix contents intimately. Let stand 5 min to secure equilibrium. Equalize pressure in measuring tube, using leveling bulb, and read volume of gas in the tube. Observe temperature of air surrounding and also barometric pressure.

The total amine can be determined by titration with standard 1N HCl to methyl orange end-point.

Calculation of CO₂ loading. Multiply ml of evolved gas by factor, \( f_g \), which is given in Table A.1, for the given
temperature and pressure. The corrected reading/10 gives %CO₂ content by wt. of sample size of 1.7 g. This can be converted to moles of CO₂ by

\[
((\text{ml of evolved gas}) \times f_g/10)/100) \times (1.7/40)
\]

Sample calculation.

sample size = 5.0 ml
ml of 1 N HCl = 10 ml
evolved gas = 55 ml
Temp. = 16 °C, Pressure = 758.5 mmHg, \( f_g = 1.07 \)

Therefore,
total amine = \((10/5) \times 1.0 = 2.0 \text{ ml}\)
moles of CO₂ = \(55 \times 1.07 \times 1.7/(10 \times 100 \times 40)\)
= \(2.5 \times 10^{-3}\) moles of CO₂
CO₂ loading = \(2.5 \times 10^{-3}/(2 \times 5/1000)\)
= \(0.25\) moles of CO₂/mole of amine

The major errors associated in this analysis are as follows:

* measurement of evolved gas ± 1.0 ml
  (affect the CO₂ content by 1.8 %)

* measurement of room temperature ± 1.0 °C
  (affect \( f_g \) by 0.5 %)

* measurement of HCl ± 0.1 ml
  (affect the total amine ± 1.0 %)

Therefore, the error in CO₂ loading is in the order of 3.3 % which is approximately 40 % more than the [OH⁻] determination.
Table A.1: The values of $f_g$ for a variety of temperatures and pressure [114].

(Multiply number of ml gas evolved from 1,700 g sample by factor that corresponds with existing atmospheric conditions and divide by 10 to obtain % CO2 by wt in sample.)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>mm</th>
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<th>mm</th>
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<td>0.38002</td>
<td>0.28735</td>
<td>0.27565</td>
<td>0.37055</td>
<td>0.37055</td>
</tr>
<tr>
<td>750</td>
<td>0.91194</td>
<td>0.90906</td>
<td>0.90818</td>
<td>0.88573</td>
<td>0.83429</td>
<td>0.38002</td>
<td>0.28735</td>
<td>0.27565</td>
<td>0.37055</td>
<td>0.37055</td>
</tr>
<tr>
<td>760</td>
<td>0.91194</td>
<td>0.90906</td>
<td>0.90818</td>
<td>0.88573</td>
<td>0.83429</td>
<td>0.38002</td>
<td>0.28735</td>
<td>0.27565</td>
<td>0.37055</td>
<td>0.37055</td>
</tr>
<tr>
<td>770</td>
<td>0.91194</td>
<td>0.90906</td>
<td>0.90818</td>
<td>0.88573</td>
<td>0.83429</td>
<td>0.38002</td>
<td>0.28735</td>
<td>0.27565</td>
<td>0.37055</td>
<td>0.37055</td>
</tr>
<tr>
<td>780</td>
<td>0.91194</td>
<td>0.90906</td>
<td>0.90818</td>
<td>0.88573</td>
<td>0.83429</td>
<td>0.38002</td>
<td>0.28735</td>
<td>0.27565</td>
<td>0.37055</td>
<td>0.37055</td>
</tr>
</tbody>
</table>

* Calc'd from 1.9% = wt 1 L CO2 at 0°C, 760 mm pressure, & 41° latitude. Formula given by W. Parr, J. Am. Chem. Soc. 31, 237(1909).

(Continued)
Table A.1 (Con't): The values of $f$ for a variety of temperature and pressure [19].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$f$ at 700 mm Hg</th>
<th>$f$ at 714 mm Hg</th>
<th>$f$ at 712 mm Hg</th>
<th>$f$ at 708 mm Hg</th>
<th>$f$ at 704 mm Hg</th>
<th>$f$ at 720 mm Hg</th>
<th>$f$ at 716 mm Hg</th>
<th>$f$ at 758 mm Hg</th>
<th>$f$ at 750 mm Hg</th>
<th>$f$ at 738 mm Hg</th>
<th>$f$ at 726 mm Hg</th>
<th>$f$ at 712 mm Hg</th>
<th>$f$ at 702 mm Hg</th>
<th>$f$ at 707 mm Hg</th>
<th>$f$ at 712 mm Hg</th>
<th>$f$ at 717 mm Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0°C</td>
<td>0.94541</td>
<td>0.39739</td>
<td>0.39796</td>
<td>0.39432</td>
<td>0.93159</td>
<td>0.92885</td>
<td>0.92612</td>
<td>0.92322</td>
<td>0.92043</td>
<td>0.91753</td>
<td>0.91457</td>
<td>0.91150</td>
<td>0.90839</td>
<td>0.90526</td>
<td>0.90204</td>
<td>0.89873</td>
</tr>
<tr>
<td>25.5°C</td>
<td>0.94381</td>
<td>0.39508</td>
<td>0.39498</td>
<td>0.39170</td>
<td>0.92824</td>
<td>0.92544</td>
<td>0.92267</td>
<td>0.92003</td>
<td>0.91710</td>
<td>0.91410</td>
<td>0.91103</td>
<td>0.90788</td>
<td>0.90461</td>
<td>0.90134</td>
<td>0.89796</td>
<td>0.89453</td>
</tr>
<tr>
<td>26.0°C</td>
<td>0.94122</td>
<td>0.39272</td>
<td>0.39206</td>
<td>0.38879</td>
<td>0.92528</td>
<td>0.92252</td>
<td>0.91967</td>
<td>0.91687</td>
<td>0.91390</td>
<td>0.91086</td>
<td>0.90772</td>
<td>0.90450</td>
<td>0.90120</td>
<td>0.89782</td>
<td>0.89441</td>
<td>0.89100</td>
</tr>
<tr>
<td>26.5°C</td>
<td>0.93864</td>
<td>0.38936</td>
<td>0.38800</td>
<td>0.38473</td>
<td>0.92233</td>
<td>0.91962</td>
<td>0.91676</td>
<td>0.91391</td>
<td>0.91090</td>
<td>0.90777</td>
<td>0.90463</td>
<td>0.90136</td>
<td>0.89798</td>
<td>0.89460</td>
<td>0.89120</td>
<td>0.88779</td>
</tr>
<tr>
<td>27.0°C</td>
<td>0.93607</td>
<td>0.38600</td>
<td>0.38464</td>
<td>0.38136</td>
<td>0.91938</td>
<td>0.91672</td>
<td>0.91386</td>
<td>0.91094</td>
<td>0.90788</td>
<td>0.90472</td>
<td>0.90153</td>
<td>0.89815</td>
<td>0.89477</td>
<td>0.89138</td>
<td>0.88799</td>
<td>0.88460</td>
</tr>
</tbody>
</table>

(Multiply number of mg ice evolved from 1,700 g sample by factor that corresponds with existing atmospheric conditions and divide by 10 to obtain % CO$_2$ by wt in sample.)
APPENDIX B
ERROR ANALYSIS

The following error analysis is derived from Mickley et al. [144]. Consider a quantity $Q$ which is a function of the independent variables $x_1, x_2, x_3, ..., x_n$

$$Q = f (x_1, x_2, x_3, ..., x_n)$$

When there are small finite increments $x_1, x_2, ..., x_n$, the corresponding error in $Q$ is

$$Q + \Delta Q = f (x_1 + \Delta x_1, x_2 + \Delta x_2, ..., x_n + \Delta x_n)$$  \hspace{1cm} (b.2)

By Taylor's series expansion

$$Q + \Delta Q = f (x_1, x_2, x_3, ..., x_n)$$
$$+ (\frac{\partial f}{\partial x_1})\Delta x_1 + (\frac{\partial f}{\partial x_2})\Delta x_2 +...+ (\frac{\partial f}{\partial x_n})\Delta x_n$$
$$+ (\frac{\partial^2 f}{\partial x_1^2})\Delta x_1^2 +...(\text{higher order terms})$$
$$..... \hspace{1cm} (b.3)$$

When $\Delta x_1, \Delta x_2, \Delta x_3, ..., \Delta x_n$ are sufficiently small, the higher order terms are negligible. The following equation would result in a good approximation
\[ \Delta Q = \left( \frac{\partial f}{\partial x_1} \right) \Delta x_1 + \left( \frac{\partial f}{\partial x_2} \right) \Delta x_2 + \ldots + \left( \frac{\partial f}{\partial x_n} \right) \Delta x_n \]

That is,

\[ \Delta Q = \text{(error caused by } \Delta x_1) \]
\[ + \text{(error caused by } \Delta x_2) \]
\[ + \ldots + \text{(error caused by } \Delta x_n) \]

It should be noted that Equation (b.4) may overestimate the error involved in the calculation, because it considers only the simultaneous occurrence of the errors and does not take into account the possibility of compensating effects. Nonetheless, error estimates in engineering analysis are often calculated by the above procedure because they are known to be conservative and hence, allow for an additional 'margin-of-safety'.

The above mentioned procedure is used to analyze uncertainty associated with the \( R_v \) value determination. The operating conditions of Run T9 are used as an example. \( R_v \) from first principles can be written as:

\[ R_v = \left\{ I k_L^o a_v (H P Y_A - C_A^*) / [1+I H (k_L^o/k_G)] \right\} \]
The uncertainties associated with the estimates of $k_g$, $k_L^\circ$, $a_v$, $H$ and $I$ are generally in the order of ±25% [85] (see Chapter 2). Assuming that the accuracy of the measurements of the gas composition and pressure are within ±2.5%. For CO$_2$-NaOH system, the free CO$_2$ in the liquid phase is virtually zero.

Since $R_v$ is a function of many parameters, it is difficult to determine the gradients analytically. Therefore, the monitor program NLMON, which is available at UBC Computing Center, is used to provide the value of $\partial f/\partial x_i$ for each parameter. These values of gradients are then used to determine uncertainty in $R_v$ by means Equation b.4. The results are shown in Table B.1.

Table B.1: Propagation of Errors for Run T9.

<table>
<thead>
<tr>
<th>Uncertainty in variable</th>
<th>Uncertainty in $R_v$ Using Eq. b.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_g$ ±25%; $k_L^\circ$ ±25%; $a_v$ ±25%; $H$ ±25%; $I$ ±25%; $P$ ±25%; $y_A$ ±25%</td>
<td>$R_v$ ±95%</td>
</tr>
</tbody>
</table>
As can be seen from Table B.1, the uncertainty associated with the computed value of $R_v$ from equation b.4 could be as high as 95% because a number of parameters are involved.

For the case of using laboratory models, $R_v$ can be acquired from the product of $R_a$ and $a_v$. Before $R_v$ can be determined from experimental testing, $k_G$ and $k_L^0$ of the system must be matched.

According to Alper [62] and Laurent [130], the accuracy of obtaining $R_a$ is within ±10% to 20%. For comparison purposes, the average value of ±15% is assigned. Since $R_v$ is determined by direct multiplication of $R_a$ and $a_v$, the error for this case is the sum of the errors associated with $R_a$ and $a_v$, which is ±40%.

For the case of using the PPT, the accuracy in obtaining $R_v$ depends only on the accuracy in measuring the inert gas flow rate, $G_I$, and the gas composition, $Y_A$. The error in measuring the distance along the column axial may be neglected. The accuracy in measuring the gas flow rate using a rotameter is about 5%. To measure the CO$_2$ composition using infrared analyzer, the accuracy would be in the order of ±2%. However, the error in mass balance as well as the liquid composition measurements could increase the uncertainty. If we adopt a worst case scenario and set
the uncertainty of the former and latter parameters to ±5 % and ±15% respectively, the maximum error that could occur for this case is ±20 %. A summary of the potential maximum uncertainties in determining the $R_v$ provided by Table B.2.

Table B.2: Estimates of potential uncertainties in $R_v$

<table>
<thead>
<tr>
<th>Determination of specific absorption rate</th>
<th>Potential max. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>First principles</td>
<td>95 %</td>
</tr>
<tr>
<td>Laboratory models</td>
<td>40 %</td>
</tr>
<tr>
<td>PPT</td>
<td>20 %</td>
</tr>
</tbody>
</table>
APPENDIX C

COMPUTER PROGRAM LISTINGS

C1. PROGRAM FOR PREDICTING CO$_2$-AMP SOLUBILITY

C PREDICT LOADING ********new fitted for pK1
C MODIFIED FROM SOL9/5 (PREDICTION OF PCO2)
C SOLUBILITY CALCULATION FOR CO2 - AMP SYSTEM
C >>>> CALCULATE =========== *********
C ***********

IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(10),F(10),AJINV(10,10),W(500),IPERM(20)
COMMON CK1,CK3,CK4,CK5,CK6
COMMON AMP,T,PCO2,ALFA

DATA AA1,AB1/-2.3091D+3,-4.9828D-01/
DATA AC1,AD1/7.0850E+4,3.8803D+2/
DATA AE1,AF1/6.3899D+00,9.5221D-2/
DATA AG1/-3.8508D-2/

DATA A3,B3,C3/-241.818D0, 298.253D3, -148.528D6/
DATA D3,E3/332.648D8, -282.394D10/

DATA A4,B4,C4/39.5554D0, -987.9D2, 568.828D5/
DATA D4,E4/-146.451D8, 136.146D10/

DATA A5,B5,C5/-294.74D0, 364.385D3, -184.158D6/
DATA D5,E5/415.793D8, -354.291D10/

DATA A6,B6,C6/22.2819D0, -138.306D2, 691.346D4/
DATA D6,E6/-155.895D7, 120.037D9/
AVE=0.
NP=60

C ** READ DATA FROM K1-DATA/5
NE =8
DO 5 I=1,NP
READ (5,10) AMP,T,ALFA,PCO2,CK1
10 FORMAT (5D12.4)
C WRITE (6.12) CK1
C 12 FORMAT (' DATA OF K1 = ',D12.4)
C
C CALCULATE CONSTANTS
CK3 = DEXP(A3 + B3/T +(C3/(T**2)) +(D3/(T**3)) +(E3/(T**4)))
CK4 = DEXP(A4 + B4/T +(C4/(T**2)) +(D4/(T**3)) +(E4/(T**4)))
CK5 = DEXP(A5 + B5/T +(C5/(T**2)) +(D5/(T**3)) +(E5/(T**4)))
CK6 = DEXP(A6 + B6/T + (C6/(T**2)) + (D6/(T**3)) + (E6/(T**4)))

CK6 = CK6/(780./101.15)

CO2=PCO2/CK6
CK1 =AA1 + AB1*T + (AC1/(T**1)) + (AD1*DLOG(T))
         + AE1*(CO2) + (AF1*DLOG(CO2)) + AG1*(AMP)

CK1 = 10.**CK1
C WRITE (6,11) CK1
C 11 FORMAT(' FITTED K1 = ',D12.4)

C SET INITIAL VALUE
C X(1)=H+, X(2)=RRNH, X(3)=RRNH2+, X(4)=HC03-
C X(5)= CO2, X(6)=OH-, X(7)=CO3-, X(8)=ALFA (CAL)
C
XALFA = 0.75
IF(T.GT.(273.+60.)) XALFA=.75
IF(T.GT.(273+60.)) XALFA=.75

X(1)= 1.D-8
X(2)= AMP*(1.-XALFA)
X(3)= AMP*XALFA
X(4)= AMP*XALFA
X(5)= X(1)*X(4)/CK3
X(6)= CK4/X(1)
X(7)= 1.D-5
X(8)= XALFA
C
X(1)= 1.D-8
C X(5)= PCO2/CK6
C X(4)= CK3*X(5)/X(1)
C X(6)= CK4/X(1)
C X(7)= 1.D-4
C X(3)= X(4)
C X(2)= CK1*X(3)/X(1)
C X(8)= (X(5)+X(4)+X(7))/AMP
C
C WRITE (6,50) X(1),X(2),X(3),X(4),X(5),X(6),X(7),X(8)
C 50 FORMAT (/INIT= '/.8D9.2)

C SET INPUT FOR NDINVT
C
DSTEP=1.D-7
DMAX = 10.
ACC = 1.D-20
MAXFUN = 15000
LOG = 00

EXTERNAL FCN
C
CALL QNEWT
CALL QNEWT(NE,X,F,NE,AJINV,DSTEP,DMAX,ACC,MADFUN,LOG,W,IPERM, 
> FCN,&70)

C
C PRINT X1 TO X9
C
EER = (ALFA-X(8))*100/ALFA
WRITE (6,52) AMP,T,PCO2,ALFA,X(8),EER
AVE = AVE +DABS(EER)
52 FORMAT (6D12.4)
5 CONTINUE

WRITE (6,75)
75 FORMAT ('AMP',9X,'TEMP',9X,'PCO2',9X,'ALFA',8X,'CAL.PCO2')

AVE = AVE/NP
WRITE (6,85) AVE
85 FORMAT ('AVE ERR = ',F9.3)
STOP
70 WRITE (7,100)
100 FORMAT ('?? ERR FORM NDINVT')
STOP 1
END

C
C SUBROUTINE FCN
C
SUBROUTINE FCN(X,F)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(1),F(1)

COMMON CK1,CK3,CK4,CK5,CK6
COMMON AMP,T,PCO2,ALFA

C DO 1 IJ=1,8
C3 IF (X(IJ).LT.1.D-20) X(IJ)=1.D-20

F(1) = X(3) + X(1) - X(6) - X(4) - 2.*X(7)
F(2) = X(8)*AMP - X(5) - X(4) - X(7)
F(3) = AMP - X(2) - X(3)
F(4) = PCO2 - (CK6)*X(5)
F(5) = CK5 - (X(1)*X(7)/X(4))
F(6) = CK4 - (X(1)*X(6))
F(7) = CK3 - (X(1)*X(4)/X(5))
F(8) = CK1 - (X(1)*X(2)/X(3))

RETURN
END
C2. PROGRAM FOR PREDICTING COLUMN PERFORMANCE FOR RUN T9
(NaOH-CO₂)

C RUN-T9 (RUN44)
C FULL SCALE RUN **********
C
IMPLICIT REAL*8(A-H,J-M,O-Z)
DIMENSION PYA(900),PYS(900),PCR(900),T(900),HT(900)
DIMENSION PTG(900),PEG(15),PEC(15),PET(15),PHT(20)
C
WRITE(6,321)
321 FORMAT(/' **** RUN # (T9) 44 ****'/
> '==============/)
C
WRITE(7,323)
323 FORMAT(/' **** RUN # (T9) 44 ****'/
> '==============/)
C
C CALCULATION OF CO₂ - AMINE SYSTEM.
C
C 1. ASSUME THE TEMP. AND SOLVENT VAPOR CONCENTRATION (YS)
C  OF THE OUTLET GAS.
C  TG(C), TGK(K), YS(MOLE FRACTION)
C
TGOUT = 15.0
YSOUT = 0.031
C
C 2. COMPUTE THE ENTHALPIES OF THE ENTERING STREAMS
C  AND THE OUTLET GAS . BY THE MATERIAL AND ENTHALPY
C  BALANCES FOR THE ENTIRE TOWER, COMPUTE THE OUTLET
C  LIQUID RATE, COMPOSITION AND TEMPERATURE.
C
NDUM=0
C
C P = TOTAL PRESSURE.
P = 1.0
C
C CONC. IN LIQUID = G-MOL/CC.
C
CRIN = 2.00
CPIN = (2.00-CRIN)/2.
LMIN= (1.00)*(1820./(60*80))
TLIN = 15.0
C
GB =1.475E-3
SYAIN = 18.45/100.
YAIN = SYAIN/(1.-SYAIN)
YBIN = 1.0
YSIN = 0.001
TGIN = 15.

CROUT = 0.37
CPOUT = (2.0 - CROUT) / 2.

C TLOUT IS ASSUMED FROM OVERALL ENERGY BALANCE.
TLOUT = 35.0
SYAOUT = 1.00 / 100
YAOUT = SYAOUT / (1. - SYAOUT)
YBOUT = 1.

C YSOUT AND TGOUT ARE ASSUME AS ABOVE

C
C STEP BY STEP CALCULATIONS NOW BEGIN FROM THE BOTTOM
C OF THE TOWER.

CR = CROUT
CP = CPOUT
TL = TLOUT
LM = LMIN + 0.0005

YA = YAIN
YB = YBIN
YS = YSIN
TG = TGIN
Z = 0.

C GBin and GBout are the same.

C
C 3. OBTAIN ALL THE NECESSARY PHYSICAL AND CHEMICAL PROPERTIES
C OF THE GAS AND LIQUID.
C  EG. VISCOSITY, DENSITY, HEAT CAPACITY, THERMAL CONDUCTIVITY,
C DIFFUSIVITIES, VAPOR PRESSURE OF SOLVENT S,
C CHEMICAL EQUILIBRIUM CONSTANT Kc,
C FORWARD REACTION RATE CONSTANT K2.

C
C SEE TABLE I P.356

C
N = 1
NOUT = 1
NSET = 900

C

300 STOI = 2.
CPA = 8.8
CPS = 8.1
CPB = 6.0
HLH2O = 10761
CL = 1.0
PL = 1.0
HR = -24400.

TLK = TL+273.15

DA = (1.65D-5)*(((647.3-298.)/(647.3-TLK))**3)
DR = DA/1.7

THE REACTION RATE CONSTANT K2.

ASI = CR + (((2.*CP)+(CP*4.))/2)
ALK2 = 11.895 - (2382/TLK) +(0.221*ASI)-(.016*(ASI**2))
K2 = 10.**(ALK2)

K2 = L/G-M OL SEC.

THE SOLUBILITY OF GAS IN SOLUTION.

( SEE COMMENTS ON P.356 )

HW= 10.**(9.1229-(.059044*TLK)+(7.8857D-5*(TLK**2)))
AHG = 0.124515-(.00047*(TLK))
SHI=(CR*(.091+.066+AHG))+(((2.*CP+CP*4.)/2)*(.09H-.066-|-AHG))
H = HW*(10.**(-SHI))

WRITE (7,221) DA,ASI,K2,HW,H
C221 FORMAT (/5D10.3)

4. ESTIMATE KLA, KGA, KGS, HGA FROM THE AVAILABLE CORRELATIONS.

SEE TABLE II P.356

A = 1.500
KLA = (2.6*DA)**(.5)
KGA = 3.2 D-5
KGS = 3.2 D-5
HGA = 2.478 D-3

STORE DATA

PYA(N)=YA
PYS(N)=YS
PCR(N)=CR
T(N) = TL
PTG(N) = TG
HT(N) = Z

5. ASSUME PAI = PA

PA = P*(YA/(YA+YS+YB))
PAI =PA

CAI = H*PAI
REAL*8 M,M2

C

200 IF(CR.LT.0.0005) E=1.
   IF(CR.LT.0.0005) GOTO201

   M2 = K2*CR*DA/(KLA**2)
   EI = DSQRT(M2)/DTANH(DSQRT(M2))
   C EI = 1. + ((CR*DR)/(2.*CAI*DA))
   EI = (DSQRT(DA/DR))+(CR/(2.*CAI)*(DSQRT(DR/DA))
   C
   ASSUME LIQUID HOLD UP = 5% OF TOTAL VALUE
   C
   HU = 0.05
   XXX = HU*K2*CR/(KLA*A)
   C
   IF (XXX.LT.20.) GO TO 550
   C
   EA = 1./((EI-1.)**1.35)
   EB = 1./((EI-1.)**1.35)
   E=1.+((1./((EA+EB)**(1./1.35)))

201 CONTINUE

C
C550 WRITE (6,555)
   C555 FORMAT (1X,' !!! E OUT OFF RANGE.' )
   C GOTO 900
   C
C560 WRITE (6,565)
   C565 FORMAT ('/ ! ! E >> 1. ???'/)
   C
   C CHACK E VALUE?
   C WRITE (6,566)
   C566 FORMAT ('/ CHACK E CALCULATION. '/)
   C WRITE (6,567)M2,M,SRM
   C567 FORMAT (' ',F15.4/F15.4/F15.4/)
   C WRITE (6,568)Q,QM,XXX,E
   C568 FORMAT (' ',F15.4/F15.4/F15.4/,..>> E',F15.4/)
   C
   C GO TO 900
   C

C
C 6. ASSUME CAE = 0.0
C
   R = (E*KLA*PA*H*1.D-3)/(1.+(E*KLA*H)*1.D-3)/(KGA))
   CAINEW = (PA*H)-(R*H/KGA)
   PAIN = CAI/H
C
IF (DABS(CAINEW-CAI).LE.DABS(0.00010*(CAINEW+CAI))) GOTO 700

CAI = CAINEW
GO TO 200

700  PSI = 0.90*( 2.7182818**(16.5362-(3985.44/(TLK-38.9974))))/
> 101.13
YSI = PSI/(P-PAIN-PSI)
YAI = PAIN/(P-PAIN-PSI)
PS = P*(YS/(YA+YB+YS))

DYADZ = -KGA*A*(PA-PAIN)/GB
DYSDZ = -KGS*A*(PS-PSI)/GB
HDGA = (-1.*GB)*(CPA*DYADZ + CPS*DYSDZ)/
> (1-DEXP(GB*(CPA*DYADZ + CPS*DYSDZ)/HGA))
DTGDZ = -HDGA*(TG-TL)/(GB*(CPB+YA*CPA+YS*CPS ))

C
C REF. TEMP. T0 = 25 C.

T0 = 25.
DTLDZ = (1./(LM*CL))*((GB*(CPB+YA*CPA+YS*CPS)*DTGDZ)
> + (GB*(CPA*(TG-T0) - HR)*DYADZ))

C
C 8. CHOOSE A SUITABLY SMALL VALUE OF DYA ,
C AN INCREMENT OF GAS COMPOSITION, SO THAT THE
C GRADIENTS DYA/DZ,DYS/DZ,DTG/DZ, AND DTL/DZ
C WILL NOT CHANGE TOO GREATLY.

DELYA = -0.00025*4.
DELZ = DELYA/DYADZ

C
WRITE(6,10) CR,PA,PAIN,PSI,Z,DELZ,E
C10  FORMAT(' ',F10.6,'(CR)',F10.6,
> F10.6,'(PA)',F10.6,'(PAI)',
> F12.4,'(PSI)',F12.4,'(DZ)',F12.4,'(Z)',F12.4,'(E)')

C
WHERE Z=0. FOR THE BOTTOM OF THE TOWER.

Z = Z + DELZ

C
9. COMPUTE THE CIRCUMSTANCES AT Z-NEXT.

YA = YA + DELYA
YS = YS + DELZ*DYSDZ
TG = TG + DELZ*DTGDZ
TL = TL + DELZ*DTLDZ
LMOLD = LM
LM = LM + GB*DELZ*(DYADZ+DYSDZ)*29.
CR=(((LMOLD*CR/1000.) - STOI*GB*DELYA)/LM)*1000.
CP=(((LMOLD*CP/1000.) + GB*DELYA)/LM)*1000.

C
C PRINT SOME RESULTS
C
NIN = N/50
IF(NIN.GE.NOUT) CALL CHACK (NIN,CR,CP,LM,TL,
> YA,YB,YS,TG,Z,NOUT)

IF(NDUM.EQ.0.AND.Z.GT.110.) CALL CKOUT(Z,CR,YA,TL,N,NDUM)
IF(Z.GT.110..AND.Z.LT.220.) GOTO 850
IF(NDUM.EQ.1.AND.Z.GT.220.) CALL CKOUT(Z,CR,YA,TL,N,NDUM)
IF(Z.GT.220..AND.Z.LT.330) GOTO 850
IF(NDUM.EQ.2.AND.Z.GT.330,) CALL CKOUT(Z,CR,YA,TL,N,NDUM)
IF(Z.GT.330..AND.Z.LT.435.) GOTO 850
IF(NDUM.EQ.3.AND.Z.GT.435.) CALL CKOUT(Z,CR,YA,TL,N,NDUM)
IF(Z.GT.440..AND.Z.LT.550) GOTO 850
IF(NDUM.EQ.4.AND.Z.GT.550.) CALL CKOUT(Z,CR,YA,TL,N,NDUM)
IF(Z.GT.550..AND.Z.LT.650) GOTO 850

850 CONTINUE
IF(YA.LT.YAOUT) CALL CKOUT(Z,CR,YA,TL,N,NDUM)

C
10. REPEAT STEP 3 TO 9 UNTIL YA FOR THE OUTLET GAS
IS REACHED.
C
IF(YA.LT.YAOUT) GO TO 900
N=N+1
IF(N.GT.NSET) GO TO 900

C
WRITE(8,1111) Z,PA,CR,TL,TG,E
1111 FORMAT(6F11.6)
C
GOTO 300
C
C
11. CHECK THE ASSUMPTION OF STEP 1.
C IF NOT MATCHED, IT MAY BE APPROPRIATE GUESS FOR
C THE NEXT ITERATION. HOWEVER, IF THE SOLUTION IS FOUND
C TO BE INSENSITIVE TO THE ASSUMED VALUES OF TG AND YS
C (THROUGH THE BACK CALCULATION OF OUTLET LIQUID TEMP.
C FROM AN OVERALL ENTHALPY BALANCE) FURTHER ITERATION
C WILL NOT BE REQUIRED.
C
900 WRITE(6,905)
905 FORMAT('/' ***** THE END CONDITION *****'/)
WRITE(6,910) CRIN
910 FORMAT('/' INLET CONCN. OF MEA ','F10.5,' G-MOL/L')
WRITE(6,915) CPIN
915  FORMAT(' INLET CONCN. OF PROD. ',F10.5,' G-MOL/L')
WRITE(6,920) LMIN
920  FORMAT(' INLET L. MOLAR VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,925) TLIN
925  FORMAT(' INLET LIQUID TEMP. ',F10.5,' C.')
WRITE(6,930) CROUT
930  FORMAT(' OUTLET CONCN. OF MEA ',F10.5,' G-MOL/L')
WRITE(6,935) CPOUT
935  FORMAT(' OUTLET CONCN. OF PROD. ',F10.5,' G-MOL/L')
WRITE(6,945) TLOUT
945  FORMAT(' OUTLET LIQUID TEMP. ',F10.5,' C.')
WRITE(6,950) GB
950  FORMAT(' INLET AIR MOL. VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,955) YAIN
955  FORMAT(' INLET MOL FRAC. OF CO2 ',F10.5)
WRITE(6,960) YBIN
960  FORMAT(' INLET MOL FRAC. OF AIR ',F10.5)
WRITE(6,965) TGIN
965  FORMAT(' INLET GAS TEMP. ',F10.5,' C. ')
WRITE(6,970) YAOUT
970  FORMAT(' OUTLET MOL FRAC. OF CO2 ',F10.5)
WRITE(6,975) YBOUT
975  FORMAT(' OUTLET MOL FRAC. OF AIR ',F10.5)
WRITE(6,980) YSOUT
980  FORMAT(' OUTLET MOL FRAC. OF H2O ',F10.5)
WRITE(6,985) TGOUT
985  FORMAT(' OUTLET GAS TEMP. ',F10.5,' C. ')
WRITE(6,990)
990  FORMAT(' *** >> CALCULATION RESULTS')
WRITE(6,991) CR
991  FORMAT(' INLET CONCN. OF MEA ',F10.5,' G-MOL/L')
WRITE(6,992) CP
992  FORMAT(' INLET CONCN. OF PROD. ',F10.5,' G-MOL/L')
WRITE(6,993) LM
993  FORMAT(' INLET L. MOLAR VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,994) TL
994  FORMAT(' INLET LIQUID TEMP. ',F10.5,' C. ')
WRITE(6,995) YA
995  FORMAT(' OUTLET MOL FRAC. OF CO2 ',F10.5)
WRITE(6,996) YB
996  FORMAT(' OUTLET MOL FRAC. OF AIR ',F10.5)
WRITE(6,997) YS
997   FORMAT( ' OUTLET MOL FRAC. OF H2O ',F10.5)
WRITE(6,998) TG
998   FORMAT( ' OUTLET GAS TEMP. ',F10.5,' C.' )
WRITE(6,999) Z
999   FORMAT( ' THE TOTAL HEIGHT ',F10.5,' CM.' )

C SCALING
DO 1 I=1,N
   HT(I) = 2. + (HT(I)/(1.*100.))
   PMIX = 1.+PYS(I) +PYA(I)
   PMIXX = 1. + PYA(I)
   PYA(I) = 1. +((PYA(I)/(PMIXX))/0.03)
   PYS(I) = 1. +((PYS(I)/(PMIX))/0.03)
   PCR(I) = 1. + (PCR(I)/.6)
   T(I)  = 1. + (T(I)*5./50.)
   PTG(I) = 1. + (PTG(I)*5./50.)
1 CONTINUE

C PLOTTING
CALL AXIS(1.,1.,'P. CO2',-6,7.,0.,0.,0.03)
CALL AXIS(1.,1.,'P. H2O',-6,7.,0.,0.,0.03)
CALL AXIS(1.,1.5,'MEA (MOL/L)',-11,7.,0.,0.,0.6)
CALL AXIS(1,2.,'TEMP. (C)',-9,7.,0.,10.)
CALL AXIS(1,2.,'HEIGTH (M)',10,7.,90,0.,1.)

CALL PLOT(1.,2.,3)
CALL PLOT(2.,2.,2)
CALL PLOT(2.,9.,2)
CALL PLOT(3.,9.,2)
CALL PLOT(3.,2.,2)
CALL PLOT(4.,2.,2)
CALL PLOT(4.,9.,2)
CALL PLOT(5.,9.,2)
CALL PLOT(5.,2.,2)
CALL PLOT(6.,2.,2)
CALL PLOT(6.,9.,2)
CALL PLOT(7.,9.,2)
CALL PLOT(7.,2.,2)
CALL PLOT(8.,2.,2)
CALL PLOT(8.,9.,2)
CALL PLOT(7.,9.,2)
CALL PLOT(8.,3.,3)
CALL PLOT(1.,3.,2)
CALL PLOT(1.,4.,2)
CALL PLOT(8.,4.,2)
CALL PLOT(8.,5.,2)
CALL PLOT(1.,5.,2)
CALL PLOT(1.,6.,2)
CALL PLOT(8.,6.,2)
CALL PLOT(8.,7.,2)
CALL PLOT(1.,7.,2)
CALL PLOT(1.,8.,2)
CALL PLOT(8.,8.,2)
CALL PLOT(8.,9.,2)
CALL PLOT(1.,9.,2)
CALL PLOT(1.,2.,3)

DO 2 I=1,N
   CALL SYMBOL(PYA(I),HT(I),0.010,0,0.,-2)
2 CONTINUE

CALL PLOT(1.,2.,3)

DO 3 I=1,N
   CALL SYMBOL(PYS(I),HT(I),0.010,1,0.,-2)
3 CONTINUE

CALL PLOT(1.,2.,3)

DO 4 I=1,N
   CALL SYMBOL(PCR(I),HT(I),0.010,2,0.,1)
4 CONTINUE

CALL PLOT(1.,2.,3)

DO 5 I=1,N
   CALL SYMBOL(T(I),HT(I),0.010,11,0.,-1)
5 CONTINUE

CALL PLOT(1.,2.,3)

DO 6 I=1,N
   CALL SYMBOL(PTG(I),HT(I),0.015,0.,-2)
6 CONTINUE

CALL SYMBOL(2.0,10.0,0.08,0.0,0.,-1)
CALL SYMBOL(2.2,10.0,0.08,'P-CO2 (ATM)',0.,11)
CALL SYMBOL(3.5,10.0,0.08,1,0.,-1)
CALL SYMBOL(3.7,10.0,0.08,'P-H2O (ATM)',0.,13)

CALL SYMBOL(5.0,10.0,0.08,2.0.,-1)
CALL SYMBOL(5.2,10.0,0.08,'NAOH (MOL/L)',0.,12)
CALL SYMBOL(2.0,9.7,0.08,11.0.,-1)
CALL SYMBOL(2.2,9.7,0.08,'LIQUID TEMP. (C)',0.,16)
CALL SYMBOL(3.5,9.7,0.08,5.0.,-1)
CALL SYMBOL(3.7,9.7,0.08,'GAS TEMP. (C)',0.,13)
CALL PDATA(PEG,PEC,PET,PHT,NEX)

DO 1001 I=1,NEX
   EG = 1. + (PEG(I)/0.03)
   EC = 1. + (PEC(I)/0.6)
   ET = 1. + (PET(I)/10.)
   EH = 2. + (PHT(I)/100.)
   CALL SYMBOL(EG,EH,.12,0,0.,-1)
   CALL SYMBOL(EC,EH,.12,2,0.,-1)
   CALL SYMBOL(ET,EH,.12,11,0.,-1)
1001 CONTINUE

CALL SYMBOL(4,9.25,.25,'RUN#  T09',0.,8)
CALL PLOTND
STOP
END

C **********************************************
C SUBROUTINE CHACK(NIN,CR,CP,LM,TL,YA,YB,YS,TG,Z,NOUT)
C
IMPLICIT REAL*8(A-M,O-Z)

WRITE(6,990)
990 FORMAT(/'  ::::  INTERMEDIAD CALCULATION RESULTS')

WRITE(6,991) CR
991 FORMAT(/' CONCN. OF MEA ',F10.5,' G-MOL/L')

WRITE(6,992) CP
992 FORMAT(/' CONCN. OF PROD. ',F10.5,' G-MOL/L')

WRITE(6,993) LM
993 FORMAT(' LIQUID MOLAR VEL. ',F10.5,' G-MOL/SEC.CM2')

WRITE(6,994) TL
994 FORMAT(' LIQUID TEMP. ',F10.5,' C.')

WRITE(6,995) YA
995 FORMAT(' MOL FRAC. OF CO2 ',F10.5)

WRITE(6,996) YB
996 FORMAT(' MOL FRAC. OF AIR ',F10.5)

WRITE(6,997) YS
997 FORMAT(' MOL FRAC. OF H2O ',F10.5)

WRITE(6,998) TG
998 FORMAT(' GAS TEMP. ',F10.5,' C.')

WRITE(6,999) Z
999 FORMAT(' THE HEIGHT ',F10.5,' CM./')

NOUT = NOUT + 1
C
RETURN
END

C

SUBROUTINE CKOUT(Z,CR,YA,TL,N,NDUM)
C
IMPLICIT REAL*8(A-M,O-Z)
C
WRITE(7,990)
990 FORMAT(/'  ::::  INTERMEDIAD CALCULATION RESULTS')

WRITE(7,999) Z
999 FORMAT(/' THE HEIGHT ',F10.5,' CM.'/)
PYA = 100.*YA/(1.+YA)
WRITE(7,995) PYA
995 FORMAT('  C02 CONC. (%) ',F10.5)
WRITE(7,991) CR
991 FORMAT('  CONCN. OF NAOH ',F10.5,' G-MOL/L')

WRITE(7,994) TL
994 FORMAT('  LIQUID TEMP. ',F10.5,' C')

C
NDUM=NDUM+1
RETURN
END

C

SUBROUTINE PDATA(EG,EC,ET,EH,NEX)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION EG(20),EC(20),ET(20),EH(20),G(20),C(20),T(20),H(20)

NEX=5
DATA H/0.000,110..220.,330.,435./
DATA G/.1845,.1155,.0580,.0265,.0100/
DATA C/.41,1.08,1.625,1.900,2.00/
DATA T/35.0,29.0,22.0,17.0,15.0/

DO 10 I=1,NEX
EH(I)=H(I)
EG(I)=G(I)
EC(I)=C(I)
10 ET(I)=T(I)
RETURN
END
C3. PROGRAM FOR PREDICTING COLUMN PERFORMANCE FOR RUN T22

(IMEA-CO₂)

C

C RUN-T22(RUN41)
C FULL SCALE RUN **********
C
IMPLICIT REAL*8(A-H,J-M,O-Z)
DIMENSION PYA(1900),PYS(1900),PALF(1900),T(1900),HT(1900)
DIMENSION PTG(1900),PEG(15),PEC(15),PET(15),PHT(20)
C
WRITE(6,321)
321 FORMAT(/' ***** RUN # (T22)41 ****'/
       '=---------------------------------'/)
C
WRITE(7,323)
323 FORMAT(/' **** RUN # (T22)41 ****'/
       '=---------------------------------'/)
C
C CALCULATION OF CO₂ - AMINE SYSTEM.
C
1. ASSUME THE TEMP. AND SOLVENT VAPOR CONCENTRATION (YS)
   OF THE OUTLET GAS .
   TG(C), TGK(K), YS(MOLE FRACTION)
C
TGOUT = 19.0
YSOUT = 0.031
C
2. COMPUTE THE ENTHALPIES OF THE ENTERING STREAMS
   AND THE OUTLET GAS . BY THE MATERIAL AND ENTHALPY
   BALANCES FOR THE ENTIRE TOWER, COMPUTE THE OUTLET
   LIQUID RATE, COMPOSITION AND TEMPERATURE.
C
NDUM=0
C
P = TOTAL PRESSURE.
P = 1.0
C
CONC. IN LIQUID = G-MOL/CC.
C
CTOT = 3.00
ALFIN = .000
LMIN = (1.00)*(1270./(60*80))
TLIN = 19.0
GB =1.475E-3
SYAIN = 19.10/100.
YAIN = SYAIN/(1.-SYAIN)
YBIN = 1.0
YSIN = 0.001
TGIN = 15.

ALFOUT = 0.443

C TLOUT IS ASSUMED FROM OVERALL ENERGY BALANCE.
TLOUT = 47.0
SYAOUT = 0.05/100
YAOUT = SYAOUT/(1.-SYAOUT)
YBOUT = 1.

C YSOUT AND TGOUT ARE ASSUME AS ABOVE

C
C STEP BY STEP CALCULATIONS NOW BEGIN FROM THE BOTTOM
C OF THE TOWER.

ALF = ALFOUT
TL = TLOUT
LM = LMIN+0.0005

YA = YAIN
YB = YBIN
YS = YSIN
TG = TGIN
Z = 0.

C GBin and GBout are the same.

C
C 3. OBTAIN ALL THE NECESSARY PHYSICAL AND CHEMICAL PROPERTIES
C OF THE GAS AND LIQUID.
C EG. VISCOSITY, DENSITY, HEAT CAPACITY, THERMAL CONDUCTIVITY,
C DIFFUSIVITIES, VAPOR PRESSURE OF SOLVENT'S,
C CHEMICAL EQUILIBRIUM CONSTANT Kc,
C FORWARD REACTION RATE CONSTANT K2.
C
C SEE TABLE I P.356
C
N = 1
NOUT = 1
NSET = 1900

C
C
C

300 STOI = 2.
CPA = 8.8
CPS = 8.1
CPB = 7.0
HLH2O = 10761
CL = 1.0
PL = 1.0
HR = -20166.
TLK = TL + 273.15

\[ DA = (0.64) \times (2.0D-5) \times ((647.3 - 298.) / (647.3 - TLK))^{**3} \]
\[ DR = (0.80D-5) \times ((647.3 - 298.) / (647.3 - TLK))^{**3} \]

C
C THE REACTION RATE CONSTANT K2.
C
ASI = ALF \times CTOT
IF(ALF.GE.0.5) ASI = 0.5 \times CTOT

ALK2 = 11.069 - (2142.34/TLK)
K2 = 10.**(ALK2)
C K2 = L/G-M OL.SEC.
C
THE SOLUBILITY OF GAS IN SOLUTION.
C
( SEE COMMENTS ON P.356 )
C

\[ HW = 10.**((9.1229 - (0.059044 \times TLK) + (7.8857D-5 \times (TLK**2))) \]
\[ AHG = 0.124515 - (0.00047 \times (TLK)) \]
\[ SHI = (0.031 + 0.021 + 0.021 + AHG) \times ASI \]
\[ H = HW \times (10.**(-SHI)) \]

C CAL. FREE AMINE
CALL SOL(TLK, CTOT, ALF, PECO2)
CAB = H \times PECO2
CR = CTOT - (2. \times CTOT \times ALF) + CAB

C WRITE (7,221) DA,ASI,K2,HW,H
C221 FORMAT (/5D10.3)
C
4. ESTIMATE KLA, KGA, KGS, HGA FROM THE AVAILABLE CORRELATIONS.
C
( SEE TABLE II P.356 )
C
A = 1.350
KLA = (2.4 \times DA)**(.5)
KGA = 3.2 \times D-5
KGS = 3.2 \times D-5
HGA = 2.478 \times D-3
C
C STORE DATA
PYA(N) = YA
PYS(N) = YS
PALF(N) = ALF
T(N) = TL
PTG(N) = TG
HT(N) = Z
C
5. ASSUME PAI = PA
C
PA = P*(YA/(YA+YS+YB))
PAI = PA

CAI = H*PAI

REAL*8 M,M2

200 IF(CR.LT.0.00005) E=1.
IF(CR.LT.0.00005) GOTO201

M2 = K2*CR*DA/(KLA**2)
E1 = DSQRT(M2)/DTANH(DSQRT(M2))
EI = 1. + ((CR*DR)/(2.*CAI*DA))
EI = (DSQRT(DA/DR))+(CR/(2.*CAI))*(DSQRT(DR/DA))

C
C ASSUME LIQUID HOLD UP = 5% OF TOTAL VALUE.

C HU = 0.05
C XXX = HU*K2*CR/(KLA*A)
C
C IF (XXX.LT.20.) GO TO 550
C
EA = 1./(((EI-1.)**1.35)
EB = 1./(((EI-1.)**1.35)
EIR=1.+((1./((EA+EB)**(1./1.35))
E=EIR*(CAI-CAB)/CAI
IF(E.LT.1.0) WRITE(6,565)
565 FORMAT ('!! E < 1. ???'/)
C IF(E.LT.1.0) E=1.
201 CONTINUE

C
C550 WRITE (6,555)
C555 FORMAT (1X,' !!! E OUT OFF RANGE.'

C560 WRITE (6,565)
C565 FORMAT ('!! E < 1. ???'/)

C C CHACK E VALUE?
C WRITE (6,566)
C566 FORMAT ('/ C CHACK E CALCULATION. '/)
C WRITE (6,567)M2,M,SRM
C567 FORMAT ('',F15.4/F15.4/F15.4/
C WRITE (6,568)Q,QM,XXX,E
C568 FORMAT ('',F15.4/F15.4/F15.4/,..>> E',F15.4/
C C GO TO 900

C
C 6. CAL. ABSORPTION RATE

\[ R = \frac{(E \cdot KLA \cdot 1.0 - (H \cdot PA - CAB))}{(1.0 + ((E \cdot KLA \cdot H) \cdot 1.0 - KGA))} \]
\[ \text{CAINEW} = (PA \cdot H) - (R \cdot H / KGA) \]
\[ \text{PAIN} = \text{CAI} / H \]

C IF (DABS(CAINEW-CAI) .LE. DABS(0.00010*(CAINEW+CAI))) GOTO 700
C
C CAI = CAINEW
GO TO 200

C 7. COMPUTE DYA/DZ, DYS/DZ, DTG/DZ, AND
C DTG/DZ FROM THE EQ.S 30,31,32,..29)
C
700 PSI = 0.90*(2.7182818**((16.5362-(3985.44/(TLK-38.9974)))))/
> 101.13
YSI = PSI/(P-PAIN-PSI)
YAI = PAIN/(P-PAIN-PSI)
PS = P*(YS/(YA+YB+YS))

DYADZ = -KGA*A*(PA-PAIN)/GB
DYSDZ = -KGS*A*(PS-PSI)/GB
HDGA = (-1.0*GB)*(CPA*DYADZ + CPS*DYSDZ)/
> (1-DEXP(GB*(CPA*DYADZ + CPS*DYSDZ)/HGA))
DTGDZ = -HDGA*(TG-TL)/(GB*(CPB+YA*CPA+YS*CPS))

C REF. TEMP. T0 = 25 C.
T0 = 25.0
DTLDZ = (1.0/(LM*CL))*((GB*(CPB+YA*CPA+YS*CPS)*DTGDZ)
> + (GB*(CPS*(TG-T0) + HLH2O )*DYSDZ)
> + (GB*(CPA*(TG-T0) - HR)*DYADZ))

C 8. CHOOSE A SUITABLY SMALL VALUE OF DYA ,
C AN INCREMENT OF GAS COMPOSITION, SO THAT THE
C GRADIENTS DYA/DZ,DYS/DZ,DTG/DZ, AND DTL/DZ
C WILL NOT CHANGE TOO GREATIY .
C
DELYA = -0.00025*2.
IF(ALF.GT.0.4) DELYA = -0.00005*2.
DELZ = DELYA/DYADZ

C WRITE(6,10) ALF,PA,PAIN,PSI,Z,DELZ,E
C10 FORMAT( 'ALF',F10.6,'PA',F10.6,'PAIN',F10.6,'PSI',F10.6,'Z',F12.4,'DELZ',F12.4,'E')

C WHERE Z=0. FOR THE BOTTOM OF THE TOWER .
C
Z = Z + DELZ
9. COMPUTE THE CIRCUMSTANCES AT Z-NEXT.

\[
\begin{align*}
\text{YA} &= \text{YA} + \text{DELYA} \\
\text{YS} &= \text{YS} + \text{DELYS} \times \text{DYSDZ} \\
\text{TG} &= \text{TG} + \text{DELYS} \times \text{DTGDZ} \\
\text{TL} &= \text{TL} + \text{DELYS} \times \text{DTLDZ} \\
\text{LMOLD} &= \text{LM} \\
\text{LM} &= \text{LM} + \text{GB} \times \text{DELYS} \times (\text{DYADZ} + \text{DYSDZ}) \times 29.
\end{align*}
\]

\[
\begin{align*}
\text{CR} &= \frac{(\text{LMOLD} \times \text{CR}/1000.) - \text{STOI} \times \text{GB} \times \text{DELYA}}{\text{LM}} \times 1000. \\
\text{CP} &= \frac{(\text{LMOLD} \times \text{CP}/1000.) + \text{GB} \times \text{DELYA}}{\text{LM}} \times 1000. \\
\text{ALF} &= \frac{(\text{CTOT} - \text{CR} + \text{CAB})}{\text{CTOT} \times 2}.
\end{align*}
\]

C PRINT SOME RESULTS

\[
\begin{align*}
\text{NIN} &= \frac{\text{N}}{100} \\
\text{IF} (\text{NIN} \geq \text{NOUT}) \text{ CALL} \text{ CHACK} \ (\text{NIN}, \text{ALF}, \text{LM}, \text{TL}, > \text{YA}, \text{YB}, \text{YS}, \text{TG}, \text{Z}, \text{NOUT}) \\
\text{IF} (\text{NDUM} \text{EQ} \text{0.AND.} \text{Z.GT.}110.) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM}) \\
\text{IF} (\text{Z.GT.110.AND.Z.LT.220.}) \text{ GOTO} 850 \\
\text{IF} (\text{NDUM} \text{EQ} \text{1.AND.} \text{Z.GT.}220.) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM}) \\
\text{IF} (\text{Z.GT.220.AND.Z.LT.330}) \text{ GOTO} 850 \\
\text{IF} (\text{NDUM} \text{EQ} \text{2.AND.} \text{Z.GT.}330.) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM}) \\
\text{IF} (\text{Z.GT.330.AND.Z.LT.440.}) \text{ GOTO} 850 \\
\text{IF} (\text{NDUM} \text{EQ} \text{3.AND.} \text{Z.GT.}440.) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM}) \\
\text{IF} (\text{Z.GT.440.AND.Z.LT.550}) \text{ GOTO} 850 \\
\text{IF} (\text{NDUM} \text{EQ} \text{4.AND.} \text{Z.GT.}550.) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM}) \\
\text{IF} (\text{Z.GT.550.AND.Z.LT.650}) \text{ GOTO} 850 \\
\text{IF} (\text{NDUM} \text{EQ} \text{5.AND.} \text{Z.GT.}655.) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM}) \\
\text{IF} (\text{Z.GT.655.}) \text{ GOTO} 850
\end{align*}
\]

850 CONTINUE

\[
\begin{align*}
\text{IF} (\text{YA} \lt \text{YAOUT}) \text{ CALL} \text{ CKOUT} \ (\text{Z}, \text{ALF}, \text{YA}, \text{TL}, \text{N}, \text{NDUM})
\end{align*}
\]

10. REPEAT STEP 3 TO 9 UNTIL YA FOR THE OUTLET GAS IS REACHED.

\[
\begin{align*}
\text{IF} (\text{YA} \lt \text{YAOUT}) \text{ GO TO} 900 \\
\text{N}=\text{N}+1 \\
\text{IF} (\text{N.GT.NSET}) \text{ GO TO} 900 \\
\text{WRITE}(8,1111) \text{Z,PA,ALF,TL,TG,E} \\
1111 \text{ FORMAT}(6F11.6) \\
\text{GOTO} 300
\end{align*}
\]

11. CHECK THE ASSUMPTION OF STEP 1.

\[
\begin{align*}
\text{IF NOT MATCHED, IT MAY BE APPROPRIATE GUESS FOR} \\
\text{THE NEXT ITERATION. HOWEVER, IF THE SOLUTION IS FOUND} \\
\text{TO BE INSENSITIVE TO THE ASSUMED VALUES OF TG AND YS}
\end{align*}
\]
(THROUGH THE BACK CALCULATION OF OUTLET LIQUID TEMP. FROM AN OVERALL ENTHALPY BALANCE) FURTHER ITERATION WILL NOT BE REQUIRED.

WRITE(6,905)
FORMAT(/' ***** THE END CONDITION *****'/)
WRITE(6,910) CTOT
FORMAT(/' TOTAL CONCN. OF MEA ',F10.5,' G-MOL/L')
WRITE(6,915) ALFIN
FORMAT(/' CO2 LOADING (IN) ',F10.5,' ')
WRITE(6,920) LMIN
FORMAT(/' INLET L. MOLAR VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,925) TLIN
FORMAT(/' INLET LIQUID TEMP. ',F10.5,' C.')
WRITE(6,930) ALFOUT
FORMAT(/' CO2 LOADING (OUT) ',F10.5,' ')
WRITE(6,945) LOUT
FORMAT(/' INLET LIQUID TEMP. ',F10.5,' C.')
WRITE(6,950) GB
FORMAT(/' INLET AIR MOL. VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,955) YAIN
FORMAT(/' INLET MOL FRAC. OF CO2 ',F10.5)
WRITE(6,960) YBIN
FORMAT(/' INLET MOL FRAC. OF AIR ',F10.5)
WRITE(6,965) TGIN
FORMAT(/' INLET GAS TEMP. ',F10.5,' C.')
WRITE(6,970) YAOUT
FORMAT(/' OUTLET MOL FRAC. OF CO2 ',F10.5)
WRITE(6,975) YBOUT
FORMAT(/' OUTLET MOL FRAC. OF AIR ',F10.5)
WRITE(6,980) YSOUT
FORMAT(/' OUTLET MOL FRAC. OF H2O ',F10.5)
WRITE(6,985) TGOUT
FORMAT(/' OUTLET GAS TEMP. ',F10.5,' C.')
WRITE(6,990)
FORMAT(/' *** >> CALCULATION RESULTS')
WRITE(6,991) ALF
FORMAT(/' CO2 LOADING (IN) CAL. ',F10.5,' /L')
WRITE(6,993) LM
FORMAT(/' INLET L. MOLAR VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,994) TL
FORMAT(' INLET LIQUID TEMP. ',F10.5,' C.')

WRITE(6,995) YA
FORMAT(' OUTLET MOL FRAC. OF CO2 ',F10.5)
WRITE(6,996) YB
FORMAT(' OUTLET MOL FRAC. OF AIR ',F10.5)
WRITE(6,997) YS
FORMAT(' OUTLET MOL FRAC. OF H2O ',F10.5)
WRITE(6,998) TG
FORMAT(' OUTLET GAS TEMP. ',F10.5,' C.')
WRITE(6,999) Z
FORMAT(' THE TOTAL HEIGHT ',F10.5,' CM.')

C SCALING
DO 1 1=1,N
   HT(I) = 2. + (HT(I)/(1.*100.))
   PMIX = 1.+PYS(I) +PYA(I)
   PMIXX = 1. + PYA(I)
   PYA(I) = 1. +((PYA(I)/(PMIXX))/0.03)
   PYS(I) = 1. +((PYS(I)/(PMIX))/0.03)
   PALF(I) = 1. + (PALF(I)/.1)
   T(I) = 1. + (T(I)*5./50.)
   PTG(I) = 1. + (PTG(I)*5./50.)
1 CONTINUE

C PLOTTING
CALL AXIS(1.,5,'P. CO2',-6,7.,0.,0.,0.03)
CALL AXIS(1.,1.,'P. H2O',-6,7.,0.,0.,0.03)
CALL AXIS(1.,1.5,'CO2 LOADING',-11,7.,0.,0.,0.6)
CALL AXIS(1.,2.,'TEMP. (C)',-9,7.,0.,0,10.)
CALL AXIS(1.,2.,'HEIGTH (M)',10,7.,90.,0.,1.)
CALL PLOT(1.,2.,3)
CALL PLOT(2.,2.,2)
CALL PLOT(2.9,2)
CALL PLOT(3.,9.,2)
CALL PLOT(3.,2.,2)
CALL PLOT(4.,2.,2)
CALL PLOT(4.,9.,2)
CALL PLOT(5.,9.,2)
CALL PLOT(5.,2.,2)
CALL PLOT(6.,2.,2)
CALL PLOT(6.,9.,2)
CALL PLOT(7.,9.,2)
CALL PLOT(7.,2.,2)
CALL PLOT(8.,2.,2)
CALL PLOT(8.,9.,2)
CALL PLOT(7.,9.,2)
CALL PLOT(8.,3.,3)
CALL PLOT(1.,3.,2)
CALL PLOT(1.,4.,2)
CALL PLOT(8.,4.,2)
CALL PLOT(8.,5.,2)
CALL PLOT(1.,5.,2)
CALL PLOT(1.,6.,2)
CALL PLOT(8.,6.,2)
CALL PLOT(8.,7.,2)
CALL PLOT(1.,7.,2)
CALL PLOT(1.,8.,2)
CALL PLOT(8.,8.,2)
CALL PLOT(8.,9.,2)
CALL PLOT(1.,9.,2)

CALL PLOT(1.,2.,3)

DO 2 I=1,N
   CALL SYMBOL(PYA(I),HT(I),.010,0,0.,-2)
2 CONTINUE

CALL PLOT(1.,2.,3)

DO 3 I=1,N
   CALL SYMBOL(PYS(I),HT(I),.010,1,0.,-2)
3 CONTINUE

CALL PLOT(1.,2.,3)

DO 4 I=1,N
   CALL SYMBOL(PALF(I),HT(I),.010,2,0.,-2)
4 CONTINUE

CALL PLOT(1.,2.,3)

DO 5 I=1,N
   CALL SYMBOL(T(I),HT(I),.010,11,0.,-2)
5 CONTINUE

CALL PLOT(1.,2.,3)

DO 6 I=1,N
   CALL SYMBOL(PTG(I),HT(I),0.01,5,0.,-2)
6 CONTINUE

CALL SYMBOL(2.0,10.0,0.08,0,0.,-1)
CALL SYMBOL(2.2,10.0,0.08,'P-CO2 (ATM)',0.,11)
CALL SYMBOL(3.5,10.,0.08,1,0.,-1)
CALL SYMBOL(3.7,10.,0.08,'P-H2O (ATM)',0.,11)

CALL SYMBOL(5.0,10.0,0.08,2.,0.,-1)
CALL SYMBOL(5.2,10.0,0.08,'CO2 LOADING',0.,11)
CALL SYMBOL(2.0,9.7,0.08,11,0.,-1)
CALL SYMBOL(2.2,9.7,0.08,'LIQUID TEMP. (C)',0.,16)
CALL SYMBOL(3.5,9.7,0.08,5,0.,-1)
CALL SYMBOL(3.7,9.7,0.08,'GAS TEMP. (C)',0.,13)

CALL PDATA(PEG,PEC,PET,PHT,NEX)

DO 1001 I=1,NEX
   EG = 1.+ (PEG(I)/0.03)
   EC = 1. + (PEC(I)/.1)
   ET = 1.+(PET(I)/10.)
   EH = 2.+ (PHT(I)/100.)
   CALL SYMBOL(EG,EH,.12,0,0.,-1)
   CALL SYMBOL(EC,EH,.12,2,0.,-1)
   CALL SYMBOL(ET,EH,.12,11,0.,-1)
1001 CONTINUE

C+++++-----------------------------------------------
CALL SYMBOL(4.,9.25,.25,'RUN# T22',0,8)
C+++++-----------------------------------------------
CALL PLOTND
STOP
END

SUBROUTINE CHACK(NIN,ALF,LM,TL,YA,YB,YS,TG,Z,NOUT)
IMPLICIT REAL*8(A-M,O-Z)
WRITE(6,990)
990 FORMAT(/' :::: INTERMEDIAD CALCULATION RESULTS')
WRITE(6,991) ALF
991 FORMAT(/' C02 LOADING ',F10.5,' ')
WRITE(6,993) LM
993 FORMAT(' LIQUID MOLAR VEL. ',F10.5,' G-MOL/SEC.CM2')
WRITE(6,994) TL
994 FORMAT(' LIQUID TEMP. ',F10.5,' C.')
WRITE(6,995) YA
995 FORMAT(' MOL FRAC. OF CO2 ',F10.5)
WRITE(6,996) YB
996 FORMAT(' MOL FRAC. OF AIR ',F10.5)
WRITE(6,997) YS
997 FORMAT(' MOL FRAC. OF H2O ',F10.5)
WRITE(6,998) TG
998 FORMAT(' GAS TEMP. ',F10.5,' C.')
WRITE(6,999) Z
999 FORMAT(' THE HEIGHT ',F10.5,' CM./')

NOUT = NOUT + 1
C
RETURN
END

******************************************************************
C
SUBROUTINE CKOUT(Z,ALF,YA,TL,N,NDUM)
C
IMPLICIT REAL*8(A-M,O-Z)
C
WRITE(7,990)
990 FORMAT(/' :::: INTERMEDIAD CALCULATION RESULTS')

WRITE(7,999) Z
999 FORMAT(/' THE HEIGHT ',F10.5,' CM./')
PYA = 100.*YA/(1.+YA)
WRITE(7,995) PYA
995 FORMAT(' CO2 CONC. (%) ',F10.5)
WRITE(7,991) ALF
991 FORMAT(' CO2 LOADING ',F10.5,' ')

WRITE(7,994) TL
994 FORMAT(' LIQUID TEMP. ',F10.5,' C.)
C
NDUM=NDUM+1
RETURN
END

******************************************************************
C
SUBROUTINE PDATA(EG,EC,ET,EH,NEX)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION EG(20),EC(20),ET(20),EH(20),G(20),C(20),T(20),H(20)

NEX=7
DATA H/0.000,110.,220.,330.,440.,550.,655./
DATA G/.1910,.1280,.0530,.0120,.0010,.0000,.0000/
DATA C/.443,.292,.1250,.0330,.0000,.0000,.0000/
DATA T/47.0,45.0,29.0,21.0,19.0,19.,19./
C
DO 10 I=1,NEX
EH(I)=H(I)
EG(I)=G(I)
EC(I)=C(I)
10 ET(I)=T(I)
RETURN
END
SUBROUTINE SOL(TLK, CTOT, ALF, PECO2)
IMPLICIT REAL*8(A-H,O-Z)

C CAL PCO2 AT EQUILIBRIUM

IF(ALF.LE.0.3) PECO2=0.0
IF(ALF.LE.0.3) GOTO 100

DX1 = 2.9410 + (1.5940D+01)*(ALF) - (6.3439D-00)*(ALF**2)
DX2=(2.6218D-01)*(1./ALF)+7.2388D-1*CTOT-(7.881D-02)*(CTOT**2)
DX3 = -(8.9512D-02)*(TLK) + (1.8524D-04)*(TLK**2)

PECO2 = (DX1+DX2+DX3)/760.
100 CONTINUE
RETURN
END