RATE-BASED MODELING OF ACID GAS ABSORPTION AND STRIPPING USING AQUEOUS ALKANOLAMINE SOLUTIONS

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by

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THESIS

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To my parents

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Abstract

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Two models for the simultaneous absorption and stripping of H_2S and CO_2 using aqueous alkanolamines were developed. The first model is a rate-based approach to modeling methyldiethanolamine (MDEA) systems which uses DeCoursey's method to calculate the CO_2 enhancement factor. The second model was developed within the framework of the process simulator ASPEN PLUS™ to model MEA, DGA, DEA, MDEA, and mixed amines. A kinetic subroutine was developed that contains complex kinetic expressions for each of these amine systems. The MDEA model was used to explore the effect of changing operating conditions on the system performance of a typical Claus tail gas cleanup application. A reasonable liquid rate and steam rate resulted in an absorber H_2S leak of 98 ppm. Addition of a strong acid to this system reduces the leak to 6 ppm. Similarly, reducing the stripper pressure from 2 atm to 0.5 atm increases performance to a leak of 4 ppm. In both cases, the improved performance is due to linearization of the H_2S equilibrium. In the case of reducing the stripper pressure, an increase in the gas phase mass transfer coefficient and number of transfer units also contributes to the improved performance. The ASPEN PLUS™ model was used to generate equilibrium data for the various amine systems. This model satisfactorily represents the amine equilibrium, including data for mixed amine systems. The kinetic subroutine developed calculates reasonable reaction rates and can be used with either an equilibrium-based or a rate-based column model.

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Chapter 1

Introduction

The removal of H_2S and CO_2 from gas streams, commonly referred to as acid gas treating, is necessary in many industrial processes including oil and gas purification, ammonia manufacture, ethylene manufacture, and sulfur recovery. The most common method used to remove these acidic components is absorption into a liquid solvent, particularly aqueous alkanolamine solutions (Astarita et al., 1983). The alkanolamine treating process was first introduced in 1930 when Bottoms patented the process. Since that time, the process has remained virtually unchanged. This work discusses computer simulation of the aqueous alkanolamine process used to remove H_2S and CO_2 from gas streams.

1.1 The Acid Gas Treating Process

Figure 1.1 illustrates the basic absorption/stripping process used to remove H_2S and CO_2 with alkanolamines. The feed gas containing undesirable amounts of H_2S and/or CO_2 enters the absorber and contacts the amine solution countercurrently. The typical absorber is a trayed or packed column operated at pressures from atmospheric for Claus tail gas cleanup to several hundred atmospheres for a natural gas application. The typical amine inlet temperature is 40°C; however, this temperature changes throughout the column because the H_2S and CO_2 react exothermically with the amine solution. The gas exiting the absorber contains the desired amount of H_2S and/or CO_2 and is further processed. The loaded (or rich) amine solution exiting the absorber passes through a cross-exchanger and serves as the liquid feed to the regenerator (stripper).

In the stripper, the chemical reactions between the acid gases and the amine solution are reversed by supplying energy, usually live or reboiled steam. A stripper is also a trayed or packed column but is usually operated at 1 to 2 atm to

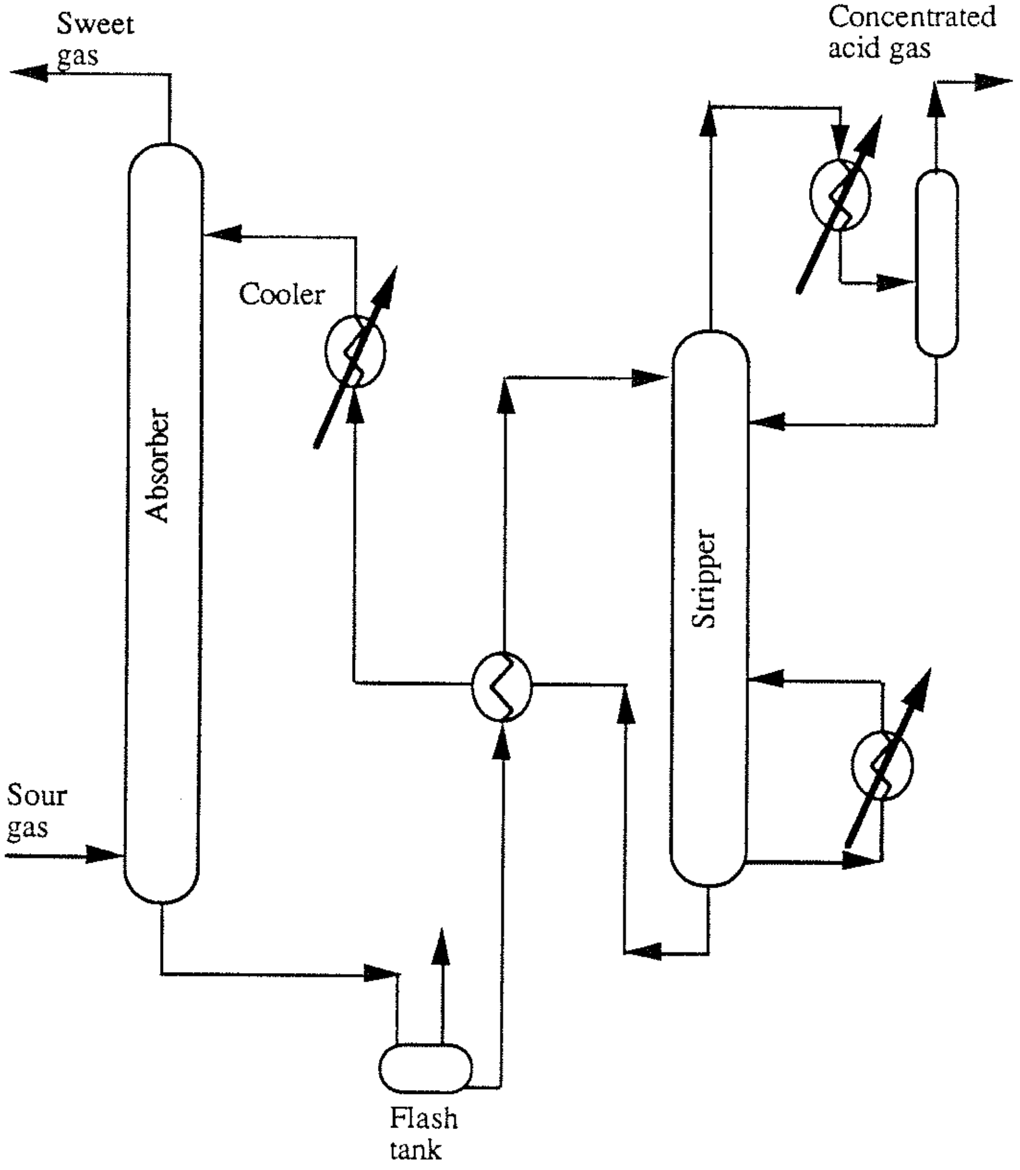

Figure 1.1: Typical Acid Gas Treating Process Flow Diagram

assist in the regeneration process. The liquid amine feed from the absorber is heated to about 120°C before entering the stripper. The steam supplies the additional energy necessary to reverse the chemical reactions and "strip" the H_2S and CO_2 from solution. The amine exiting the stripper is now regenerated and returns to the absorber. The outlet gas from the stripper typically has a high H_2S concentration; therefore, in many cases this gas stream is sent to a Claus or other type of sulfur recovery unit which converts the H_2S into useful elemental sulfur. Many times the Claus process includes an acid gas treating system which recovers the unconverted H_2S in the Claus tail gas. In this way the maximum amount of H_2S is converted into elemental sulfur. If the cost of a sulfur recovery system can not be justified, the gas from the stripper is sent to a flare and burned.

1.2 Characteristics and Types of Amines

Alkanolamines are basic in nature with the amine nitrogen able to accept a proton; therefore, amines easily react with the acidic components H_2S and CO_2. The most common industrial alkanolamines include monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Considering the acid gas treating applications using alkanolamine solutions in 1987, DEA based solvents were used to process 47% of the treated volume while MEA and MDEA based solvents were used to process 23% and 17%, respectively (Cross et al., 1990). Other commercially available amines include diglycolamine (DGA) and diisopropanolamine (DIPA). Recently, some companies have developed proprietary hindered amines.

MEA is typically used as a 10-20 wt% solution in water. The acid gas loading (moles of acid gas absorbed/mole of amine) is usually limited to 0.4 due to corrosion problems. Loadings much higher than this require the use of stainless steel equipment or corrosion inhibitors. MEA is the most corrosive of the common amines and has a high heat of reaction, 20 kcal/mole, with CO_2 (Polasek and Bullin, 1984). This high heat of reaction results in high energy costs in the stripper.

DEA is typically used as a 25-35 wt% solution in water. The acid gas loading is limited to the same value as MEA again due to corrosion problems; however, because DEA solutions generally are more concentrated than MEA solutions, the DEA solvent circulation rate is smaller. Because DEA is a secondary amine, the reaction between CO_2 and DEA is slower than the equivalent reaction with MEA; therefore, under certain conditions DEA may not be able to remove the required amount of CO_2. Although DEA is generally not used for selective removal of H_2S, certain conditions allow DEA to be selective (Polasek and Bullin, 1984). DEA is the most widely used of the amines because it generally does a good job of removing H_2S and CO_2 and has a heat of reaction with CO_2 of only 16 kcal/mole.

DGA can be used up to 60 wt% in water with a loading of 0.4 with no corrosion problems. The high DGA concentration results in lower solvent circulation rates than with MEA or DEA. DGA has a tendency to react preferentially with CO_2 and to absorb most sulfur compounds (Polasek and Bullin, 1984). Unfortunately, DGA has the highest heat of reaction with CO_2 of any of the common amines (20.8 kcal/mole).

Finally, MDEA is considerably less corrosive than the other amines and is typically used as a 50 wt% solution. Other advantages of MDEA are its low heat of reaction with CO_2 (14 kcal/mole) and its ability to selectivity remove H_2S over CO_2. Because MDEA can be used in high concentrations and has a low heat of reaction with CO_2, energy savings can be significant. MDEA is not able to remove a large amount of CO_2 without providing large gas-liquid contact times in the absorber.

1.3 Amine Applications

1.3.1 Bulk H_2S and CO_2 Removal

Many acid gas applications require bulk removal of both H_2S and CO_2. Bulk removal means purifying the feed gas to very low concentrations of H_2S and CO_2. For example, a typical natural gas purification application might process a feed gas with 1% H_2S and 30% CO_2 down to an outlet gas composition of less than 4 ppm H_2S and 1% CO_2 (Astarita et al., 1983). Other processes that might be generalized as bulk removal applications include hydrogen, ammonia, and ethylene manufacture, coal gasification, and refinery processes.

Primary and secondary amines (MEA, DEA, DGA) are generally used for bulk H_2S and CO_2 removal. These amines react directly with both acid gases. Primary and secondary amines react with H_2S through an instantaneous proton transfer mechanism. The reaction with CO_2, although not instantaneous, is very fast and forms a carbamate species. These fast reactions result in easy removal of H_2S and CO_2. DEA is generally used more than MEA because DEA is less corrosive and has a lower heat of reaction.

1.3.2 Selective Removal of H_2S

For many applications, a feed gas may contain both H_2S and CO_2 but only the H_2S needs to be removed. These applications require selective removal of the H_2S. For example, the feed gas to a Claus unit needs to be rich in H_2S to obtain a reasonable efficiency. Therefore, a gas stream containing both H_2S and CO_2 can be selectively treated so that the gas leaving the stripper is rich in H_2S and can be fed to a Claus unit. Other selective applications include Claus tail gas cleanup and recovery of CO_2 for well injection.

Tertiary amines (MDEA) and hindered amines are generally used to perform selective processes. This selective process is possible because these amines react very quickly with H_2S but slowly with CO_2. Before reacting with tertiary or hindered amines, CO_2 must first react with water to form carbonic acid which is a slow reaction; however, H_2S is able to react directly with these amines through a very fast proton transfer mechanism. Thus, tertiary and hindered amines exhibit large kinetic selectivity for H_2S over CO_2 because CO_2 can not react directly with them. This kinetic selectivity is much greater with tertiary and hindered amines than with primary or secondary amines.

1.3.3 Amine Blends

The most recent trend in the use of alkanolamines is the use of mixed amine solutions, usually a combination of MDEA and either MEA or DEA. Recent work has shown that the DEA or MEA greatly increases the absorption of CO_2 over MDEA alone while exhibiting a lower heat of reaction than DEA or MEA alone (Polasek et al., 1990; Campbell and Weiland, 1989; Critchfield, 1988; Katti and Wolcott, 1987). Therefore, the absorption characteristics of MEA or DEA are retained to remove bulk CO_2 while the presence of MDEA enhances the regeneration process. These blends are best suited for bulk removal of acid gases.

1.4 Modeling the Amine Process

Due to the importance of absorption using alkanolamine solutions, the development of computer models to simulate the absorption/stripping process using these solutions is important for design and retrofit purposes. This system is governed by complicated mass transfer with simultaneous chemical reaction. Mass transfer models have been developed based on rigorous, numerical solution of the differential equations describing the simultaneous transfer of H_2S and CO_2 with chemical reaction (Bou-Hamra, 1990; Glasscock, 1990; Versteeg, 1986; Blauwhoff and van Swaaij, 1985a; Cornelisse et al., 1980). Unfortunately, these rigorous solutions generally require a large amount of computer time and are not practical for use in a complete process simulator. Therefore, some simplifying approximations must be chosen in order to solve for the mass transfer analytically in a process model.

Many approaches have been used in representing the mass transfer which occurs for simultaneous absorption and desorption of H_2S and CO_2 in alkanolamines. The simplest and crudest assumption is that the system is not mass transfer but equilibrium controlled. This type of model is sometimes useful for nonselective, ethanolamine systems (Vaz et al., 1981); however, this approximation is inadequate for design of a selective treating system because typical design procedures include estimation of stage efficiencies. The effect of chemical reactions in this system makes the prediction of stage efficiencies difficult because efficiencies are different for H_2S and CO_2 and vary at each stage. Stage efficiencies are usually underestimated as a safety factor; however, this overdesign destroys the selectivity of an absorption/stripping system. The more recent approach to modeling H_2S and CO_2 absorption into alkanolamines is the rate or nonequilibrium approach. This approach avoids the standard use of efficiencies by basing the amount of absorption at each stage on actual mass fluxes. The effect of chemical reaction on the mass fluxes is usually calculated with an analytical expression for the mass transfer enhancement factor. The enhancement factor is defined as the actual flux occurring across the gas-liquid interface divided by the flux that would occur without the chemical reaction. An extensive literature review of rate-based models is presented in Chapter 2.

1.5 Summary of This Work

This work is concerned with the rate-based modeling of alkanolamine absorption/stripping systems, specifically selective absorption using MDEA and absorption using blended amines. MDEA modeling was done by extending the absorption/stripping model developed by Hermes (1987). The simulation program ASPEN PLUS™ by Aspen Technology, Inc., was developed to model MEA, DGA, DEA, and amine blends.

This work extends Hermes (1987) is several ways. The system physical property calculations were extended by adding expressions to calculate diffusion coefficients, MDEA solution viscosity and density, and water viscosity. A subroutine was also added to calculate the mass transfer coefficients and interfacial area for both sieve and bubble cap trays. The Henry's constant expressions and some of the chemical reaction equilibrium constants were changed. Using these new equilibrium expressions, the CO_2 and H_2S equilibrium constants were fit to an empirical expression with six adjustable parameters. Finally, the CO_2-MDEA rate constant expression was updated. The extended model continues to use an analytical expression for the CO_2 enhancement factor by solving the diffusion equations using the approximation of DeCoursey (1982) for the reaction rate term. The model was used to investigate the effect of adding a strong acid to the solvent, reducing the stripper pressure, and reducing the number of stripper stages on system performance. The sensitivity of the model results to values of the H_2S equilibrium constant, H_2S heat of reaction, mass transfer coefficients, and CO_2-MDEA rate constant is also investigated.

The second modeling effort in this work consisted of developing Aspen Technology's ASPEN PLUS™ to model all of the common alkanolamine systems. ASPEN PLUS™ was chosen because it contains an accurate thermodynamic model for electrolytes, a rate-based column model, and the ability to include complicated reaction rate expressions. Input files containing physical properties and chemical reaction equilibrium constants specific to the alkanolamine systems were developed. In addition, subroutines were developed to calculate the reaction rate for rate limited reactions. These files can be used to perform equilibrium or rate-based modeling. Aspen Technology is in the process of developing a rate-based column model, but this model was not available with the current version of ASPEN PLUS™. Therefore, the files developed in this work were tested using the equilibrium column model.

Chapter 2

Literature Review

Accurate computer process simulators are needed to model acid gas treating using alkanolamines for purposes of process designs and retrofits. The traditional modeling approach of assuming equilibrium stages and then applying an efficiency is not satisfactory for most amine applications due to the complication of mass transfer with chemical reaction. Therefore, several rate-based process simulators have been developed over the past several years. These models provide a much more accurate simulation of process conditions than an equilibrium approach.

As part of this work, the various rate-based models for simulation of acid gas treating using aqueous alkanolamines have been reviewed. These models can be classified as either academic, commercial, or industrial models. The academic models focus primarily on the selective process while the commercial and industrial models are more general.

2.1 Academic Models

The need for accurate design of selective absorption systems resulted in rate-based modeling research efforts. Although many problems existed in designing other amine systems, typical MEA or DEA systems were common, and design was based on experience. Selective systems were relatively new and required accurate design because design errors could easily destroy the selective capability of the system. Therefore, all of the academic models were developed to model only MDEA in order to gain a better understanding of the basic principles of this important, selective system.

Table 2.1 summarizes the models considered to be academic efforts. The first attempt to use the rate-based approach for the aqueous alkanolamine-H_2S-CO_2 system appears to be Cornelissen (1980). Many of the basic assumptions used in his model are used in later models. The details of the thermodynamic model used

Table 2.1: Summary of Academic Rate-Based Alkanolamine Models

Model	Flow Sheet Options	Validation Method	Thermodynamic Models		CO2 Kinetic Model
			Liquid	Gas	
Cornelissen	Trayed absorber	Exptl data from a 0.11 m diameter absorber	H2S-amine equil. determined by experiment.	not available	Uses irreversible, pseudo-first order in CO2. Rate constants for CO2 with H2O and OH-: Pinsent et al. (1956). The amine rate constant was determined experimentally.
Yu and Astarita	packed absorbers	none	Semi-empirical fit to data from Jou et al. (1981).	not available	Reversible, second order kinetics are considered. The rate constant is from Yu et al. (1985).
Kelly et al.	Packed absorbers	Exptl data from a 0.053 m i.d. absorber	Edwards (1974). Several other methods were compared.	Redlich-Kwong modified by Cheuh and Prausnitz (1967)	Reversible, second order kinetics are considered. CO2 kinetic data is taken from Yu (1985).
van Swaaij et al.	absorber/stripper, Claus sulfur recovery unit, Shell Claus off-gas treater tail gas unit	none	Blauwhoff and van Swaaij (1980)	Soave-Redlich-Kwong	Reversible reactions are considered. Rate constants from Danckwerts and Sharma (1966), Blauwhoff et al. (1984), and Blauwhoff (1982)
This work	trayed absorbers and strippers	none	Empirical fit to experimental data of Jou et al. (1982, 1986)	Ideal gas	Reversible, second order kinetics are considered. CO2-MDEA rate constant is from Littel et al. (1990). CO2-OH- value is from Astarita et al (1983).

Table 2.1 (cont.): Summary of Academic Rate-Based Alkanolamine Models

Model	Mass Transfer Model	Numerical Approach	Computer Specifications	References
Cornelissen	Uses analytical expressions from Danckwerts (1970). The concentration profiles are linearized to yield algebraic equations. Mass transfer parameters are from experiments.	Single trays are solved using Kevorkian and Snoek (1973) A second method iterates on the absorber tray-by-tray	not available	Cornelissen (1980)
Yu and Astarita	Algebraic model that uses the pseudo-first order enhancement factor with the amine concentration included Mass transfer parameters: Onda et al. (1968)	Runge-Kutta		Yu (1985); Yu and Astarita (1987a); Yu and Astarita (1987b)
Kelly et al.	Instantaneous rxns: Olander (1960) CO2 rxn: differential equations Mass transfer parameters: Onda et al.(1968) Considers axial dispersion and liquid holdup	Pseudo Newton-Raphson for set of nonlinear equations. Orthogonal collocation for differential equations.	Micro-VAX II requires about 90 minutes.	Lindner (1988); Lindner et al. (1987); Lindner et al. (1988).
van Swaaij et al.	Fluxes are calculated analytically using Secor and Beutler (1967) for H2S and Hikita and Asai (1963) for CO2 or numerically using Cornelisse et al. (1980).Mass transfer parameters: Sharma and Gupta (1967)	Tray-by-tray calculations using a Newton-Raphson technique.	not available	Blauwhoff et al. (1985b)
This work	Enhancement factor from DeCoursey (1982) Mass transfer parameters: Sharma et al. (1969) or Chan and Fair (1984).	Tray-by-tray calculations using secant method and two variable secant method	VAX 6410 (5 to 10 min) VAX 11/780	Hermes (1987); Hermes and Rochelle (1987)

were unavailable; however, the H_2S-amine equilibrium was determined experimentally and then incorporated into the model. The model uses Lewis's two-film theory with linearized concentration profiles in the interface which results in algebraic rather than differential equations. The assumption of irreversible kinetics does not allow simulation of a regenerator. Using the model, Cornelissen showed that under certain conditions the simultaneous absorption of CO_2 and H_2S can cause H_2S to desorb despite an absorptive driving force. Experimental data from a lab scale absorber were used to verify the model.

The work of Yu and Astarita (see Table 2.1 for references) and Lindner et al. (see Table 2.1 for references) focused entirely on absorption using MDEA in packed columns. The model by Yu and Astarita was the first academic effort to model this system in packed columns. Yu and Astarita consider the CO_2 kinetics to be reversible and second order; however, they do not discuss simulation of a regenerator. The pseudo-first order enhancement factor expression is expanded by including an amine concentration term to account for the effect of H_2S absorption on CO_2 absorption. The model was used to simulate both isothermal and adiabatic absorbers. As expected, the results indicated that considering an absorber to be isothermal can result in significant absorber design errors.

The work of Lindner et al. (see Table 2.1 for references) is unique because it was concerned not only with producing a packed tower model for MDEA that was accurate but also one that was computationally efficient. They used the same kinetic representation for the CO_2-amine reaction as Yu and Astarita; however, this model contains more rigorous thermodynamic and mass transfer models. As a test of both accuracy and efficiency, several equilibrium models were compared including the assumption of an ideal liquid, the method of Edwards (1974), the method of Chakravarty (1985), and the addition of more data to the method of Chakravarty (1985). A detailed hydrodynamic model which considers both axial dispersion and static liquid holdup was used. By changing certain parameters of this model, the validity of various hydrodynamic assumptions could be investigated under different absorption conditions. The model results agreed well with experimental data from a laboratory packed tower.

The work of Blauwhoff et al. (1985b) is the most flexible of the models classified as academic efforts. This model has the ability to model an entire sour gas plant including sulfur recovery. This work is unique in three other ways. First, in addition to a typical trayed absorber, this work also looked at modeling the absorption process as a series of trickle bed reactors. Second, the model has the ability to solve the mass transfer problem both analytically and numerically. For the conditions investigated, the analytical method proved to be competitive with the numerical approach in the accuracy of the results while using less computation time. The authors used the analytical method to generate most of their results. Finally, a fairly detailed economic analysis was done for eight different sulfur recovery plants based on results from the model.

For completeness, the MDEA model described in Chapter 3 of this thesis is summarized in Table 2.1. As mentioned earlier, this MDEA model is an extension of Hermes (1987); therefore, his work is not detailed here. In addition, the academic work done by Weiland et al. has expanded into a commercial model; therefore, this model is described in the next section.

2.2 Commercial Models

Prior to the academic effort to develop selective models, several researchers developed general amine simulators for commercial use. These models began to have a selective design capability about the same time the academic models were developed. Table 2.2 compares these commercial models. The models by Bullin et al., Tomcej et al., and Weiland et al. are commercially known as TSWEET, AMSIM, and GASPLANT (or GASPLANT-PLUS), respectively. The model by Weiland et al. began as an academic effort before expanding commercially. Because of their commercial use, all of these models have been verified against several sets of pilot plant or full-scale operating data.

The model developed by Bullin et al. (see Table 2.2 for references) uses the flexible flowsheet approach which allows the user to arrange the process flow diagram using various unit operation blocks. Including the amines shown in

Table 2.2: Summary of Commercial and Industrial Rate-Based Alkanolamine Models

Model	Type of Amine Simulated	Flow Sheet Options	Thermodynamic Models Liquid	Thermodynamic Models Gas	CO_2 Kinetic Model
Bullin et al.	MEA, DEA DGA, MDEA, mixed amines	Trayed or packed absorbers/strippers, flash tanks, heat exchangers, column side streams, pumps, reclaimer, holdup tank	Modified Kent and Eisenberg (1976) model	Soave-Redlich-Kwong	Developed a kinetic model to predict effect of residence time, solution concentration, pressure, temperature, and type of amine on the CO_2 absorption rate.
Tomcej et al.	MEA, DEA, MDEA	Trayed absorbers and strippers, flash tanks, heat exchangers, column side streams	Modified Kent and Eisenberg (1976).	not available	MEA/DEA - Uses an apparent first order constant based on Laddha and Danckwerts (1981). MDEA - Uses a pseudo-first order rate constant from Tomcej et al (1986).
Weiland et al.	MEA, DEA, DIPA, MDEA, DGA, mixed amines	Trayed or packed absorbers/strippers, flash tanks, heat exchangers, column side streams	Chakravarty (1985) added to Deshmukh and Mather (1981).	Peng-Robinson	The MEA /DEA reactions are second order, irreversible in the absorber. All reactions are considered instantaneous in the stripper.
Dow Chemical Company	MEA, DEA, MDEA based solvents and mixed amines	Trayed absorbers and strippers	Chakravarty (1985) added to Deshmukh and Mather (1981). Separate model for low loadings.	Peng-Robinson	MDEA - second order overall using a kinetic expression similar to that of Yu et al. (1985). Other amines rate expressions not available.

Table 2.2 (cont.): Summary of Commercial and Industrial Rate-Based Alkanolamine Models

Model	Mass Transfer Model	Numerical Approach	Computer Specifications	References
Bullin et al.	not available	Rigorous tray-by-tray calculations using Ishii-Otto (1973)	PC version	Bullin et al. (1981); Holmes et al. (1984); Polasek et al. (1983); Polasek et al. (1990)
Tomcej et al.	Enhancement factor: Uses pseudo-first order expression Mass transfer coefficients: Bubble cap trays - Sharma et al. (1969)	Rigorous tray-by-tray calculations using a revised version of Ishii-Otto (1973)	Amdahl 470V (1 to 3 cpu seconds) PC version	Tomcej et al. (1983); Tomcej et al. (1986); Tomcej and Otto (1986); Tomcej et al. (1987)
Weiland et al.	Enhancement factor: Abs: MEA/DEA - Welleck et al. (1978) MDEA - 1.0. Str: Olander (1960) Mass transfer coefficients: Packing - Onda et al. (1968) Trays - Scheffe (1984)	Simultaneous solution of equations using Newton-Raphson (Jacobi evaluated using finite differences)	IBM 4341 or VAX 11/780. (2 to 5 cpu minutes) PC version	Chakravarty et al. (1985); Sardar et al. (1985a,1985b); Sivasubramanian et al. (1985a, 1985b); Sivasubramanian (1985); Vickery and Weiland (1986); Vickery et al. (1988)
Dow Chemical Company	CO_2 enhancement factor: Calculated from the free amine profile. The amine profile is determined by the H_2S absorption rate assuming CO_2 has no effect on this rate. Mass transfer coefficients: AIChE correlation (1958), proprietary correlations, and Scheffe (1984).	Restructure the nonlinear equations to reduce the degree of the system and solve using Newton-Raphson or substitution	VAX 11/780 (5 to10 cpu seconds)	Katti and Langfitt (1986); Katti and Wolcott (1987); Katti et al. (1988)

Table 2.2, this program contains the necessary properties for 24 common liquid and gas components. The unique feature of this model is the development of a kinetic model that predicts the effect of residence time, temperature, solution concentration, pressure, and amine type on the rate of CO_2 absorption. The details or features of this development are not available in the literature. The model has been used extensively to investigate the feasibility of various process flow schemes and the effect of operating conditions on performance. The ability to perform selectivity calculations for any of the amines has recently been added.

The program AMSIM developed by Tomcej et al. (see Table 2.2 for references) differs from the other models because it uses a stage efficiency approach to perform nonequilibrium modeling; however, the model does assume thermal equilibrium on each stage. The model has been used to successfully model the common amines but, at least publicly, has not been used for mixed amines. The model has been used to explore the component efficiencies found in typical absorbers. In addition, sensitivity analysis to liquid depth, interfacial area, and number of absorber stages has been done.

The program by Weiland et al. (see Table 2.2 for references) began as an academic effort and developed into a commercial model. Many of the specific details listed in Table 2.2 were obtained from academic publications; therefore, some of the model correlations may be different in the commercial model. For primary and secondary amines, this model uses a more complex expression for the CO_2 enhancement factor than the other models; however, for tertiary amines (MDEA), the enhancement factor in the absorber is simply set equal to one. The model GASPLANT-PLUS was the first amine simulator with a complete range of mixed and single amine capabilities within a flexible flowsheet environment. This model has been compared extensively to actual operating data for the various amine systems with the results published in the references cited in Table 2.2.

2.3 Industrial Models

Several companies are known to have amine plant simulators including Exxon, Dow, Union Carbide, and Shell. The model by Cornelissen, although listed with the academic models because of its fundamental nature, was part of some model development at Shell. Most of the company models are considered proprietary; therefore, these models are not discussed in the literature. Dow Chemical Company is the only company which has published significant details about their amine simulator.

Table 2.2 summarizes the model developed by the Gas Spec Technology group at Dow Chemical Company. This model is very similar to the model by Weiland. The same basic thermodynamic model is used with some slight modification. Dow has also developed some expressions and empirical factors to improve the model's prediction of mass transfer parameters. The unique feature of Dow's model is the numerical solution of the equations. The equations describing the column have been reformulated to give a substantial decrease in computer time when compared to Weiland's model. The details of this reformulation are not available. Because Dow deals with proprietary solvents that are formulated from the common amines, some of the physical properties and equilibrium parameters are probably somewhat different. The model has been used to investigate the effect of changing the number of absorber trays, amine concentration, temperature, amine circulation rate, weir height, and interstage cooling on system performance. In addition, the model has been used to simulate mixed amines, including a comparison to actual operating data.

2.4 Research Needs

The review of the available alkanolamine computer models identified several research needs. The following three research needs have been partially addressed in this work:

1. Investigation of stripper performance

Most of the modeling work in the literature concentrates on evaluating absorber performance under various operating conditions. Investigation of stripper performance or system performance using both columns under various operating conditions might provide further insights into system performance. This work investigates the effect of changing certain operating conditions in the stripper on system performance.

2. Investigation of acid addition on system performance

Union Carbide (1984) reports significant performance improvements after adding a strong acid to MDEA solutions. None of the modeling work reviewed has been used to verify or investigate this acid effect. This work successfully modeled the claim of Union Carbide and showed how the acid affects performance.

3. Representation of CO_2 absorption in mixed amine systems

For mixed amine systems, correct representation of the CO_2 distribution between bicarbonate and carbamate needs to be addressed. The present modeling efforts dealing with mixed amines do not specifically address how this problem is handled. This work presents a method for handling the CO_2 distribution in mixed amine systems which uses an approximation developed by Glasscock and Rochelle (1990a).

The remaining research needs identified as a result of the literature review but not addressed in this work include:

1. Verification and use of mixed amine models

The accuracy of current amine models when modeling mixed amine systems has not been verified over a wide range of operating conditions. Only one set of actual operating data for a MDEA-DEA system has been compared to the models by Weiland and Dow Chemical Company. In addition, the advantages of using mixed amine systems have only recently been investigated.

2. *Numerical techniques*

As computer speed increases, the incorporation of a rigorous solution to the differential equations describing mass transfer with chemical reaction might be feasible if solved with efficient numerical techniques. Development of specific algorithms for solving the amine system would also be helpful. Dow Chemical Company has developed an efficient technique for solving the system of equations describing an amine absorber; however, the details of this technique are unavailable.

Chapter 3

MDEA Modeling

Process modeling using MDEA solutions was done by expanding the model created by Hermes (1987). In order to represent the CO_2-H_2S-MDEA-H_2O system, expressions representing the vapor-liquid equilibrium, chemical equilibrium, and mass transfer occurring at each stage are needed. Although the model is not based on the assumption of equilibrium at each stage, representation of the equilibrium is important because it establishes the driving forces available for mass transfer. Mass fluxes can then be calculated by knowing diffusion coefficients, mass transfer parameters, and the enhancement factor. This chapter describes the expressions used in the model to represent these properties. Before presenting these expressions, a general summary of the model structure is given.

3.1 Description of the Process Model

The overall objective of the model is to calculate the absorber and stripper outlet gas streams given the feed gas to the absorber, the steam rate to the stripper, the solvent circulation rate, and the column specifications. The mass and energy balance equations describing both the absorber and the stripper are solved by performing stage-by-stage calculations. The user has the option of modeling the absorber and the stripper individually or as a system. The cross exchanger is not modeled; therefore, the inlet liquid temperature to both columns is specified.

The general approach for solving the absorber/stripper system is the following:

1. Guess the rich solution loading of H_2S and CO_2 out of the absorber.
2a. Perform individual, stage-by-stage calculations up the absorber.
2b. Update the temperature profile using direct substitution until the column temperature profile has converged.

3. Use the calculated lean solution into the absorber as the starting point at the bottom of the stripper. Perform steps 2a and 2b for the stripper.
4. Compare the calculated rich loading into the stripper to the guessed rich loading. Update the rich loading guesses and repeat the process until the desired tolerance is obtained.

This procedure requires iterative solutions for the temperature profiles and for the rich loading values. Individual column convergence is based on the tolerance of the liquid temperature profile, and overall system convergence is obtained when the loading values are within a given tolerance.

3.1.1 Stage Calculations

Each stage is modeled assuming the liquid is well mixed with the gas moving in plug flow. The reboiler is treated like any other stage except the number of gas phase mass transfer units is set to a high value. At the beginning of each stage calculation, the component flow rates and temperature of the inlet gas, the component flow rates of the outlet liquid, and the estimated liquid temperatures are known. With this initial information, the stage routine is designed to calculate the component flow rates of the outlet gas by mass transfer, the component flow rates of the inlet liquid by material balance, the temperature of the outlet gas by heat transfer, and the outlet liquid temperature by interface pressure balance. The obvious starting point is then at the bottom of the absorber where the desired information for the feed gas (component flow rates, temperature, and pressure) is known. To obtain the other initial information, the H_2S and CO_2 rich loadings are guessed as well as a temperature profile to obtain the liquid temperatures. Two iterative loops are needed to converge the material and energy balances on each stage. The inner loop converges the component flow rates of the outlet gas, and the outer convergence loop calculates the outlet liquid temperature for the stage.

The outlet gas composition is determined by the amount of mass transfer occurring on the stage which implies that the driving force (DF) for mass transfer in the gas phase must be determined. This driving force is the difference between the bulk partial pressure and the interface partial pressure. Because the inlet gas composition is known, the driving force associated with the inlet gas can be calculated; however, the composition of the outlet gas must be guessed in order to calculate the outlet driving force. With the guessed values for the outlet gas, a log mean average driving force is used for mass transfer in the gas phase. This average driving force is then used to calculate the outlet gas flow rates of H_2S and CO_2 based on mass transfer. This process consists of solving the following equations:

$$V_{out,k} = V_{in,k} + y_k [V_{out} - V_{in}] + k_g a' DF_{avg,k} \tag{3.1}$$

where k is CO_2 or H_2S and

$$DF_{avg,k} = \frac{DF_{in,k} - DF_{out,k}}{\ln \frac{DF_{in,k}}{DF_{out,k}}} \tag{3.2}$$

$$DF_{in,k} = P_{in,k,i} - P_{in,k,b} \tag{3.3}$$

$$DF_{out,k} = P_{out,k,i} - P_{out,k,b} \tag{3.4}$$

The amount of water in the outlet gas is calculated by an energy balance using the number of heat transfer units to determine the outlet gas temperature:

$$T_{V_{out}} = T_{L_{out}} + (T_{V_{in}} - T_{L_{out}}) \exp(-N_q) \tag{3.5}$$

$$\begin{aligned} V_{out,w} (\Delta H_{V_{out,w}} + \Delta H_{rxn,w}) = & \sum_{k=1}^{n} V_{in,k} \, \Delta H_{V_{in,k}} - \\ & \sum_{k=1}^{n} L_{out,k} \, \Delta H_{L_{out,k}} - \sum_{k=1}^{n-1} V_{out,k} \, \Delta H_{V_{out,k}} + \\ & \sum_{k=1}^{n-1} (V_{in,k} - V_{out,k}) \, \Delta H_{rxn,k} + V_{in,w} \, \Delta H_{rxn,w} \end{aligned} \tag{3.6}$$

In equation (3.6), n is the number of molecular components and n-1 is every molecular component except water. The calculated outlet gas flow rates from (3.1) and (3.6) are now compared to the guessed values and updated until the desired tolerance is obtained. After converging the outlet gas flow rates, the composition of the liquid into the stage is calculated by component material balances:

$$L_{in,k} = L_{out,k} + V_{out,k} - V_{in,k} \tag{3.7}$$

The outer convergence loop solves for the temperature of the outlet liquid on each stage by minimizing the error in the sum of the interface partial pressures. The following equation is solved to within a specified tolerance:

$$P - P_{H_2S,i} - P_{CO_2,i} - P_{w,i} - P_{inert,i} = 0 \tag{3.8}$$

In order to calculate the partial pressure of water at the interface, water is assumed to be in equilibrium at the interface at the temperature of the outlet liquid. The outlet liquid temperature is changed and the above material balance procedure performed until (3.8) is satisfied. At this point, the process proceeds up the column with the now calculated outlet gas and inlet liquid becoming the inlet gas and outlet liquid for the next stage.

3.1.2 Temperature Convergence

To begin the stage-by-stage calculations, initial temperature profiles must be generated for both columns. These initial profiles can be generated by the program internally or supplied in an input file. To generate a temperature profile for the absorber, linear interpolation between the input top tray temperature and the guessed bottom tray temperature is used. For the stripper, an expression representing a common stripper temperature profile is used (Hermes, 1987). The alternative to internal generation of the temperature profiles is the use of an input file containing the initial profiles for both columns. This method is very beneficial when the converged temperature profiles from a previous simulation are available.

Using the initial profiles, the program begins the stage-by-stage calculations. After every stage in the column has been converged using the initial profile, the new outlet liquid temperature profile is compared to the previous profile. If the old profile and the new profile are not within the desired tolerance, the new temperature profile is stored and then used to repeat the stage-by-stage calculations. Once the desired tolerance is achieved for each temperature in the column, the column has converged and the calculations proceed to the next column.

3.1.3 System Convergence

After the absorber and stripper temperature profiles are converged, the calculated rich amine stream into the stripper is known. The calculated rich liquid loadings are now compared to the starting guesses in order to generate an error for H_2S and CO_2. A two variable secant method is used to update the guesses and the towers are repetitively converged until the rich loadings of H_2S and CO_2 converge to within a given tolerance. In order to save effort in converging the towers, the temperature profiles and composition of the outlet gas of each tray are stored. This provides good guesses in converging each stage and the temperature profile the next time calculations proceed to that tower.

While the H_2S and CO_2 loadings have to be converged, the amounts of water and amine in the liquid are specified. Unlike the amine, water is transferred between phases; therefore, some water exits with the absorber and stripper gases. In order to conserve water in the system, the water in the gas leaving the stripper is condensed and sent back to the top of the column, and water make up is added at this point. The amount of water made up is the difference between the amount of water in the feed gas and the absorber off gas.

3.1.4 Model Inputs

To begin the system calculations the following information is input to the program:

Column Specifications:
- Number of stages for each tower
- Tray characteristics (tray type, approach to flood, liquid depth, froth height)
- Reboiled stripper or live steam
- Number of gas phase transfer units for the reboiler

Operating Variables:
- Flow rates (mole/s): Feed gas to the absorber (H_2S, CO_2, H_2O, inert)
  - Steam to the stripper
  - Rich liquid out of the absorber (H_2O, amine, acid anion)
- Temperatures (°K): Feed gas and steam
  - Liquid into each tower
- Column pressures (atm)
- Pressure drop per stage for each tower

Physical properties at the conditions of each tower:
- Heats of reaction (cal/mole): H_2S dissociation
  - H_2CO_3 dissociation
  - Amine protonation
  - Heat of vaporization of H_2O (cal/mole)

Initial Guesses:
- Rich solution loadings (mole/s): Two guesses for both H_2S and CO_2
- Liquid temperature profile for each tower

Program execution options:

- Absorber, stripper, or absorber/stripper system
- Print option
- Maximum number of temperature convergence iterations for each tower
- Maximum number of system convergence iterations
- Secant method damping factors

3.2 MDEA Solution Physical Properties

3.2.1 MDEA Viscosity and Density

Glasscock and Rochelle (1990b) present the following viscosity relationship for unloaded amine solutions based on the data of Al-Ghawas et al. (1989), Critchfield (1988), and Sada et al. (1978):

$$\ln \mu^o = B_1 + \frac{B_2}{T} + B_3 T \qquad (3.9)$$

$$B_1 = -19.52 - 23.40\text{wam} - 31.24\text{wam}^2 + 36.17\text{wam}^3$$

$$B_2 = 3912 + 4894\text{wam} + 8477\text{wam}^2 - 8358\text{wam}^3$$

$$B_3 = 0.02112 + 0.03339\text{wam} + 0.0278\text{wam}^2 - 0.04202\text{wam}^3$$

$$\text{wam} = \text{wmdea} + 0.980\text{wdea} + 0.876\text{wmea}$$

where wmdea, wdea, and wmea represent the weight fraction of MDEA, DEA, and MEA, respectively. The above expression is valid for 0 to 50 wt% total amine and on the temperature range 20°C to 50°C.

Using (3.9), the desired viscosity expression is entered into the program by editing the correct subroutine. For the case of 50 wt% MDEA, the following expression is obtained:

$$\ln \mu^o = -34.51 + \frac{7443}{T} + 0.03951\,T \qquad (3.10)$$

Toman and Rochelle (1989) report the effect of CO_2 loading at 25°C on the viscosity of 50 wt% MDEA solutions:

$$\ln \frac{\mu}{\mu^o} = 0.7527\ [CO_2 \text{ loading}] \tag{3.11}$$

where μ^o is given by equation (3.10) and CO_2 loading is the total moles of CO_2 absorbed divided by the total moles of amine. The effect of loading on viscosity is expected to diminish at higher temperatures because the effect of temperature will dominate the viscosity. Therefore, the following arbitrary adjustment is made to equation (3.11):

$$\ln \frac{\mu}{\mu^o} = 0.7527 \left(\frac{298}{T}\right)^2 [CO_2 \text{ loading}] \tag{3.12}$$

Equation (3.12) is used to calculate the viscosity of loaded, 50 wt% MDEA solutions by assuming that it is valid for all temperatures of interest.

A temperature dependent expression for the density of 50 wt% MDEA solutions was fit to data of Al-Ghawas et al. (1989) on the range 15-60°C. The following expression was obtained:

$$\rho^o_{MDEA} = 1.0589 - 6.2606 \times 10^{-4}\ (T - 273) \tag{3.13}$$

Equation (3.13) was then corrected for CO_2 loading using data from Toman and Rochelle (1989) to obtain:

$$\rho_{MDEA} = \rho^o_{MDEA} + 0.009998[\text{wt\% } CO_2] \tag{3.14}$$

Equation (3.14) is used to calculate the density of loaded, 50 wt% MDEA solutions by assuming that it is valid for all temperatures of interest.

3.2.2 *Water Viscosity and Density*

Both the water viscosity and density were obtained from data in the *CRC Handbook of Physics and Chemistry*. The following expressions are used in the model:

$$\ln \mu_w = 0.55479 - 0.028401\,(T\text{-}273) + 0.000104\,(T\text{-}273)^2 \tag{3.15}$$

$$\rho_w = \frac{999.84 + 16.945\,(T\text{-}273) - 0.007987\,(T\text{-}273)^2}{1000\,[\,1.0 + 0.01688\,(T\text{-}273)\,]} \tag{3.16}$$

Both equations (3.15) and (3.16) were fit over the temperature range 0-100°C.

3.2.3 *Liquid Diffusion Coefficients*

An estimation of the liquid diffusion coefficients for all of the species is needed to calculate the liquid fluxes. The liquid diffusion coefficients for H_2S, CO_2, and MDEA are functions of temperature and viscosity. The diffusion coefficients for the ionic species are considered to be equal and arbitrarily set equal to the value for MDEA.

The CO_2 diffusion coefficient in MDEA is obtained using the N_2O analogy (see section 3.3). Tomcej and Otto (1989) plotted $\ln(D_{N_2O}/T)$ as a function of viscosity for unloaded, 40 wt% MDEA and obtained a straight line. To obtain an expression for 50 wt% MDEA, the value for D_{N_2O} in 50 wt% MDEA at 25°C reported by Al-Ghawas et al. (1989) was used with the same slope for 40 wt% MDEA to obtain:

$$\ln \frac{D_{N_2O}}{T} = -30.7509 - 0.7785 \ln \mu^o \tag{3.17}$$

The value of the CO_2 diffusivity for unloaded, 50 wt% MDEA ($D^o_{CO_2}$) is then given by multiplying D_{N_2O} from equation (3.17) by 1.1. The value of the CO_2 diffusivity for the loaded solution is then (Toman and Rochelle, 1989):

$$D_{CO_2} = D^o_{CO_2}\left(\frac{\mu^o}{\mu}\right)^{0.6} \tag{3.18}$$

Toman and Rochelle used 0.7 instead of 0.6 but indicated that using 0.7 may over estimate the diffusivity in MDEA solutions with acid added; therefore, the value of 0.6 was used to offset this over estimation.

The MDEA diffusion coefficient in water is approximately the same as the diffusion coefficient of DEA. Versteeg and van Swaaij (1988) report the DEA diffusion coefficient at 25°C to be 8.08 x 10^{-10} m^2/s. To correct this diffusivity for temperature and viscosity, the modified Stokes-Einstein relationship is used:

$$D_{MDEA} = 8.08 \times 10^{-10}\left(\frac{T}{298}\right)\left(\frac{\mu_w}{\mu}\right)^{0.6} \tag{3.19}$$

The diffusion coefficient for H_2S is calculated in an analogous way to MDEA. From the *CRC Handbook of Physics and Chemistry* the diffusion coefficient for H_2S in water at 16°C is 1.77 x 10^{-9} m^2/s. Using the modified Stokes-Einstein equation:

$$D_{H_2S} = 1.77 \times 10^{-9}\left(\frac{T}{289}\right)\left(\frac{\mu_w}{\mu}\right)^{0.6} \tag{3.20}$$

3.2.4 Conversion of Molality to Molarity

Liquid concentrations throughout the model are represented in units of molality (mole/kg H_2O). Certain expressions in the literature were only available in units of molarity; therefore, a conversion factor must be used. The conversion factor for converting molarity to molality is

$$C_M = \frac{0.044\ TCO_2 + 0.034\ TH_2S + 0.119\ TAM + 1.0}{\rho_{MDEA}} \tag{3.21}$$

where TCO_2, TH_2S, and TAM represent the molal concentration of CO_2, H_2S, and MDEA, respectively. This conversion factor is used internally wherever necessary.

3.3 Vapor-Liquid Equilibrium

An equilibrium-based model would assume that the bulk vapor and bulk liquid obtain total equilibrium on each stage; however, because this model is a rate-based model, vapor-liquid equilibrium is assumed to exist only at the gas-liquid interface. The difference between the bulk partial pressure and the interface partial pressure for a given component establishes the gas phase driving force for mass transfer. The interface partial pressures of H_2S and CO_2 are calculated from the interfacial liquid concentrations using Henry's law.

The physical absorption of CO_2 and H_2S into aqueous alkanolamines can not be measured directly because both gases react with these solutions. In the case of H_2S, this fact forces the use of a Henry's constant at infinite dilution in water. The following expression for 0°C to 150°C is used (Edwards et al., 1978):

$$\ln (H_{H_2S}) = 342.595 + 0.0595651(T) - 55.0551 \ln(T) - \frac{13236.8}{T} \qquad (3.22)$$

In the case of CO_2, many researchers have obtained the CO_2 Henry's constant by measuring the N_2O Henry's constant in aqueous amine solutions and assuming the following relationship holds:

$$\frac{H_{CO_2}}{H_{N_2O}} = \frac{H^{\infty}{}_{CO_2}}{H^{\infty}{}_{N_2O}} \qquad (3.23)$$

where $H^{\infty}{}_{CO_2}$ and $H^{\infty}{}_{N_2O}$ are aqueous, infinite dilution values (Haimour et al., 1985). Using data based on this N_2O analogy, an expression for the CO_2 Henry's constant was developed that depends on temperature, MDEA weight percent, and acid gas loading.

To establish the temperature dependence of the CO_2 Henry's constant, an expression at infinite dilution in water was used (Edwards et al., 1978):

$$\ln (H^{\infty}_{CO_2}) = 94.4914 - 0.010454(T) - 11.4519 \ln(T) - \frac{6789.04}{T} \quad (3.24)$$

The above temperature dependence is valid from 0°C to 250°C.

Haimour et al. (1985) have presented Henry's constant data for N_2O in MDEA as a function of temperature (0-35°C) and amine concentration (0-40 wt%). Al-Ghawas et al. (1989) present similar data for 50 wt% MDEA for 0-50°C. Using these data, the CO_2 Henry's constant in units of atm-L/mole was plotted as a function of MDEA weight percent for 0-35°C. Figure 3.1 shows this plot. Each set of weight percent data was represented well by a second order polynomial. Correcting this polynomial to yield the correct units gives the following expression:

$$\begin{aligned} H^{o}_{CO_2} = {} & H^{\infty}_{CO_2} + C_M [\, 0.032361(\text{wt \% MDEA}) + \\ & 0.0035283(\text{wt \% MDEA})^2 \,] \end{aligned} \quad (3.25)$$

As it should, equation (3.25) reduces to the infinite dilution in water value for 0.0 wt% MDEA.

Finally, Toman and Rochelle (1989) present data for CO_2 Henry's constant as a function of liquid charge concentration in equivalents per liter. The data fit the following at 25°C:

$$\log_{10} \frac{H}{H^{o}} = 0.09[MDEAH^{+}] \quad (3.26)$$

where H^{o} is the Henry's constant for unloaded solution at 25°C and $[MDEAH^{+}]$ is the protonated amine concentration in molarity. This relationship is extended to other temperatures by evaluating H^{o} from equation (3.25) at the desired temperature. The final expression for the CO_2 Henry's constant is then:

$$\log_{10} (H_{CO_2}) = \log_{10} (H^{o}_{CO_2}) + C_M \,(\, 0.09[MDEAH^{+}] \,) \quad (3.27)$$

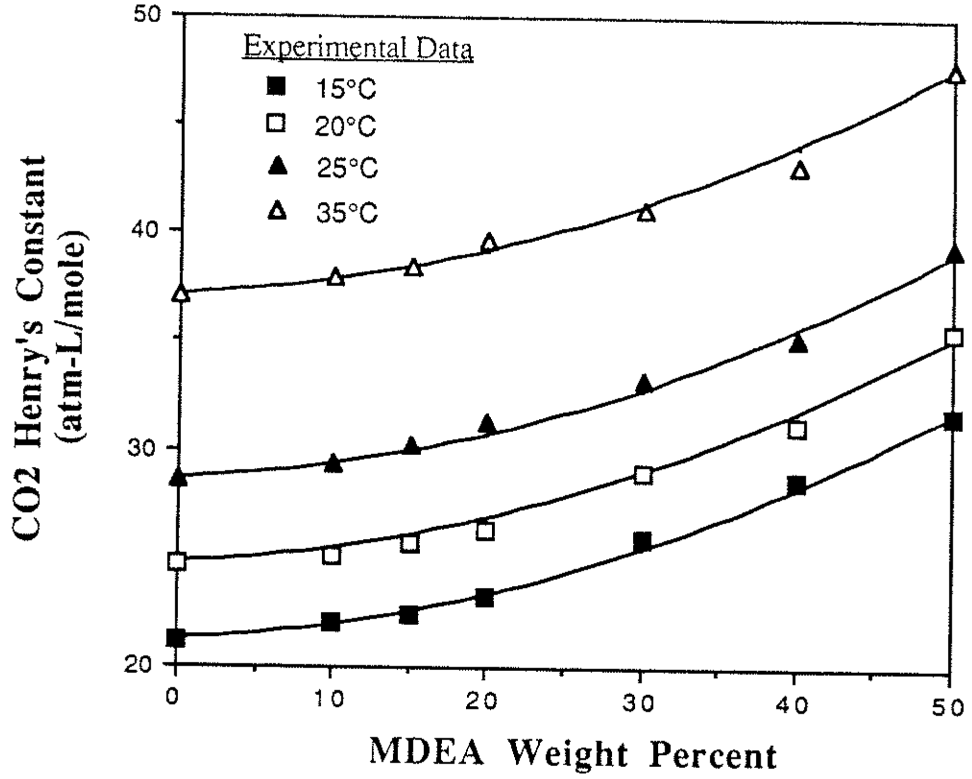

Figure 3.1: Comparison of CO_2 Henry's Constant to Experimental Data. (—) = prediction. Data Sources: wt% MDEA = 0: Edwards et al. (1978); wt% MDEA = 10, 15, 20, 30, and 40: Haimour et al. (1985); wt % MDEA = 50: Al-Ghawas et al. (1989).

3.4 Chemical Equilibrium

Whereas the vapor-liquid equilibrium establishes the component partial pressures at the gas-liquid interface, chemical equilibrium establishes the liquid phase composition in the bulk liquid. Each reaction occurring in the liquid phase is fast enough that chemical equilibrium is established by the time each component has diffused to the bulk liquid. The equilibrium for H_2S and CO_2 in MDEA consists of the following reactions:

$$H_2S\ (aq) + R_3N \Leftrightarrow HS^- + R_3NH^+ \qquad K_{H_2S} \qquad (3.28)$$

$$CO_2\ (aq) + R_3N + H_2O \Leftrightarrow HCO_3^- + R_3NH^+ \qquad K_{CO_2} \qquad (3.29)$$

$$HCO_3^- + OH^- \Leftrightarrow CO_3^= + H_2O \qquad K_{HCO_3} \qquad (3.30)$$

$$R_3N + H_2O \Leftrightarrow R_3NH^+ + OH^- \qquad K_{MDEA} \qquad (3.31)$$

These reactions do not include either hydrogen ion or sulfide ion because their equilibrium concentrations are negligible.

In order to represent the chemical equilibrium in the liquid phase, expressions are needed for the equilibrium constants; however, obtaining accurate equilibrium constant expressions is difficult because the liquid phase becomes very nonideal as CO_2 and H_2S are absorbed. In a rigorous model, the equilibrium constants are represented using activity coefficients and concentrations; however, calculation of activity coefficients is very time consuming. To account for the solution nonideality without using activity coefficients, the CO_2 and H_2S constants, equations (3.28) and (3.29) above, have been fit to equilibrium data as a function of ionic strength, amine concentration, and temperature. Ionic strength serves to indicate the degree of nonideality. In order to represent the wide range of conditions present in an absorber/stripper system and the wide range of operating conditions over which a good model should be useful, the following functional form was used:

$$\ln\frac{H}{K} = (\frac{H}{K})_o + aI + bI^{1/2} + c[R_3N]^d + \frac{\Delta H}{R}\ (\frac{1}{T} - \frac{1}{298}) \tag{3.32}$$

$$I = 0.5\ \Sigma\ (\text{Ion Charge})_k^2\ [\text{Ion}]_k \tag{3.33}$$

where $(\frac{H}{K})_o$, a, b, c, d, and $\frac{\Delta H}{R}$ are adjustable parameters and $[\text{Ion}]_k$ is the molal concentration of the k^{th} ionic species. The variable $\frac{H}{K}$ is the Henry's constant divided by the equilibrium constant for either H_2S or CO_2. Astarita et al. (1983) have reported the form of the ionic strength dependence, $aI + bI^{1/2}$.

The CO_2 equilibrium constant was fit to data from Jou et al. (1982) and Austgen (1989) for 2.0 and 4.28 molar MDEA solutions on the temperature range 25°C to 120°C. The H_2S equilibrium constant was fit to data from Jou et al. (1982) and Jou et al. (1986) for 1.0, 2.0, 3.04, 4.28 and 4.39 molar MDEA solutions on the same temperature range. The adjustable parameters of equation (3.32) were optimized for the H_2S and CO_2 data separately using the objective function:

$$\sum_{i=1}^{\text{ndata}} \left[\frac{\ln(H/K)_{i,\text{data}} - \ln(H/K)_{i,\text{calc}}}{(\text{std dev})_i}\right]^2 \tag{3.34}$$

Table 3.1 shows values for the constants obtained from the fit for H_2S and CO_2. With data for only two amine concentrations reported for CO_2, the fit of constant d is arbitrary; therefore, the value of d was set equal to one.

Accounting for the solution nonidealities through the CO_2 and H_2S constants allows the remaining constants to be handled with infinite dilution expressions. The water concentration does not appear in any of the equilibrium constant expressions; therefore, water is accounted for through the use of the water equilibrium constant defined as the product of the hydroxide and hydronium ion

Table 3.1: Nonlinear optimization fit of experimental data over all temperatures and MDEA concentrations reported.

Parameter	H_2S	CO_2
$(H/K)_o$	-17.28	2.961
a	-0.1119	0.3932
b	-0.5602	-2.178
c	19.390	0.1082
d	0.01	1.0
$\Delta H/R$	-4896	-7036

concentrations. An expression for this constant, K_w, was fit to data found in the *CRC Handbook of Chemistry and Physics*. An expression for the MDEA protonation equilibrium constant based on data from Schwabe et al. (1959) is given by Haimour et al. (1985). The equilibrium constant for the bicarbonate/carbonate equilibrium is from Edwards et al. (1978). These literature expressions are then manipulated to represent the chemical reactions as written in equations (3.30) and (3.31). The final expressions are:

$$\log_{10} K_w = 285.52 - \frac{11988}{T} + .061656\,T - 48.737 \ln T \tag{3.35}$$

$$\log_{10} \left(\frac{K_{MDEA}}{K_w} \right) = 14.309 - 0.019416\,T \tag{3.36}$$

$$\ln (K_{HCO_3} K_w) = 220.067 - 35.4819 \ln T - \frac{12431.7}{T} \tag{3.37}$$

The above set of equilibrium expressions were used to compare the calculated partial pressure of CO_2 and H_2S to the experimental values over which the equilibrium constants were fit. The results of this comparison for CO_2 and H_2S are shown in Figures 3.2 and 3.3, respectively. For both CO_2 and H_2S the fit is within 20% for loadings greater than about 0.1; however, the predictions show a

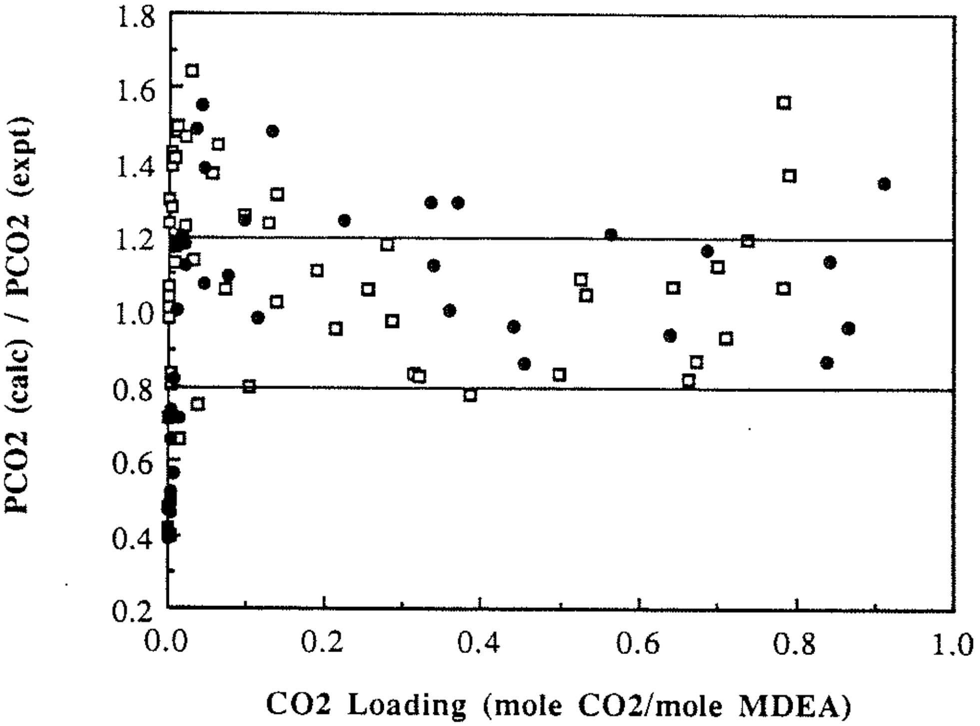

Figure 3.2: Comparison of the Calculated CO_2 Partial Pressures to Experimental CO_2 Partial Pressures over Aqueous MDEA Solutions. Data from Jou et al. (1982) for 25-120°C: (☐) - 4.28M, (•) - 2.0M.

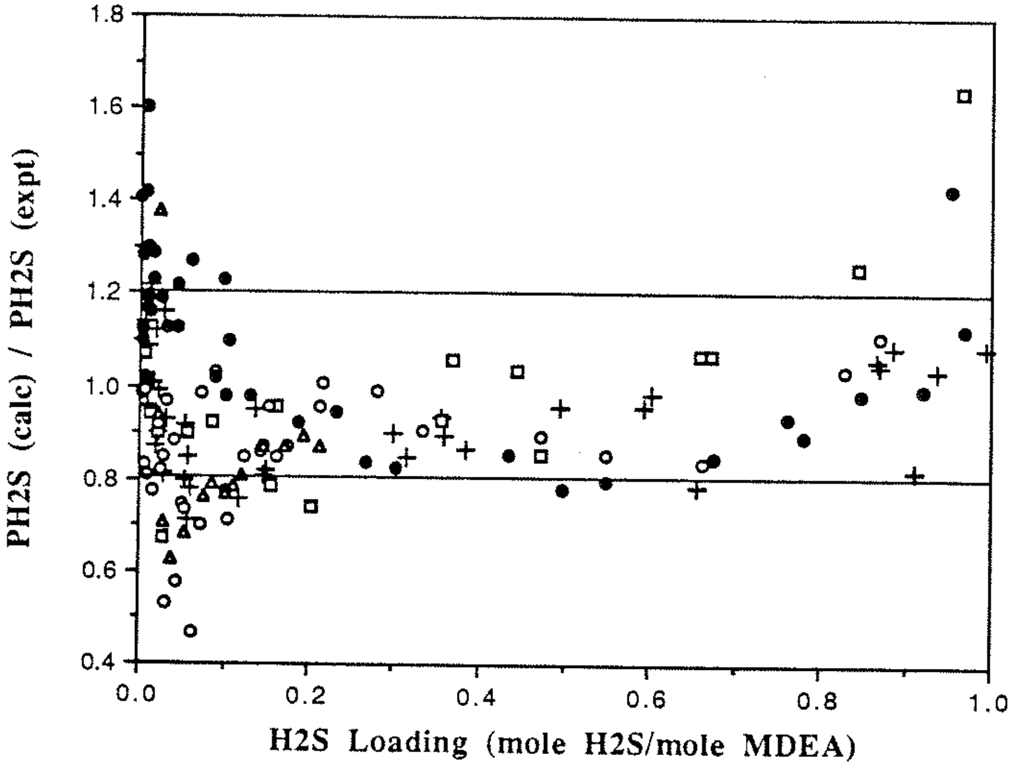

Figure 3.3: Comparison of Calculated H_2S Partial Pressures to Experimental H_2S Partial Pressures over Aqueous MDEA Solutions. Data from Jou et al. (1982) for 25-120°C: (+) - 1.0M, (❐) - 2.0M, (•) - 4.28M. Data from Jou et al. (1986) for 40°C and 100°C: (o) - 3.04M, (Δ) - 4.39M.

large scatter outside of 20% at low loadings. This scatter is primarily due to uncertainty in the experimental data.

The model has a species distribution routine which calculates the equilibrium constants at the conditions needed. Given known total amounts of H_2S, CO_2, and amine, this subroutine divides the totals into species molalities for the bulk solution. Given that there are eight unknown species concentrations (OH^-, R_3NH^+, R_3N, HS^-, H_2S, HCO_3^-, $CO_3^=$, CO_2) the eight equations to be solved are:

1-4) Equilibrium equations for reactions (3.28)-(3.31)

5) $[R_3N]_{total} = [R_3N] + [R_3NH^+]$ (3.38)

6) $[H_2S]_{total} = [H_2S] + [HS^-]$ (3.39)

7) $[CO_2]_{total} = [CO_2] + [HCO_3^-] + [CO_3^=]$ (3.40)

8) $[R_3NH^+] = [HS^-] + [HCO_3^-] + 2\,[CO_3^=]$ (3.41)

These equations are solved by converging on the OH^- concentration. Solution of these equations determines the liquid bulk concentrations; however, the interface concentrations are determined by mass transfer relationships.

3.5 Mass Transfer Relationships

Whereas every component is at chemical equilibrium in the bulk liquid, every component is not at chemical equilibrium at the liquid interface. The reaction of H_2S with aqueous MDEA is a proton transfer and is instantaneous with respect to diffusion; therefore, H_2S is at equilibrium at the interface. The reaction of CO_2 with MDEA is slow with respect to diffusion; therefore, CO_2 has to diffuse partially into the liquid phase before its reaction reaches equilibrium. To determine the CO_2

concentration at the interface, mass transfer enhanced by the chemical reaction must be considered. This mass transfer is calculated by establishing the gas phase driving force available. In addition to the driving force, the liquid diffusion coefficients, mass transfer parameters, and the enhancement factor must be known to calculate the mass transfer.

3.5.1 Mass Transfer Parameters

The mass transfer parameters required to calculate the gas phase and liquid phase flux include the gas and liquid phase mass transfer coefficients and the area available for mass transfer. These parameters depend on the type of contacting device; therefore, the model contains an internal subroutine that calculates these parameters based on correlations for the type of contacting device to be modeled. In this way different types of trays and packings can easily be modeled. These values are calculated for the inlet conditions of each column and then considered to be constant at each stage.

Currently, the model contains expressions to calculate the mass transfer parameters for both bubble cap trays and sieve trays. The following correlations are used to obtain the needed parameters for bubble cap trays (Sharma et al., 1969):

$$k_g\left[\frac{\text{mole}}{\text{atm dm}^2\text{ s}}\right] = 0.0467\ U^{0.25}\ S^{-0.5}\ D_G^{\ 0.5} \qquad (3.42)$$

$$k_l^{\circ}\ (\text{dm/s}) = 1.3\ U^{0.25}\ S^{-0.5}\ D_L^{\ 0.5} \qquad (3.43)$$

$$a'\ (\text{dm}^2/\text{dm}^2) = 0.535\ U^{0.25}\ S^{0.83} \qquad (3.44)$$

The calculated gas phase coefficient is then used to calculate the number of gas phase transfer units:

$$N_g = \frac{k_g\ a'\ P}{G} \qquad (3.45)$$

For sieve trays, equations from Chan and Fair (1984) were manipulated to give the appropriate units used for this work. This results in the following expressions:

$$k_g a'' \left[\frac{\text{mole}}{\text{atm dm}^3\ \text{s}}\right] = \frac{10.0\ D_G^{0.5}\ (\ 1030\ f - 867\ f^2\ )}{0.08205\ T\ S^{0.5}} \tag{3.46}$$

$$k_l^{\circ} a''\ (1/s) = 10.0\ [\ 197\ D_L^{0.5}\ (\ 0.12649\ F + 0.17\ )\ ] \tag{3.47}$$

where

$$F\left[\frac{cm}{s}\left(\frac{kg}{L}\right)^{0.5}\right] = U\ \rho_g^{0.5} \tag{3.48}$$

To obtain the values of k_g and k_l°, the interfacial area is calculated from the following for weir heights of 25-75 mm (Bisio and Kabel, 1985):

$$a''\ (dm^2/dm^3) = 0.075794 + 9.8521\ F - 0.94321\ F^2 + 0.031225\ F^3 \tag{3.49}$$

Equation (3.49) represents the interfacial area quite well up to F=14 which covers reasonable operating conditions. The number of mass transfer units is then calculated by (Chan and Fair, 1984):

$$N_g = k_g\, a''\, t_g \tag{3.50}$$

where

$$t_g = \frac{(1 - \phi)\ S}{\phi\ U} \tag{3.51}$$

$$\phi = S / S_{eff} \tag{3.52}$$

Regardless of the type of tray used, the value for k_l° is calculated using the CO_2 diffusion coefficient for D_L; therefore, the other component mass transfer coefficients are calculated by assuming proportionality to the square root of the diffusion coefficient. The value of D_G is calculated using the method by Fuller et al. (1966). In the absorber, this value is calculated assuming water vapor is diffusing through nitrogen while in the stripper the assumption is CO_2 diffusing in water. This results in the following expressions:

$$D_G\,(\text{absorber}) = 1.233 \times 10^{-5}\,\frac{T^{1.75}}{P} \tag{3.53}$$

$$D_G\,(\text{stripper}) = 9.851 \times 10^{-6}\,\frac{T^{1.75}}{P} \tag{3.54}$$

The column vapor velocity is calculated based on the fractional approach to the vapor flood velocity input to the program. The vapor flood velocity is calculated from Figure 18-10, page 18-7, in *Perry's Chemical Engineers' Handbook* assuming 24 inch tray spacing (Perry and Green, 1984) .

3.5.2 Enhancement Factor

For process models of this type, the effect of chemical reaction on mass transfer is best represented through the use of an enhancement factor. The enhancement factor is defined as the ratio of the amount of mass transfer occurring with the chemical reaction to the amount occurring without chemical reaction. The enhancement factor is bounded by two limiting cases. In the case where the reaction is very slow, the chemical reaction has no effect on mass transfer and the enhancement factor is equal to one. The other limiting case occurs when the chemical reaction is instantaneous with respect to mass transfer. The reaction of H_2S with amines falls into this category. In this case, the enhancement factor has a finite value much, much greater than one but does not need to be calculated because the reaction is considered to be at equilibrium everywhere in the liquid phase.

The reaction of CO_2 with MDEA falls into the intermediate range where an estimate of the enhancement factor is needed. Various simplifying assumptions can be made along with an appropriate hydrodynamic model to give an expression for the enhancement factor. One such case is under the conditions where the reaction can be considered to be pseudo-first order. For the purposes of this model, the expression derived by DeCoursey (1982) is used. The detailed mathematical derivation can be found in his paper; however, a brief discussion of the assumptions and meaning of his method is outlined here.

The detailed derivation by DeCoursey applies specifically to reversible, second order reactions with the stoichiometry corresponding to the kinetics and equal diffusivities for all reactants. He begins with the differential equations that describe mass transfer with chemical reaction and develops some expressions that relate the concentration difference of each reactant anywhere in the liquid to the bulk concentrations. These expressions contain no reaction term. The reaction term of the differential equation is made linear and integrable by choosing an arbitrary functional form that satisfies the boundary conditions. To do this, he assumes that the reactants remain at their interface concentration throughout the reaction region and then adds a term to meet the boundary condition in the bulk liquid. Essentially, he has chosen a form for the reaction term that yields the interface reaction rate at x=0, the bulk reaction rate at x=∞, and is smooth and continuous in between. After these differential equations are solved, the following expression for the enhancement factor is obtained:

$$E_{CO_2} = 1 + (E_i - 1)\left[1 - \Theta - \frac{\Theta}{E_i + C_3} \right] \qquad (3.55)$$

$$E_i = \sqrt{1 + M} \qquad (3.56)$$

$$M = \frac{D_{CO_2}}{k_l^{o2}} \left(k_{MDEA} [R_3N]_i + k_{OH} [OH^-]_i \right) \qquad (3.57)$$

$$\Theta = \frac{[CO_2]_{ie} - [CO_2]_b}{[CO_2]_i - [CO_2]_b} \qquad (3.58)$$

Equations (3.55) through (3.58) represent a rearrangement of DeCoursey's equation (28). This enhancement factor expression was tested numerically by varying the CO_2 reaction rate over several orders of magnitude (Hermes, 1987). This test showed asymptotic behavior to an instantaneous enhancement factor when the reaction rate was increased, and an asymptotic approach to 1.0 (no enhancement) when the reaction rate approached zero in the slow reaction region. It also showed a smooth transition from these regions to a fast reaction rate region where the enhancement factor increases rapidly with the reaction rate. DeCoursey compared the predictions of this equation to those of other models for the enhancement factor and found good agreement. The details of this comparison are found in his article (DeCoursey, 1982).

This work has extended the use of DeCoursey's approximation by making two assumptions. First, the DeCoursey approximation is assumed to be valid for the case of simultaneous absorption of two components, H_2S and CO_2. Second, the DeCoursey approximation is assumed to be valid when using unequal diffusivities. Both of these assumptions seem to be reasonable and are not severe deviations from the original derivation.

To solve for the enhancement factor, interface concentrations and two reaction rate constants are needed. An interface routine similar to the bulk routine calculates the interfacial concentration of all of the species in solution. The equilibrium value of CO_2 at the interface is also calculated to evaluate equation (3.58). This interface routine iterates on the OH^- concentration with convergence depending on the actual CO_2 liquid flux based on the enhancement factor being equal to the CO_2 gas phase flux. At the interface, nine equations must to be solved. The first four equations consist of the equilibrium reactions (3.28) - (3.31). The next two equations represent the liquid flux of all ionic species and the liquid flux of the amine.

Charge flux:

$$\sqrt{D_{R_3NH}}([R_3NH^+] - [R_3NH^+]_i) = \sqrt{D_{HS}}([HS^-] - [HS^-]_i) + \sqrt{D_{HCO_3}}([HCO_3^-] - [HCO_3^-]_i) + 2\sqrt{D_{CO_3}}([CO_3^=] - [CO_3^=]_i) + \sqrt{D_{OH}}([OH^-] - [OH^-]_i) \tag{3.59}$$

Amine flux:

$$\sqrt{D_{R_3N}}\,(\,[R_3N] - [R_3N]_i\,) + \sqrt{D_{R_3NH}}\,(\,[R_3NH^+] - [R_3NH^+]_i\,) = 0 \quad (3.60)$$

The next two equations result from the H_2S and CO_2 gas fluxes being equal to their respective liquid fluxes. Interface partial pressures are calculated using Henry's law.

H_2S flux:

$$k_g\,(\,P_{H_2S_i} - P_{H_2S}\,) = \frac{k_l}{\sqrt{D_{CO_2}}}\Big[\sqrt{D_{H_2S}}\;([H_2S] - [H_2S]_i) + \sqrt{D_{HS}}\;([HS^-] - [HS^-]_i\,)\Big] \qquad (3.61)$$

CO_2 flux based on species concentrations:

$$k_g\,(P_{CO_{2i}} - P_{CO_2}) = k_l\,\Big\{[CO_2] - [CO_2]_i + \sqrt{\frac{D_{HCO_3}}{D_{CO_2}}}([HCO_3^-] - [HCO_3^-]_i) + \sqrt{\frac{D_{CO_3}}{D_{CO_2}}}([CO_3^=] - [CO_3^=]_i)\Big\} \quad (3.62)$$

The final equation is again the CO_2 flux calculation, but this CO_2 flux is based upon the enhancement factor rather than concentrations.

CO_2 flux based on enhancement:

$$k_g\,(\,P_{CO_2} - P_{CO_2}\,) = E_{CO_2}\,k_l^{\circ}\,(\,[CO_2] - [CO_2]_i\,) \qquad (3.63)$$

In order to calculate the CO_2 enhancement factor, the CO_2 reaction kinetics must be included in the model. The CO_2 reaction to bicarbonate occurs by two important mechanisms.

$$CO_2 + OH^- \Leftrightarrow HCO_3^- \qquad (3.64)$$

$$CO_2 + R_3N + H_2O \Leftrightarrow HCO_3^- + R_3NH^+ \qquad (3.65)$$

Second order rate constant expressions for each of these mechanisms are included in the model. The rate constant for the hydroxide reaction is obtained from Astarita et al. (1983) and includes an ionic strength correction. The work of Littel et al. (1990) supplied an expression for the other mechanism.

$$\log_{10} k_{OH} = 13.635 - \frac{2895}{T} + .08\ I \qquad (3.66)$$

$$k_{MDEA} = 1.34 \times 10^{9} \exp\left(\frac{-5771}{T}\right) \qquad (3.67)$$

The literature reports a large disagreement concerning the expression for k_{MDEA}. The value chosen for this work was corrected for an overestimation of the hydroxide contribution that can occur when taking experimental data. Further details can be found in the cited article and in Glasscock (1990).

3.6 Energy Balance Parameters

The expressions used to perform an energy balance at each stage are identical to those used by Hermes (1987). These expressions are reported here for completeness. The number of gas phase heat transfer units is calculated from the specified number of gas phase mass transfer units using the Chilton and Colburn analogy (Perry and Green, 1984):

$$N_q = N_g \left[\frac{\kappa}{\rho\ C_p\ D_G}\right]^{2/3} \qquad (3.68)$$

The liquid phase is assumed to have no resistance to heat transfer.

The thermal conductivity is assumed to be the value for nitrogen in the absorber and water in the stripper. The values are calculated from data by Incropera and DeWitt (1981). The overall gas diffusivity is given by equations (3.53) and (3.54). The expressions for heat capacity are given in Table 3.2.

Table 3.2: Heat Capacity Expressions

$$C_p\left(\frac{\text{J}}{\text{mole °C}}\right) = C1 + C2 \times 10^{-2}\ T + C3 \times 10^{-5}\ T^2 + C4 \times 10^{-9}\ T^3$$

Component	C1	C2	C3	C4	Source
GAS:					
H_2S	33.51	1.547	0.3012	-3.292	a
CO_2	36.11	4.233	-2.887	7.464	a
H_2O	33.46	0.688	-0.7604	-3.593	a
Inert (N_2)	29.00	0.220	0.5723	-2.871	a
LIQUID:					
H_2S	75.40	0.0	0.0	0.0	b
CO_2	75.40	0.0	0.0	0.0	b
H_2O	75.40	0.0	0.0	0.0	a
MDEA	68.00	0.0	0.0	0.0	c

a - Felder and Rousseau (1978); b - Values assumed equal to that of water for this work; c - Value assumed equal to that of DEA from Kohl and Riesenfeld (1985).

Chapter 4

Modeling with ASPEN PLUS ™

The process simulator ASPEN PLUS™ by Aspen Technology Inc. was used to establish a framework capable of modeling acid gas treating using MEA, DGA, DEA, MDEA, and mixtures of these amine solutions. ASPEN PLUS™ was used because it contains an accurate thermodynamic package for electrolytes, a rate-based column modeling feature, and the ability to include user FORTRAN subroutines. This work adapted ASPEN PLUS™ to model the removal of H_2S and CO_2 using alkanolamine solutions by supplying the necessary physical properties for DGA, DEA, and MDEA, supplying the appropriate NRTL interaction parameters, and developing appropriate mass transfer coefficient and kinetic model subroutines. The development of ASPEN PLUS™ for modeling amine systems is discussed in this chapter.

4.1 Model Overview

ASPEN PLUS™ uses a flexible flowsheet concept which means the process consists of individual unit operations which are connected together to yield the overall flow diagram. A process simulation begins with creating an ASPEN PLUS™ input file which uses a specially designed input language discussed in the ASPEN PLUS™ *User Guide*. The user begins by specifying all of the components that appear in the simulation and the physical property models to be used. Any component not found in the ASPEN PLUS™ data banks can be simulated by specifying the appropriate physical properties for that component. If the system contains chemical reactions, the reaction stoichiometry and equilibrium constants or rate expressions are specified. The desired chemical process is then simulated by defining the appropriate feed streams, unit operations, and connectivity between the unit operations. After executing the simulation, ASPEN PLUS™ reports any errors or the detailed results of each unit operation. Convergence of the process is handled automatically or can be directed by the user. In addition, user FORTRAN statements and subroutines can be incorporated to perform calculations not provided for by ASPEN PLUS™.

ASPEN PLUS™ uses a preprocessor approach to execute process simulations. After creating the input file, ASPEN PLUS™ translates the input language into a FORTRAN program. If this process is successful, the FORTRAN program is compiled, stored in a module, linked and then executed. This preprocessor approach can save computer time when making minor changes to the input file of a simulated process. ASPEN PLUS™ can determine if the old FORTRAN module can be used to simulate the new input file, thus saving compilation time. These features are discussed in Chapter 8 of the ASPEN PLUS™ *System Maintenance Manual.*

4.2 Essential Input File Information

ASPEN PLUS™ contains several data banks with the required physical properties for over 400 components including the necessary properties for many electrolyte species. Physical properties or components not found in these data banks can be specified by the user. The required physical properties for each component depends on the property set used. A property set consists of a group of property models used to calculate the system properties. ASPEN PLUS™ contains a variety of property sets to be used for different applications. If some of the property models within the property set are unsatisfactory for a particular system, the model can be replaced with a user supplied model. With the ability to specify components and physical property models, ASPEN PLUS™ can be adjusted to handle almost any system.

4.2.1 Apparent vs. True Components

When using electrolyte systems, ASPEN PLUS™ has two methods for handling the components, the apparent component approach and the true component approach. The true component approach considers each chemical species in the simulation, whether molecular or ionic, to be a component. In other words, an electrolyte's physically dissolved form and chemically combined form are represented as two separate components. The apparent component approach considers only molecular species to be components; therefore, using this approach, an electrolyte's physically dissolved form and chemically combined form are combined and represented by one component. Certain unit operations within ASPEN PLUS™ can only use the apparent approach.

The alkanolamine systems considered in this work to perform acid gas treating contain the following true components:

Molecular:	H_2O, MDEA, DEA, MEA, DGA, CO_2, H_2S, H_2CO_3, RR'NCOOH, other molecules
Cations:	H_3O^+, $MDEAH^+$, $DEAH^+$, $MEAH^+$, $DGAH^+$, other cations
Anions:	OH^-, $RR'NCOO^-$, HCO_3^-, HS^-, $CO_3^=$, other anions

The apparent components are those listed as molecular above. The components H_2CO_3 (carbonic acid) and RR'NCOOH (carbamic acid) are introduced as apparent components to simulate rate limited reactions (see section 4.3). ASPEN PLUS™ requires that all true components be listed in the input file even if the apparent approach is used. The user subroutines developed in subsequent sections of this chapter are designed such that the components shown above should always be listed in that order when creating an input file. When other molecules or ions are present, component flags are passed to the kinetic subroutine from the input file.

4.2.2 Component Physical Properties and Property Models

The property set most appropriate to represent the alkanolamine-water-CO_2-H_2S system is called SYSOP15M. This set uses the Redlich-Kwong equation of state to calculate fugacities and the NRTL equation to calculate activity coefficients. The details of the models used by this property set are found in the ASPEN PLUS™ *Electrolytes Manual* and the appendices of the ASPEN PLUS™

User Guide. The necessary properties for each component are listed in the ASPEN PLUS™ *Electrolytes Manual* or *User's Guide.*

The ASPEN PLUS™ data banks contain all of the necessary properties for the alkanolamine system components except for DGA, DEA, MDEA, and their ionic species (protonated amine and carbamate). In addition to the properties for these missing components, Henry's constant expressions for H_2S and CO_2, NRTL interaction parameters, and Rackett parameters were supplied to the model. All of this input information was included in input files through the use of a user insert library. The details of user insert libraries and their use are found in the ASPEN PLUS™ *System Maintenance Manual.*

The required information included in the insert library was obtained from Austgen (1989). The Henry's constant expressions for H_2S and CO_2 are shown in Table 4.1. Table 4.2 contains the binary parameters for the Rackett equation. These values were calculated from the following equation (Austgen, 1989):

$$k_{ij} = 1.0 - \left[\frac{2\sqrt{V_{ci}^{1/3}\, V_{cj}^{1/3}}}{V_{ci}^{1/3} + V_{cj}^{1/3}}\right]^3 \qquad (4.1)$$

where V_c is the critical volume for component i or j. Because DEA, DGA, and MDEA are not listed in the ASPEN PLUS™ data banks, several properties had to be included for these components. Critical properties and vapor pressures are listed in Tables 4.3 and 4.4, respectively. Dielectric constants for the unlisted components and MEA are shown in Table 4.5. The only required information for the unknown ions is the ion's charge, type, and molecular weight. Ion types are listed in the ASPEN PLUS™ *Electrolytes Manual.*

The NRTL model requires interaction parameter values to account for the interactions between all molecules and electrolytes (ion pairs) in the liquid phase. These parameters are specific to the chemical system and are obtained by regressing experimental data. The parameters for the alkanolamine-H_2O-CO_2-H_2S system were obtained from Austgen (1989). Austgen found that the only molecule-molecule interaction parameters that could be fit with statistical significance were

Table 4.1: Henry's Constant Expressions for H_2S and CO_2.

$$\ln H_i\,(\mathrm{Pa}) = C_1 + C_2/T + C_3 \ln T + C_4 T$$

Gas	C_1	C_2	C_3	C_4	Temperature Range (°C)	Source
H_2S	358.138	-13236.8	-55.0551	0.059565	0 - 150	a
CO_2	170.7126	-8477.711	-21.9574	0.005781	0 - 100	b

a - Edwards et al. (1978); b - Chen et al., 1979.

Table 4.2: Rackett Binary Interaction Parameters.

$$k_{ij} = 1.0 - \left[\frac{2\sqrt{V_{ci}^{1/3} V_{cj}^{1/3}}}{V_{ci}^{1/3} + V_{cj}^{1/3}}\right]^3$$

Comp.	H_2O	MDEA	DEA	MEA	DGA	CO_2	H_2S
H_2O	0.0	0.1442	0.1286	0.07696	0.1203	0.01115	0.01331
MDEA	0.1442	0.0	5.87E-4	0.01286	1.41E-3	0.08107	0.07593
DEA	0.1286	5.87E-4	0.0	7.99E-3	1.77E-4	0.06873	0.06395
MEA	0.07696	0.01286	7.99E-3	0.0	5.80E-3	0.03118	0.02788
DGA	0.1203	1.41E-3	1.77E-4	5.80E-3	0.0	0.06234	0.05776
CO_2	0.01115	0.08107	0.06873	0.03118	0.06234	0.0	9.77E-5
H_2S	0.01331	0.07593	0.06395	0.02788	0.05776	9.77E-5	0.0

Table 4.3: Pure Component Molecular Weight and Critical Properties for DEA, MDEA, and DGA.

Comp.	MW	T_c (°K)	P_c (kPa)	V_c ($m^3\ kmol^{-1}$)	Z_c	ω	Source
DEA	105.14	715.0	3270.0	0.3490	0.192	1.046	a
MDEA	119.16	677.8	3876.1	0.3932	0.192	1.242	b
DGA	105.14	674.6	4354.9	0.327	0.254	1.046	c

a - Daubert and Danner, DIPPR Data Tables (1985); b - Peng (1988) ; c - Texaco Chemical Company.

Table 4.4: Pure Component Vapor Pressures of DEA, MDEA, and DGA.

$$\ln P^o\,(\mathrm{Pa}) = D_1 + \frac{D_2}{T + D_3} + D_4 T + D_5 \ln T$$

Amine	D_1	D_2	D_3	D_4	D_5	Temp Range (°C)	Source
DEA	286.01	-20360.0	0.0	0.032378	-40.422	28-269	a
MDEA	26.137	-7588.5	0.0	0.0	0.0	120-240	b
DGA	20.86	-3314.6	-140.83	0.0	0.0	not reported	c

a - Daubert and Danner, DIPPR Data Tables (1985); b - Dow Chemical Co. (1987); c - Sheu (1989).

Table 4.5: Dielectric constants for pure MEA, DEA, MDEA, and DGA.

$$d_i = A + B\left[\frac{1}{T} - \frac{1}{273}\right]$$

Amine	A	B	Source
MEA	36.76	14836.0	a
DEA	28.01	9277.0	a
MDEA	24.74	8989.3	b
DGA	28.01	9277.0	*

a - Ikada et al. (1968); b - Austgen (1989); * - value arbitrarily set equal to DEA.

pairs that contained water. All other molecule-molecule pair values were set to zero. The only molecule-ion pair and ion pair-molecule parameters that could be fit with statistical significance were pairs containing water as the molecule and ion pairs of protonated amine combined with either bicarbonate, bisulfide, or carbamate. All other water-ion pair and ion pair-water values were set to values of 8 and -4, respectively. All other molecule-ion pair and ion pair-molecule values were set to values of 15 and -8, respectively. The molecule-molecule interaction pairs used for this work are shown in Table 4.6. The molecule-ion pair and ion pair-molecule parameters are shown in Table 4.7. Details of the NRTL interaction parameter regression are found in Austgen (1989).

4.2.3 Equilibrium Reactions

As described in Chapter 3, equilibrium calculations are important because equilibrium establishes the mass transfer driving force. In addition, ASPEN PLUS™ has the ability to perform equilibrium flash calculations which might be used to compare, analyze, or interpolate experimental data. Therefore, the stoichiometry and equilibrium constants must be included in the input file for the following equilibrium reactions:

$$2H_2O \Leftrightarrow OH^- + H_3O^+ \qquad K_w \qquad (4.2)$$

$$H_2S + H_2O \Leftrightarrow HS^- + H_3O^+ \qquad K_{H_2S} \qquad (4.3)$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^= + H_3O^+ \qquad K_{HCO_3} \qquad (4.4)$$

$$RR'R''NH^+ + H_2O \Leftrightarrow RR'R''N + H_3O^+ \qquad K_{amine} \qquad (4.5)$$

$$CO_2 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+ \qquad K_{CO_2} \qquad (4.6)$$

$$RR'NCOO^- + H_2O \Leftrightarrow RR'NH + HCO_3^- \qquad K_{carb} \qquad (4.7)$$

Equation (4.7) applies only when a primary or secondary amine is present. The dissociation of bisulfide (HS^-) to sulfide ($S^=$) is neglected due to a very small equilibrium constant. The mole fraction based equilibrium constants for each of these reactions were obtained from Austgen (1989) and are shown in Table 4.8.

Table 4.6: NRTL Molecular Interaction Parameters Used in the Model

Molecule Pair	$\tau = a + b/T$ a	b	Accentric Factor
H_2O - MEA	1.674	0.00	0.2
MEA - H_2O	0.000	-649.75	0.2
H_2O - DEA	-0.965	1317.63	0.2
DEA - H_2O	-0.661	-718.08	0.2
H_2O - MDEA *	0.000	0.00	0.2
MDEA - H_2O *	0.000	0.00	0.2
H_2O - DGA	1.992	0.00	0.2
DGA - H_2O	0.000	-770.41	0.2
H_2O - H_2S	-3.674	1155.9	0.2
H_2S - H_2O	-3.674	1155.9	0.2
H_2O - CO_2	10.064	-3268.14	0.2
CO_2 - H_2O	10.064	-3268.14	0.2

* - These values were fit by Austgen (1989) but then later set to zero when fitting the molecule-ion pair parameters.

Table 4.7: NRTL Molecule - Ion Pair Interaction Parameters Used in the Model

	$\tau = a + b/T$		
Molecule - Ion Pair	a	b	Accentric Factor
MEA = RNH_2			
H_2O - ($MEAH^+$, HS^-)	6.844	501.83	0.2
($MEAH^+$, HS^-) - H_2O	-3.560	-197.12	0.2
H_2O - ($MEAH^+$, HCO_3^-)	4.550	1218.19	0.2
($MEAH^+$, HCO_3^-) - H_2O	-4.088	0.0	0.2
H_2O - ($MEAH^+$, $MEACOO^-$)	10.268	0.0	0.2
($MEAH^+$, $MEACOO^-$) - H_2O	-5.098	0.0	0.2
DGA = RNH_2			
H_2O - ($DGAH^+$, HS^-)	7.744	375.72	0.2
($DGAH^+$, HS^-) - H_2O	-4.337	0.0	0.2
H_2O - ($DGAH^+$, HCO_3^-)	0.0	2960.94	0.2
($DGAH^+$, HCO_3^-) - H_2O	-4.251	0.0	0.2
H_2O - ($DGAH^+$, $DGACOO^-$)	11.424	0.0	0.2
($DGAH^+$, $DGACOO^-$) - H_2O	-5.328	0.0	0.2
DEA = R_2NH			
H_2O - ($DEAH^+$, HS^-)	5.199	1519.60	0.2
($DEAH^+$, HS^-) - H_2O	-2.836	-636.95	0.2
H_2O - ($DEAH^+$, HCO_3^-)	4.204	1588.19	0.2
($DEAH^+$, HCO_3^-) - H_2O	-4.434	0.0	0.2
H_2O - ($DEAH^+$, $DEACOO^-$)	11.549	102.66	0.2
($DEAH^+$, $DEACOO^-$) - H_2O	-5.580	0.0	0.2
MDEA = R_3N			
H_2O - ($MDEAH^+$, HS^-)	3.735	1036.04	0.2
($MDEAH^+$, HS^-) - H_2O	-3.225	0.0	0.2
H_2O - ($MDEAH^+$, HCO_3^-)	5.864	1147.90	0.2
($MDEAH^+$, HCO_3^-) - H_2O	-4.511	0.0	0.2
H_2O - ($MDEAH^+$, $RHNCOO^-$)	9.903	0.0	0.2
($MDEAH^+$, $RHNCOO^-$) - H_2O	-4.776	0.0	0.2
H_2O - ($MDEAH^+$, $DEACOO^-$)	10.387	0.0	0.2
($MDEAH^+$, $DEACOO^-$) - H_2O	-4.965	0.0	0.2

Table 4.8: Mole Fraction- Based Equilibrium Constants Used in the Model

$$\ln K_i = C_1 + C_2/T + C_3 \ln T + C_4 T$$

Rxn #	Comp	C_1	C_2	C_3	C_4	Source
4.2	H_2O	132.899	-13445.9	-22.4773	0.0	a
4.3	H_2S	214.582	-12995.4	-33.5471	0.0	a
4.4	CO_2	231.465	-12092.1	-367816	0.0	a
4.5	HCO_3^-	216.049	-12431.7	-354819	0.0	a
4.6	MEA	2.1211	-8189.38	0.0	-0.007484	b
4.6	DEA	-6.7936	-5927.65	0.0	0.0	c
4.6	MDEA	-9.4165	-4234.98	0.0	0.0	d
4.6	DGA	1.6957	-8431.65	0.0	-0.005037	e
4.7	MEA	2.8898	-3635.09	0.0	0.0	f
4.7	DEA	4.5146	-3417.34	0.0	0.0	f
4.7	DGA	8.8334	-5274.4	0.0	0.0	f

a - Edwards et al. (1978); b - Bates and Pinching (1951); c - Bower et al.(1962); d - Schwabe et al. (1959); e - Dingman et al. (1983); f - Austgen (1990)

4.3 Kinetic Model

The information described in section 4.2 can be used in an ASPEN PLUS™ input file to model equilibrium flashes, heat exchangers, and equilibrium columns; however, more information is required to simulate the rate limited reactions of the alkanolamine systems. The current version of ASPEN PLUS™ has a unit operation called RADFRAC which performs equilibrium-based column modeling. This model can handle rate limited reactions and can simulate nonequilibrium stages using component efficiencies; therefore, it could possibly be used to model the alkanolamine system. The other column model that can handle rate limited reactions is a rate-based model called RATEFRAC. Unfortunately, this model is not yet available. For both of these columns, rate limited reaction rates are specified by the user; therefore, a reaction rate subroutine was created to be used with either of these columns.

4.3.1 Formulation of Rate Limited Reactions

For purposes of rate modeling, the chemical reactions (4.2) through (4.5) can still be considered equilibrium reactions with the equilibrium constants given in Table 4.8; however, reactions (4.6) and (4.7) are rate limited. Rate limited reactions in ASPEN PLUS™ must contain molecular species only; therefore, the apparent component approach must be used and reactions (4.6) and (4.7) can not be used as written. Instead, these rate limited reactions are represented with the following chemical reactions:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \tag{4.8}$$

$$CO_2 + RR'NH \Leftrightarrow RR'NCOOH \tag{4.9}$$

The molecular species carbonic acid (H_2CO_3) and carbamic acid (RR'NCOOH) probably exist in the liquid phase for very short times; however, both species are very strong electrolytes and quickly dissociate. This dissociation is handled by indicating within ASPEN PLUS™ that the following reactions completely dissociate:

$$H_2CO_3 + H_2O \Leftrightarrow HCO_3^- + H_3O^+ \qquad K_{H_2CO_3} \qquad (4.10)$$

$$RR'NCOOH + H_2O \Leftrightarrow RR'NCOO^- + H_3O^+ \qquad K_{carbH} \qquad (4.11)$$

The rate subroutine is designed to calculate the rate of formation of H_2CO_3 and RR'NCOOH. The equilibrium reactions (4.10) and (4.11) then speciate these molecular components into bicarbonate and carbamate. Obviously, the rate of formation of bicarbonate is equal to that of H_2CO_3 and similarly for carbamate and RR'NCOOH.

4.3.2 Bicarbonate Formation Rate

For systems containing MDEA, the reaction of CO_2 to form bicarbonate is a rate limited reaction. The reaction rate of CO_2 is related to the formation rate of bicarbonate. Glasscock (1990) formulated rate expressions and regressed kinetic rate constants for the formation of bicarbonate. The following reactions are considered and apply when using MDEA or mixed amine solvents (Glasscock, 1990):

$$CO_2 + H_2O + MDEA \Leftrightarrow HCO_3^- + MDEAH^+ \qquad (4.12)$$

$$CO_2 + OH^- + MDEA \Leftrightarrow HCO_3^- + MDEA \qquad (4.13)$$

$$CO_2 + OH^- \Leftrightarrow HCO_3^- \qquad (4.14)$$

A rate expression for bicarbonate based on the above reactions was developed by Glasscock (1990). Although not considered in Glasscock's work, reaction (4.12) could also proceed by replacing MDEA with a primary or secondary amine in a mixed amine system. Including a rate constant for reaction (4.12) with a primary or secondary amine, the rate of bicarbonate formation for any amine system is given by:

$$R_{HCO_3} = [a_{CO_2} - a_{CO_2,HCO_3,e}]\,[k_{tam,w}\,a_{tam}a_w + k_{am,w}\,a_{am}\,a_w + k_{tam,OH}\,a_{tam}\,a_{OH} + k_{OH}\,a_{OH}] \qquad (4.15)$$

where $k_{tam,w}$ represents the rate constant for reaction (4.12), $k_{am,w}$ represents (4.12) with a primary or secondary amine, $k_{tam,OH}$ represents (4.13), and k_{OH} represents (4.14). The constants $k_{tam,w}$ and $k_{tam,OH}$ are activity based constants regressed by Glasscock (1990) and are discussed in section 4.3.4. The value for $k_{am,w}$ was not fit by Glasscock so it is set to zero. The reaction rate constant k_{OH} is given by equation (3.66) with the ionic strength term removed. The ionic strength term in (3.66) is dropped because the component activities account for the solution nonidealities. The term $a_{CO_2,HCO_3,e}$ represents the activity of CO_2 in equilibrium with the bicarbonate in solution.

An inconsistency in equation (4.15) should be noted. The rate constant for reaction (4.14) given by equation (3.66) is a second order, **concentration** based constant. In the regression work done by Glasscock, this constant was multiplied by the hydroxide **activity** as shown in equation (4.15). Multiplying the concentration based rate constant by the activity represents a thermodynamic inconsistency.

In order to evaluate the formation rate of bicarbonate, the value for $a_{CO_2,HCO_3,e}$ must be calculated. Reaction (4.14) conveniently represents the equilibrium between CO_2 and HCO_3^-. The equilibrium constant for (4.14) is represented by combining the constants for reactions (4.2) and (4.6):

$$K_{CO_2,HCO_3} = \frac{K_{CO_2}}{K_w} \qquad (4.16)$$

The equilibrium CO_2 activity is then given by:

$$a_{CO_2,HCO_3,e} = \frac{a_{HCO_3}}{K_{CO_2,HCO_3}\;a_{OH}} \qquad (4.17)$$

Equation (4.17) is used for all amine systems to calculate the equilibrium CO_2

activity associated with bicarbonate and is substituted into equation (4.15) to calculate the bicarbonate rate of formation.

4.3.3 Carbamate Formation Rate

The formation rate of carbamate must be calculated for systems containing primary or secondary amines. The rate expression for this formation depends on the type of amine. Glasscock (1990) formulated rate expressions and regressed rate constants for conversion of MEA, DGA, and DEA to carbamate.

For the primary amines MEA and DGA, carbamate formation follows a second order rate expression, first order in CO_2 and amine. For the case of MEA, the rate expression is:

$$R_{MEACOO} = k_{pam}\,[CO_2]\,[MEA] \tag{4.18}$$

The same rate expression and rate constant apply to DGA by substituting DGA for MEA in (4.18). This rate was found not to be affected in the mixed amine system (Glasscock, 1990).

The DEA system is more complicated. Carbamate can be formed by the following reactions:

$$CO_2 + DEA + H_2O \Leftrightarrow DEACOO^- + H_3O^+ \tag{4.19}$$

$$CO_2 + DEA + DEA \Leftrightarrow DEACOO^- + DEAH^+ \tag{4.20}$$

$$CO_2 + DEA + MDEA \Leftrightarrow DEACOO^- + MDEAH^+ \tag{4.21}$$

Reaction (4.21) only occurs in mixed amine systems. Based on reactions (4.18) through (4.21), the rate expression for carbamate formation in the MEA, DGA, DEA, or mixed amine system can be combined into the following expression:

$$R_{carb} = \mathbf{a}_{am}\,[\mathbf{a}_{CO2} - \mathbf{a}_{CO2,carb,e}]\,[\,k_{pam} + k_{am}\,\mathbf{a}_{am} + k_{tam}\,\mathbf{a}_{tam} + k_w\,\mathbf{a}_w\,] \tag{4.22}$$

where k_{pam} represents the rate constant for the reaction of MEA or DGA to form carbamate, k_w represents reaction (4.19), k_{am} represents (4.20), and k_{tam} represents (4.21). These rate constants are discussed in section 4.3.4. For the MEA or DGA system, k_{am}, k_{tam}, and k_w are set to zero while for the DEA system k_{pam} is set to zero. The term $a_{CO2,carb,e}$ represents the activity for CO_2 in equilibrium with the carbamate in solution and is dependent on the type of amine present.

For the DEA system, the equilibrium carbamate reaction with CO_2 is given by combining the following reactions:

$$CO_2 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+ \qquad K_{CO_2} \qquad (4.23)$$

$$DEACOO^- + H_2O \Leftrightarrow DEA + HCO_3^- \qquad K_{DEACOO} \qquad (4.24)$$

$$2H_2O \Leftrightarrow OH^- + H_3O^+ \qquad K_w \qquad (4.25)$$

The overall equilibrium constant is:

$$K_{CO_2,carb} = \frac{K_{CO_2}}{K_{DEACOO}\ K_w} \qquad (4.26)$$

The equilibrium CO_2 activity is then:

$$a_{CO2,carb,e} = \frac{a_w\ a_{DEACOO}}{K_{CO_2,carb}\ a_{OH}\ a_{DEA}} \qquad (4.27)$$

The rate of carbamate formation is then calculated by substituting (4.27) into (4.22) along with the appropriate rate constants and activities. For the MEA or DGA systems, the equilibrium CO_2 activity is obtained by replacing the DEA expressions in (4.26) and (4.27) with analogous expressions for MEA or DGA.

4.3.4 *Rate Constant Values*

Using experimental absorption data, Glasscock (1990) regressed all of the rate constants used in equations (4.15) and (4.22) except k_{OH} and k_{pam}. Expressions for k_{OH} and k_{pam} were taken from the literature. The other rate constants were fit to the following form:

$$k_i = k_{298} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right] \tag{4.28}$$

The rate constants reported in Glasscock (1990) are for concentration based activities so k_{298} has units of ($m^6/kmol^2/s$); however, the activities calculated in this work are mole fraction based and require the units ($kmol/m^3/s$). To convert from the concentration base to the mole fraction base, the values for k_{298} reported by Glasscock were multiplied by the density of water at 25°C cubed to yield the appropriate units. The original rate constants and the corrected rate constants used in the kinetic subroutine are shown in Table 4.9. These rate constant values are passed into the kinetic subroutine from the ASPEN PLUS™ input file.

4.4 Incorporating an Enhancement Factor Approach

Although the unit operation RATEFRAC was unavailable, a preliminary user's manual for this model was obtained. RATEFRAC handles mass transfer with chemical reaction using a rigorous and general approach. The differential equations are integrated through the liquid phase. Although this procedure is accurate, it will most likely be very time consuming; therefore, some work was done to develop an enhancement factor approach that might be incorporated into RATEFRAC. An algorithm with the necessary equations was developed; however, because RATEFRAC is currently unavailable, no attempt was made to code this algorithm. The details of how to incorporate the algorithm into RATEFRAC can be solved after obtaining the program.

Table 4.9: Rate Constants Used for the Kinetic Model.

Rate constant	k_{298}* ($m^6/kmol^2$-s)	Corrected k_{298} ($kmol/m^3$-s)	E_a (kcal/kmol-K)	Source
MDEA constants:				
$k_{tam,w}$	0.0157	2668.2	3710	a
$k_{tam,OH}$	1.54×10^5	2.617×10^{10}	8107	a
DEA constants:				
k_{am}	18500	3.144×10^9	9314	a
k_w	30.0	5.098×10^6	11000	a
DEA/MDEA constant:				
k_{tam}	3310	5.625×10^8	-105	a
MEA (DGA) constant:				
k_{pam}	---	5868.45	9846	b
Hydroxide constant:				
k_{OH}	---	8322.14	13245	c

a - regressed by Glasscock (1990); b - Hikita et al. (1977); c - Astarita et al. (1983)

* - Original values from Glasscock (1990).

One feature of RATEFRAC is the ability to use user supplied subroutines to calculate the mass transfer coefficients and interfacial area. If no subroutine is supplied, internal correlations are used. The mass transfer coefficients and interfacial area expressions for bubble cap and sieve trays presented in Chapter 3 were used to develop a subroutine for RATEFRAC. Although not included at this time, the enhancement factor approach would be incorporated in the subroutine for calculating mass transfer coefficients.

The enhancement factor approach involves calculating the absorption rates of CO_2 and H_2S using the CO_2 enhancement factor approximation of DeCoursey (1982). The procedure begins with calculating the liquid phase mass transfer coefficient for each apparent component and then speciating the bulk liquid phase by flashing the apparent composition. With the bulk composition known, the procedure iterates on the interface composition. Guessing the interface composition for carbamic acid (RR'NCOOH), carbonic acid (H_2CO_3), and H_2S allows calculation of the other apparent component concentrations. Using these interface concentrations, the remaining concentrations can be calculated from the following:

$$C_{MDEA,i} = C_{MDEA,b} \tag{4.29}$$

$$C_{CO_2,i} = \frac{P_{CO_2}}{H_{CO_2}} \tag{4.30}$$

$$C_{DEA,i} = C_{DEA,b} - \frac{k_l^{\circ}{}_{,carb}}{k_l^{\circ}{}_{,DEA}} \Delta C_{carb} \tag{4.31}$$

where

$$\Delta C_k = C_{k,interface} - C_{k,bulk} \tag{4.32}$$

Equations (4.29) and (4.31) result from the flux of total MDEA and DEA being equal to zero. Equation (4.30) results from assuming no gas phase resistance for CO_2. Based on these interface concentrations, the interface is now speciated by the flash routine.

The now established interface concentrations are used in the kinetic subroutine described in section 4.3 to calculate the rate of formation of CO_2 which is then used to calculate the enhancement factor of DeCoursey (1982) described in Chapter 3. The enhancement factor expression is:

$$E_{CO_2} = 1 + (E_i - 1)\left[1 - \Theta - \frac{\Theta}{E_i + C_3} \right] \tag{4.33}$$

$$E_i = \sqrt{1 + M} \tag{4.34}$$

$$M = \frac{k_1 D_{CO_2}}{k_l^{o2}} \tag{4.35}$$

$$\Theta = \frac{\mathbf{a}_{CO_2,i,e} - \mathbf{a}_{CO_2,b}}{\mathbf{a}_{CO_2,i} - \mathbf{a}_{CO_2,b}} \tag{4.36}$$

where k_1 is a pseudo-first order rate constant and the dimensionless driving force Θ is now in terms of activities. This transformation of Θ is done out of convenience because the term $\mathbf{a}_{CO_2,i,e}$ is readily available from the reaction rate subroutine. The constant k_1 can be approximated using the net reaction rate of CO_2 calculated in the reaction rate subroutine by combining (4.15) and (4.22):

$$k_1 = \frac{R_{CO_2,i}}{C_{CO_2,i}} \tag{4.37}$$

where

$$R_{CO_2,i} = R_{HCO_3,i} + R_{carb,i} \tag{4.38}$$

For equation (4.36), the CO_2 activity at the interface in equilibrium with the other species must be calculated. For the MDEA system, $\mathbf{a}_{CO_2,i,e}$ can be obtained from the equilibrium activity calculated in equation (4.17). For primary, secondary or mixed amine systems, the value for $\mathbf{a}_{CO_2,i,e}$ depends on the distribution of CO_2 between carbamate and bicarbonate. This distribution is estimated using the MCFLUX approximation (Glasscock and Rochelle, 1990a). This approximation assumes the CO_2 is distributed amongst the bicarbonate and carbamate according to the rates of reactions; therefore, the fraction of CO_2 considered to be in equilibrium with the carbamate is given by:

$$f_{carb} = \frac{R_{carb}}{R_{carb} + R_{HCO_3}} \tag{4.39}$$

The net rates of R_{HCO_3} and R_{carb} are calculated using (4.15) and (4.22), respectively. The equilibrium value for the CO_2 activity is then approximated by:

$$\mathbf{a}_{CO_2,i,e} = f_{carb}\, \mathbf{a}_{CO_2,carb,e} + (1-f_{carb})\, \mathbf{a}_{CO_2,HCO_3,e} \tag{4.40}$$

The values for $\mathbf{a}_{CO_2,HCO_3,e}$ and $\mathbf{a}_{CO_2,carb,e}$ are calculated using (4.17) and (4.27), respectively.

Using equations (4.33) through (4.40), the CO_2 enhancement factor can be calculated. The guessed interface values are now checked using the following equations:

$$N_{CO_2} = k_l^{\circ}{}_{,CO_2}\, E_{CO_2} \left[C_{CO_2,i} - C_{CO_2,b} \right] \tag{4.40}$$

$$N_{CO_2} = k_l^{\circ}{}_{,CO_2}\, \Delta C_{CO_2} + k_l^{\circ}{}_{,carb}\, \Delta C_{carb} + k_l^{\circ}{}_{,H_2CO_3}\, \Delta C_{H_2CO_3} \tag{4.41}$$

$$\frac{k_l^{\circ}{}_{,carb}\, \Delta C_{carb}}{k_l^{\circ}{}_{,H_2CO_3}\, \Delta C_{H_2CO_3}} = \frac{R_{carb}}{R_{H_2CO_3}} \tag{4.42}$$

$$k_g \left[P_{H_2S} - C_{H_2S,i,e}\, H_{H_2S} \right] = k_l^{\circ}{}_{,H_2S}\, \Delta C_{H_2S} \tag{4.43}$$

Equation (4.42) is an approximation developed by Glasscock and Rochelle (1990a). The value for $C_{H_2S,i,e}$ is obtained from the speciation at the interface. If the fluxes calculated in (4.40) and (4.41) are not equal and equations (4.42) and (4.43) are not satisfied, the guesses for the interface concentrations for RR'NCOOH, H_2CO_3, and H_2S are updated and the process repeated.

Chapter 5

Results

5.1 MDEA Modeling

The MDEA model described in Chapter 3 was used to evaluate the performance of an absorber/stripper system using 50 wt% MDEA. System performance was calculated as the amount of H_2S in the absorber off-gas (H_2S leak). Specifically, the effect of adding a strong acid to the amine solution and lowering the stripper pressure was studied. Sensitivity of the model predictions to values of the H_2S equilibrium constant, the mass transfer coefficients, and the CO_2-MDEA rate constant was also investigated.

5.1.1 Base Case

In order to compare results from the model at various operating conditions, a base case set of inputs was established. The base case conditions were selected to represent typical Claus tail gas conditions which implies the absorber is operated at low pressure. Table 5.1 shows the base case conditions chosen for both columns. The absorber feed gas is saturated with water, and the remaining composition is nitrogen. Saturated steam at 2 atm pressure has a temperature of 121°C; therefore, the steam into the stripper was assumed to be slightly superheated. The inlet liquid temperatures are specified because no attempt is made at modeling the cross-exchanger or trim cooler for the system. The inlet liquid temperature to the absorber gives a 15°C approach for the trim cooler with cooling water at 25°C. The temperature of the liquid into the stripper yields a 9°C approach for the cross-exchanger because the temperature of the liquid out of the stripper is 121°C (saturated water at 2 atm). The amine protonation heat of reaction is obtained from equation (3.36) by the relationship:

Table 5.1: MDEA Modeling Base Case Conditions

Parameter	Absorber	Stripper
Number of trays	20 bubble cap	25 bubble cap
Pressure (atm)	1.1	2
Pressure drop (atm/tray)	0.0025	0.0025
Feed gas	1% H_2S, 10% CO_2, 40°C	Live steam at 127°C
Inlet liquid temperature (°C)	40	112
Heats of reaction (cal/mole):		
H_2S dissociation	2089	2089
CO_2 dissociation	6364	6364
MDEA protonation	7889	7889
H_2O vaporization	10325	9461
Tray Specifications		
fractional approach to flood	0.7	0.7
liquid depth (cm)	7.0	7.0
effective froth height (cm)	15.0	17.0
Mass Transfer Parameters		
gas phase coefficient (mole/atm/dm^2/s)	0.02219	0.01958
liquid phase coefficient (dm/s)	0.001546	0.006441
interfacial area (dm^2/dm^2)	892.3	305.3
gas phase transfer units/tray	2.178	2.174

$$\frac{\Delta H}{R} = \frac{\partial \ln K_{MDEA}}{\partial\,(1/T)} = -0.019416 \ln(10)\, T^2 \tag{5.1}$$

The heat of reaction data for H_2S and CO_2 was obtained by subtracting the amine protonation heat of reaction from the fit of the equilibrium data. The heat of vaporization for water is used in the enthalpy balance for a stage, as are the heats of reaction. For the base case, different values were input for the absorber (10325 cal/mole) and stripper (9461 cal/mole). Values were obtained from the ASME Steam Tables (1977). The mass transfer parameters were calculated using the correlations for bubble cap trays. These values change slightly with operating conditions.

5.1.2 Optimum Liquid Rate

A base case steam rate and solvent circulation rate are not specified. For a given steam rate, an optimum liquid rate exists; therefore, for several steam rates the liquid rate was varied until the desired system performance (H_2S leak) of 100 ppm was obtained. The optimum liquid rate was determined for each set of operating conditions to provide a meaningful comparison to the base case results.

Base case results of H_2S leak as a function of liquid rate for steam rates of 0.023, 0.028, and 0.033 lb steam/SCF feed gas are presented in Figure 5.1. Each point on the plot represents one run of the model. Increasing the steam rate from 0.023 to 0.028 lb steam/SCF feed gas decreases the H_2S leak from 134 ppm to 98 ppm, while increasing the steam rate from 0.028 to 0.033 lb steam/SCF feed gas decreases the leak from 98 ppm to 77 ppm. Using a steam rate of 0.028 lb steam/SCF feed gas provides the desired system performance at the optimum liquid rate; therefore, this steam rate was used for **all** subsequent results. The curve for 0.028 lb steam/SCF feed gas shows a flat optimum liquid rate in the range 1.6 to 2.0 lb steam/gallon solvent. This optimum liquid rate is close to typical rates.

The optimum liquid rate shown in Figure 5.1 is not distinct due to tightly pinched conditions for H_2S in the stripper. This pinched condition can be seen in Figure 5.2 which is for the optimum liquid rate with 0.028 lb steam/SCF feed gas.

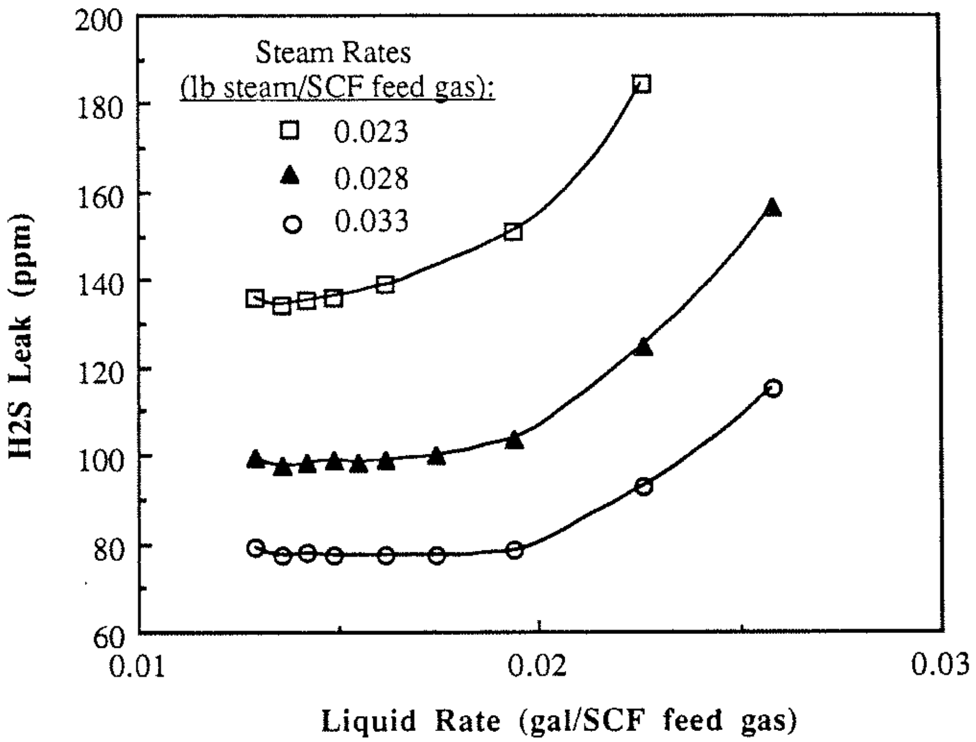

Figure 5.1: Effect of Steam Rate and Solvent Circulation Rate on System Performance (1.1 atm absorber with 20 trays, 2.0 atm stripper with 25 trays, feed gas with 1% H_2S, 10% CO_2).

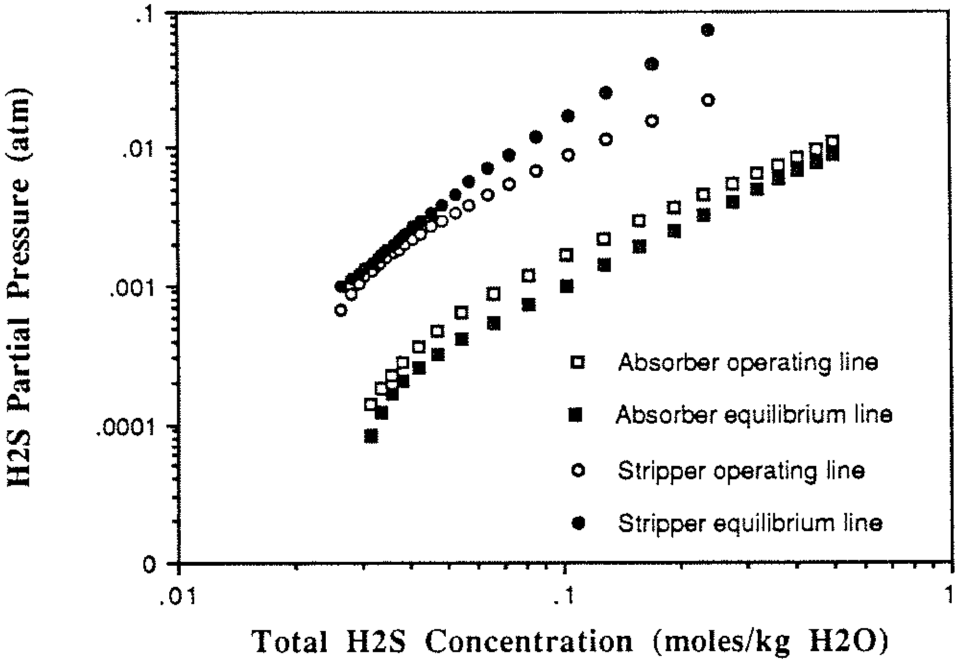

Figure 5.2: McCabe-Thiele Plot for the Base Case at the Optimum Liquid Rate (1.1 atm absorber with 20 trays, 2.0 atm stripper with 25 trays, feed gas with 1% H_2S, 10% CO_2, 1.7 lb steam/gal solvent).

This McCabe-Thiele type plot was generated from the detailed, stage-by-stage results reported by the model. The difference between the operating and equilibrium lines represents the driving force available for mass transfer. Because the data was plotted on a log-log scale, the operating line appears to be nonlinear.

Reducing the number of absorber stages to 14 and the number of stripper stages to 18 removes the stripper pinch and results in a distinct optimum liquid rate. Figures 5.3 and 5.4 illustrate the distinct optimum rate and reduced stripper pinch, respectively. Liquid rates greater than the optimum decrease performance due to energy limitations in the stripper which results in a lean absorber pinch. Liquid rates smaller than the optimum decrease performance because of the reduced absorbing capacity which results in a rich absorber pinch. Figure 5.1 does not show the performance decrease for low liquid rates because the model had trouble converging in this area due to tightly pinched conditions.

Details about an MDEA absorption/stripping system were obtained by examining the base case simulation at a steam rate of 0.028 lb steam/SCF feed gas at the optimum liquid rate. Tray efficiencies and liquid phase mass transfer resistances at the top and bottom of each tower are presented in Table 5.2. Even though large enhancement factors for H_2S occur in the absorber (from 225 at the bottom to 1050 at the top), the mass transfer of H_2S is somewhat liquid phase controlled because the gas phase coefficient is much larger than the liquid phase coefficient. Dow Chemical Company has observed similar H_2S resistances (Katti and Langfitt, 1986). In the stripper, the H_2S enhancement factor ranges from about 233 at the bottom to 31 at the top, but a smaller gas to liquid coefficient ratio causes similar mass transfer resistances.

Because of the much slower reaction rate, CO_2 mass transfer is always liquid phase controlled in an MDEA system. With an enhancement factor of about 1.2 in the absorber, CO_2 is practically under physical absorption. In the stripper, the CO_2 enhancement factor ranges from 2.5 at the top tray to 4.5 at the bottom tray. Conditions in the stripper were further analyzed to determine how close these enhancement factors are to instantaneous values. At the bottom tray the free CO_2 concentration at the interface is 0.349×10^{-5} mole/kg H_2O, and the bulk concentration is 0.108×10^{-3} mole/kg H_2O. If the CO_2 reaction was instantaneous,

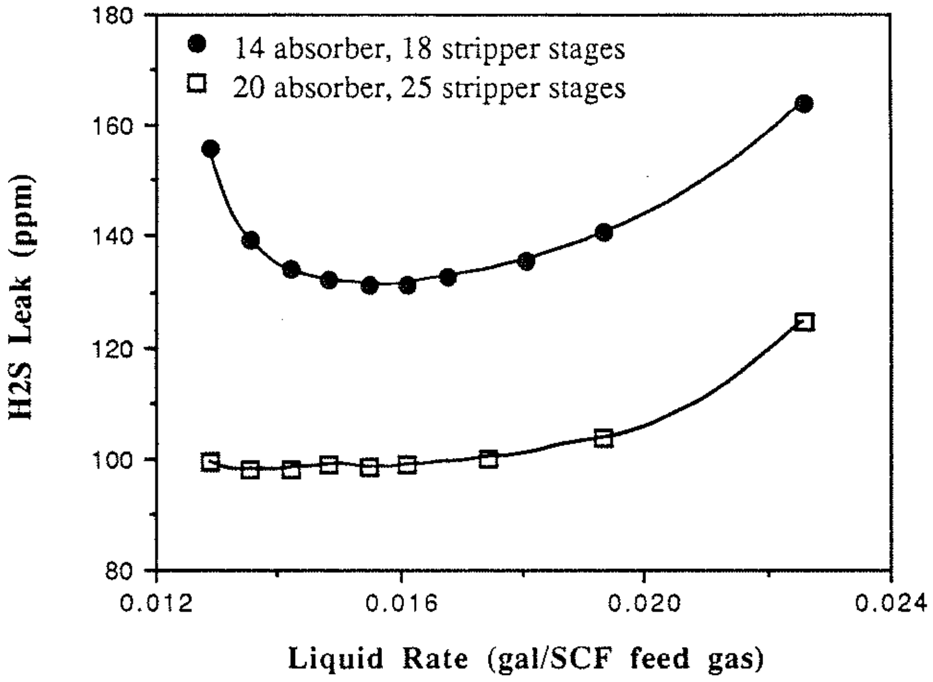

Figure 5.3: Effect of Reducing the Number of Absorber and Stripper Stages on the Liquid Rate and System Performance (1.1 atm absorber, 2.0 atm stripper, feed gas with 1% H_2S, 10% CO_2, 0.028 lb steam/SCF feed gas).

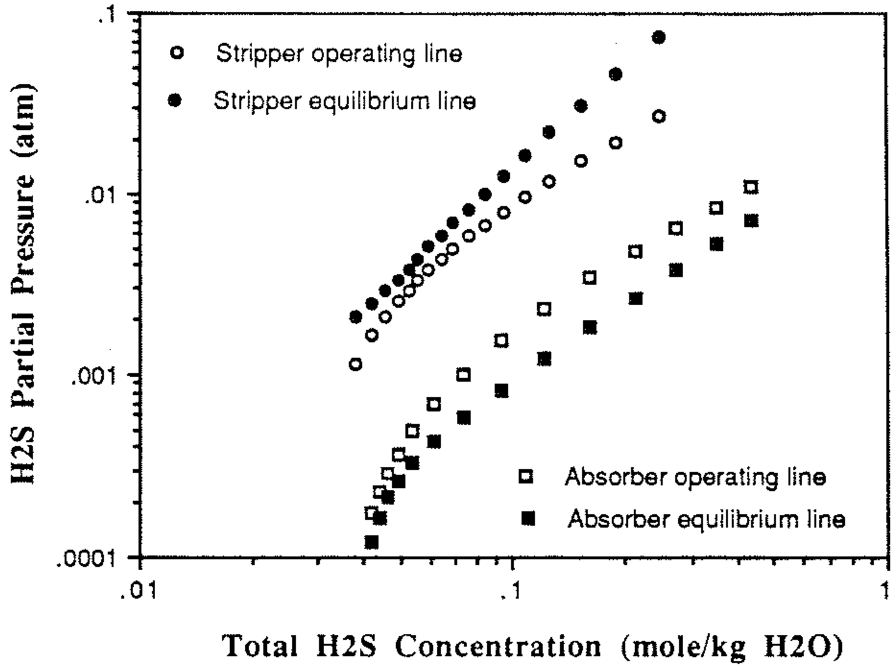

Figure 5.4: McCabe-Thiele Plot for the Optimum Liquid Rate with Reduced Absorber and Stripper Stages (1.1 atm absorber with 14 trays, 2.0 atm stripper with 18 trays, feed gas with 1% H_2S, 10% CO_2, 1.7 lb steam/gal solvent).

Table 5.2: Base Case Tray Efficiencies and Liquid Phase Mass Transfer Resistances

		Tray Efficiency (%)		Liquid Phase Resistance (%)	
		H_2S	CO_2	H_2S	CO_2
Absorber:	Bottom	61	1.0	63	100
	Top	89	0.3	27	100
Stripper:	Bottom	66	2.2	45	100
	Top	24	1.3	86	100

the CO_2 concentration at the interface would be at equilibrium and have a value of 0.895×10^{-4} mole/kg H_2O. These interface and bulk concentrations were used to estimate the CO_2 flux. Assuming the CO_2 reaction to be instantaneous would have resulted in an overestimation of the CO_2 flux by about an order of magnitude.

The base case results illustrated some other characteristics of an MDEA system. A temperature bulge of +3°C from the liquid out temperature is developed in the 20 tray absorber with the peak at the tenth stage. Similar temperature bulges have been well documented in the literature and can be much more extreme with higher absorber pressures. The selectivity for removing H_2S and leaving CO_2 in the gas is an important characteristic of the MDEA system. This case showed that 6.5% of the CO_2 and 99% of the H_2S in the feed gas is removed in the absorber, giving the off gas from the stripper a composition of 60% H_2S. This high percentage of H_2S is typical for MDEA systems and is good for Claus plant operation.

5.1.3 Acid Addition

The model was developed with the ability to predict system performance when a strong acid is added to the liquid phase. Addition of acid affects the liquid charge balance and increases the ionic strength of the solution; therefore, the model is designed to account for the addition of acid anion independent of anion type. Heinzelmann et al. (1986) have shown that sulfuric acid addition to MDEA solutions increases the H_2S selectivity. Union Carbide Corporation (1984) has also shown that adding acid to alkanolamine solvents improves H_2S removal. According to Union Carbide, typical Claus tail gas units have trouble obtaining an H_2S leak of 100 ppm with just amine solvent; however, H_2S leaks of less than 10 ppm can easily be achieved by adding acid. The pinched conditions of the base case discussed above showed difficulties in obtaining the performance level of 100 ppm with a reasonable steam rate and solvent rate; however, as shown in Figure 5.5, the model predicts performance of better than 10 ppm with acid addition.

Figure 5.5 shows two curves. One curve represents acid addition without changing the solvent circulation rate while the other curve represents acid addition with the liquid optimized at each point. The figure shows that without optimizing the liquid rate, performance is improved to about 25 ppm, but performance is improved to about 6 ppm if the liquid rate is increased about 35% while adding acid. Figure 5.6 shows the McCabe-Thiele plot for H_2S with 0.05 equiv acid/mole MDEA. Comparison of Figure 5.6 and Figure 5.2 shows that in both the absorber and stripper the equilibrium and operating lines have become almost parallel after adding acid, thus increasing the driving force for mass transfer throughout both columns.

The improved driving force illustrated in Figure 5.6 can be explained by examining what happens to the H_2S equilibrium after adding acid. The following equation represents the H_2S equilibrium:

$$P_{H_2S} = \frac{H_{H_2S}}{K_{H_2S}} \frac{[HS^-]\,[\,MDEAH^+]}{[MDEA]} \tag{5.2}$$

Examination of this equation partially explains why pinched conditions easily occur in the lean end of the stripper for the base case. At the lean end, the solution loading is very low; therefore, the protonated amine concentration is low, and the free amine concentration is high. The overall effect is a low equilibrium partial

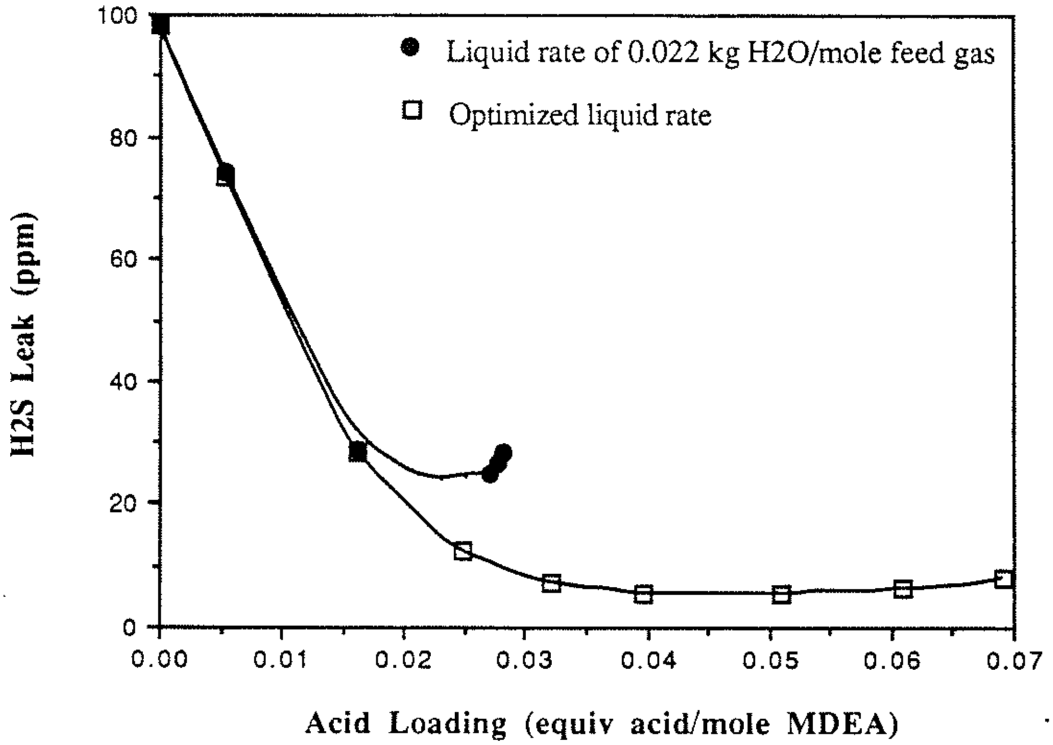

Figure 5.5: Effect of Acid Addition on System Performance (1.1 atm absorber with 20 trays, 2.0 atm stripper with 25 trays, feed gas with 1% H_2S, 10% CO_2, 0.028 lb steam/SCF feed gas).

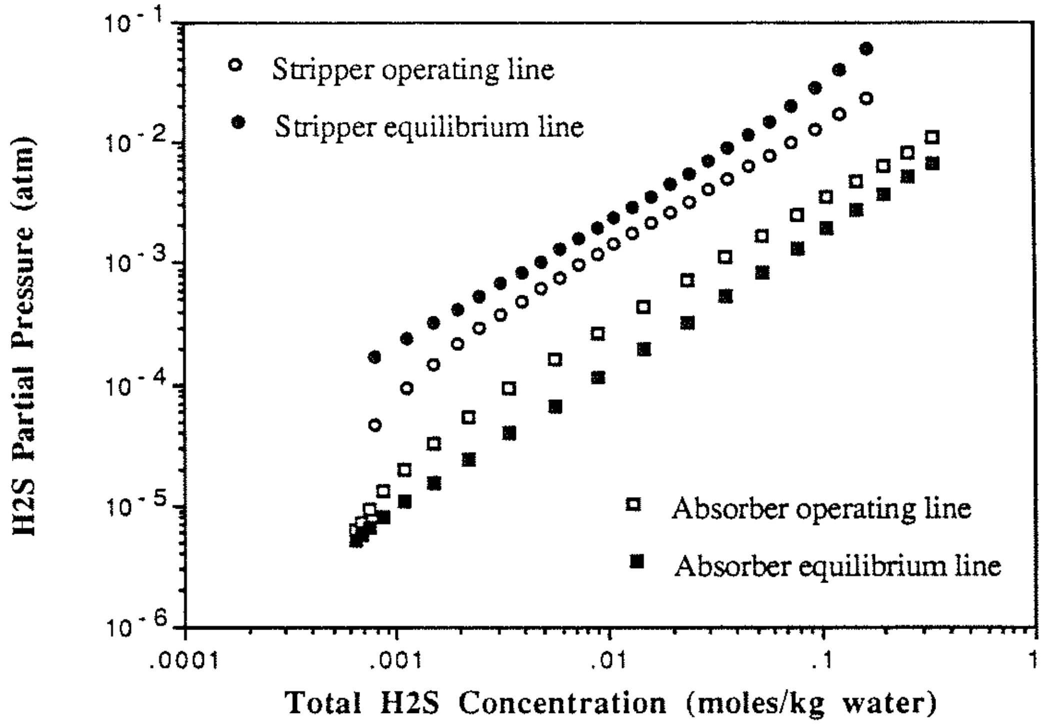

Figure 5.6: McCabe-Thiele Plot for Optimum Acid Addition (1.1 atm absorber with 20 trays, 2.0 atm stripper with 25 trays, feed gas with 1% H_2S, 10% CO_2, 1.2 lb steam/gal solvent, 0.05 equiv/mole MDEA).

pressure. The operating partial pressure is also low in this part of the stripper so that a pinch can easily occur.

Acid addition causes the following reaction:

$$\text{Acid} + \text{MDEA} \Leftrightarrow \text{Acid anion} + \text{MDEAH}^+ \tag{5.3}$$

This reaction produces a much higher protonated MDEA concentration throughout the column. If the concentration of protonated amine is very large compared to the total concentration of H_2S, which is approximately the bisulfide concentration, the ratio $[R_3NH^+]/[R_3N]$ can be considered constant at the lean end and P_{H_2S} is proportional to $[H_2S]_{total}$. Thus, the H_2S equilibrium is then given by:

$$P_{H_2S} = C_{H_2S}[HS^-] \tag{5.4}$$

where

$$C_{H_2S} = \frac{H_{H_2S}\,[MDEAH^+]}{K_{H_2S}\,[MDEA]} \tag{5.5}$$

Equation (5.4) shows that system performance improves because the H_2S equilibrium is now essentially linear and the H_2S lean loading will be lower. The increased concentration of protonated amine also explains why performance is only improved to 25 ppm without optimizing the liquid rate. The large amount of protonated amine decreases the absorption capacity of the solution; therefore, the improved stripper performance is eventually offset by reduced absorber performance.

5.1.4 Stripper Pressure Reduction

The results for acid addition indicate that increasing the concentration of protonated amine in the stripper will improve performance. Lowering the stripper pressure was expected to increase the protonated amine concentration by increasing the lean loading of CO_2. By lowering the stripper pressure, and therefore the temperature, reaction rates are slower. The lower temperature affects the CO_2 reaction rate more than that of H_2S because CO_2 has a higher heat of reaction with MDEA. The slower reaction rate lowers the CO_2 enhancement factor; therefore, the mass transfer of CO_2 in the stripper is adversely affected and more CO_2 is left in the lean solution. The extra CO_2 in solution helps to linearize the H_2S equilibrium by protonating more amine, especially in the lean end, which leads to lower H_2S lean loadings. As a test to see if this is true, the amount of CO_2 in the feed gas was reduced to see if the effect on system performance is the same.

Figure 5.7 shows the effect of reducing the stripper pressure on system performance using the base case steam rate. With 10% CO_2 feed gas, the performance is drastically improved from 98 ppm H_2S leak for the base case (2 atm) to 4 ppm at a pressure of 0.5 atm. Lowering the stripper pressure from 2 atm to 0.5 atm increased the CO_2 lean loading from 0.0012 to 0.018 mole/mole MDEA. This is evidence that the effect of the CO_2 lean loading on H_2S stripping described above is the cause for the improved performance. Figure 5.8 shows the operating and equilibrium lines for H_2S in the stripper at 0.5 atm. Because of the lower stripper temperature, the stripper operating line corresponded to the absorber equilibrium line; therefore, only the stripper is shown. Comparison of Figure 5.8 with Figure 5.2 shows the removal of the pinch at 0.5 atm. This again is due to the linearization of the H_2S equilibrium.

Figure 5.7 also shows the system performance at various pressures with only 2.5% CO_2 feed gas. Clearly, the increase in performance by reducing the pressure is reduced with only 2.5% CO_2 in the feed gas. With 2.5% CO_2 in the feed gas, the H_2S leak only drops from 68 ppm to 25 ppm with the same drop in pressure. Figure 5.9 shows the operating and equilibrium lines for the 0.5 atm stripper with 2.5% CO_2 feed gas. Comparison of Figure 5.9 with Figure 5.8 shows that a greater stripper pinch occurs with a smaller amount of CO_2 in the feed gas.

Although the presence of CO_2 is helpful in H_2S removal at lower pressures because it linearizes the equilibrium, CO_2 hinders H_2S removal at higher pressures as seen by the higher leak at 2 atm stripper pressure with 10% CO_2. At the lean end

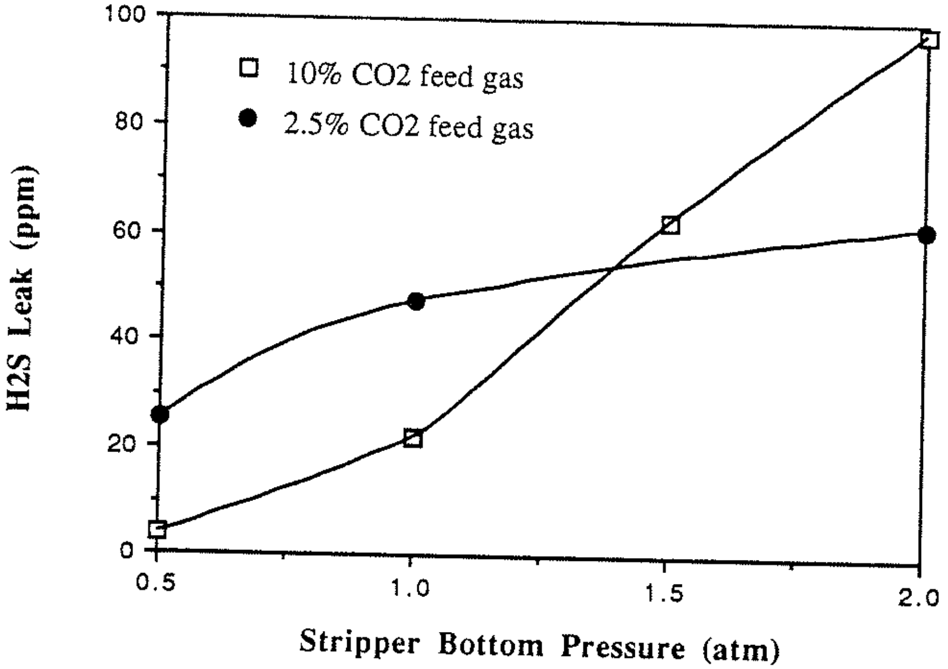

Figure 5.7: Effect of Reducing the Stripper Pressure on System Performance with Varying Amounts of CO2 in the Feed Gas (1.1 atm absorber with 20 trays, stripper with 25 trays, feed gas with 1% H_2S, 0.028 lb steam/SCF feed gas, liquid rate optimized).

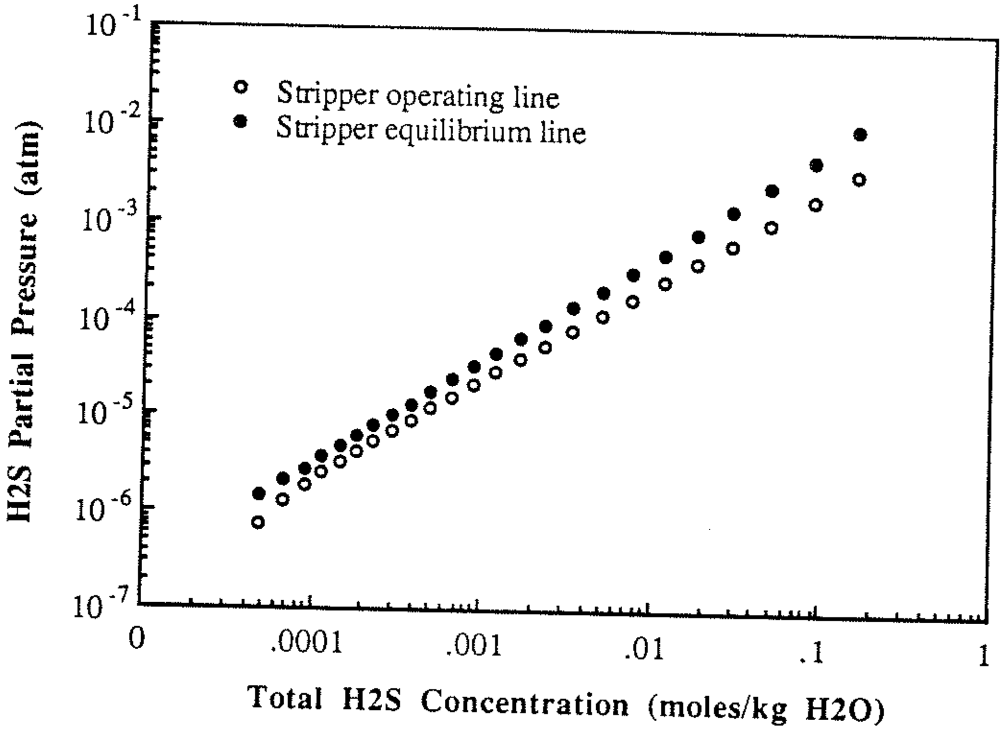

Figure 5.8: McCabe-Thiele Plot with 10% CO2 Feed Gas and a Stripper Pressure of 0.5 atm (1.1 atm absorber with 20 trays, stripper with 25 trays, feed gas with 1% H_2S, 1.9 lb steam/gal solvent).

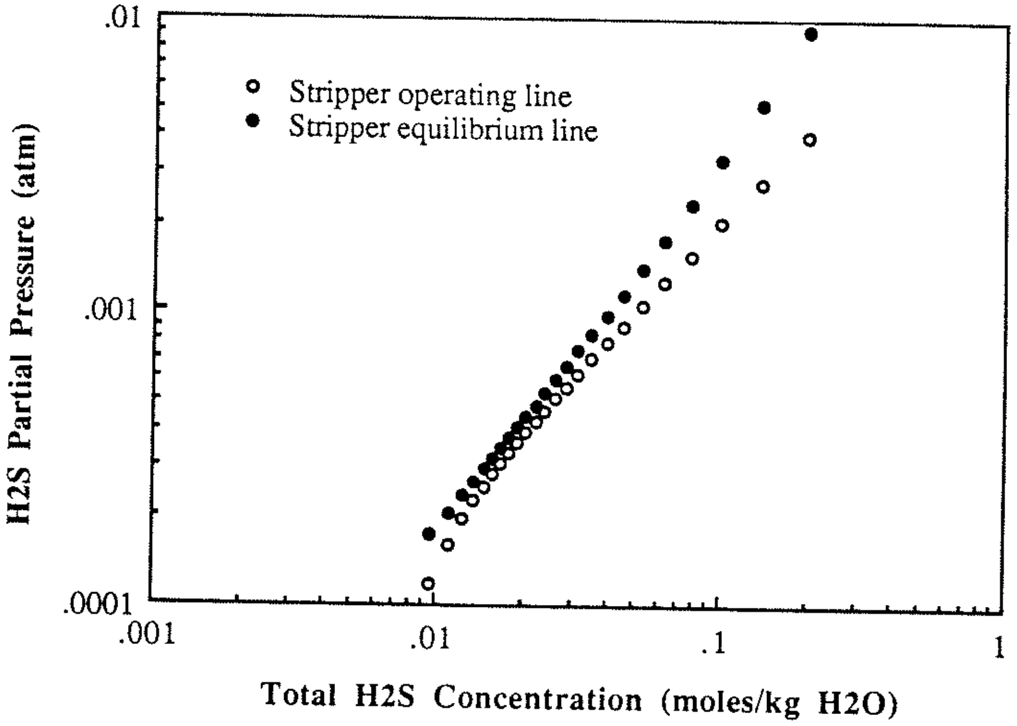

Figure 5.9: McCabe-Thiele Plot with 2.5% CO2 Feed Gas and a Stripper Pressure of 0.5 atm (1.1 atm absorber with 20 trays, stripper with 25 trays, feed gas with 1% H_2S, 1.9 lb steam/gal solvent).

of the absorber, CO_2 at the gas/liquid interface creates protonated amine which decreases the ability to absorb H_2S. This effect has also been discussed by Yu and Astarita (1987).

Figure 5.10 shows a comparison between the effect of acid addition and reduction of stripper pressure. When adding acid, an acid loading of about 0.04 is required to produce a 5 ppm H_2S leak. However, in the case of pressure reduction a CO_2 lean loading of only about 0.018 is required to produce the same leak. This large difference in acid loading and CO_2 loading suggests that linearization of the H_2S equilibrium is not the only benefit of reducing the stripper pressure. Further analysis of the simulation output showed the stripper gas phase mass transfer coefficient is increased by about a factor of 4 and the number of transfer units is increased by about 50% when reducing the stripper pressure. Addition of acid has no effect on these parameters. Because the H_2S is partially gas phase controlled as shown in Table 5.2, the increase in these mass transfer parameters improves H_2S stripping. The effect of these mass transfer parameters is further illustrated by comparing the driving forces in Figures 5.6 and 5.8. The McCabe-Thiele diagram for acid addition shows much larger driving forces throughout the stripper than the analogous diagram for pressure reduction. Larger driving forces indicate lost work and thus a larger acid loading for the same system performance.

5.1.5 Reduction of Stripper Stages

Based on the stripper pressure reduction results, increasing the CO_2 lean loading improves system performance. Conceivably, if reducing the number of stripper stages affected the stripping of CO_2 more than that of H_2S, the CO_2 lean loading in the stripper could increase. This effect was investigated using a 2 atm stripper and 14 absorber stages. The results are shown in Figure 5.11. Obviously, reducing the number of stripper stages does not improve performance under these conditions. As expected, the CO_2 lean loading increased as the number of stripper stages was reduced; however, the increase in lean loading was not as great as in the case of reducing the stripper pressure. In addition, the H_2S lean loading also

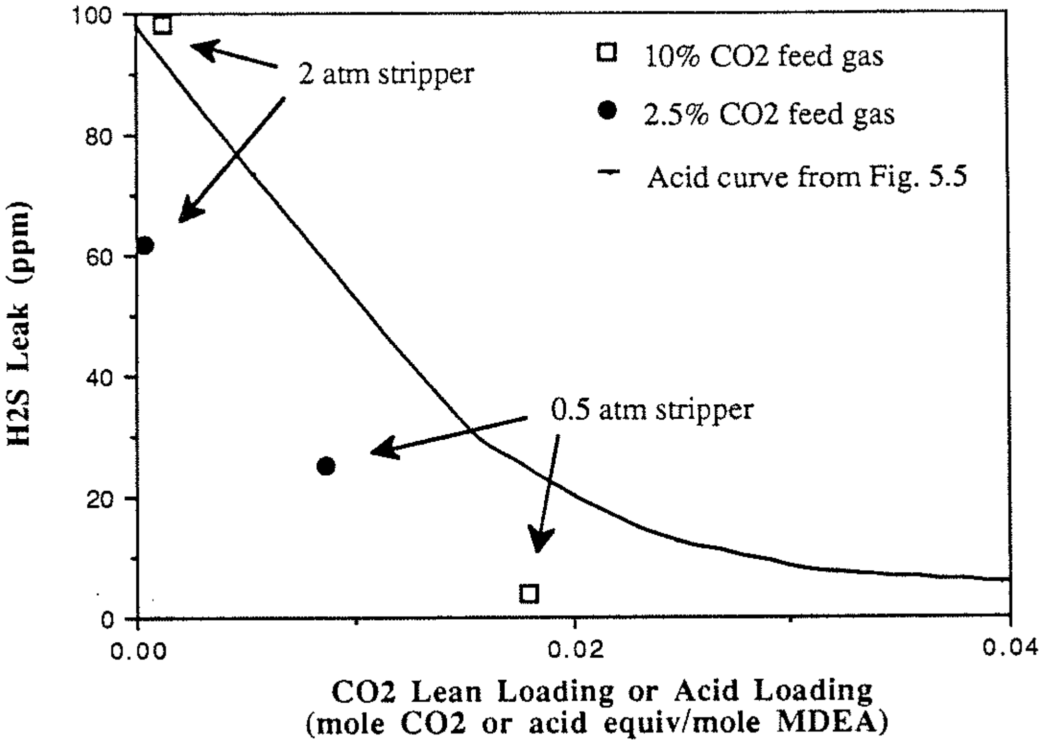

Figure 5.10: Comparison of the Effect of Acid Addition and Stripper Pressure Reduction on System Performance (1.1 atm absorber with 20 trays, stripper with 25 trays, feed gas with 1% H_2S, 0.028 lb steam/SCF feed gas).

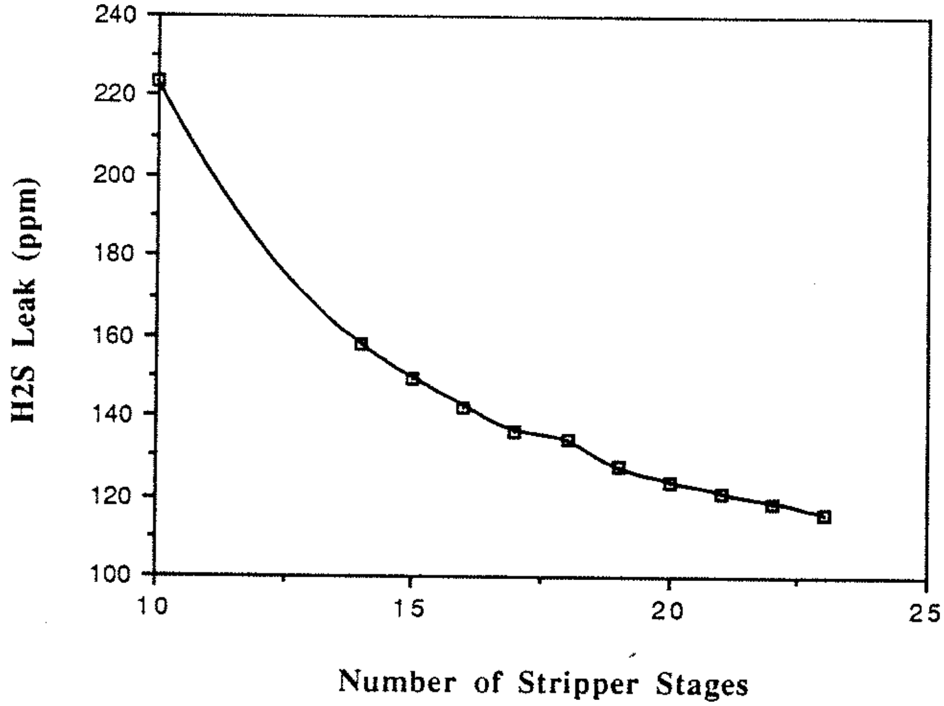

Figure 5.11: Effect of Stripper Stages on System Performance (1.1 atm absorber with 14 trays, 2.0 atm stripper, feed gas with 1% H_2S, 10% CO_2, 0.028 lb steam/SCF feed gas).

increased; therefore, H_2S stripping was hindered due to the reduced number of stages. These two effects resulted in a decrease in system performance. A similar decrease in performance was found when the number of stages was reduced from 18 to 15 for a 1 atm stripper.

5.1.6 Sensitivity Analysis

The sensitivity of the model results to the H_2S equilibrium constant, the H_2S heat of reaction, the mass transfer coefficients, and the CO_2-MDEA rate constant was tested by varying all of these parameters independently. All of the sensitivity analysis was done for the system with 14 absorber trays, 18 stripper stages, and a steam rate of 0.028 lb steam/SCF feed gas. Because no severe pinch exists in the stripper for this case as illustrated by Figure 5.4, the results from this analysis are more easily interpreted, and the model was more stable. A summary of the sensitivity of various system responses to variation of the parameters above is shown in Table 5.3. Carbon dioxide lean loading is the moles of CO_2 per moles of MDEA entering the absorber in the liquid phase. Percent CO_2 slip is the percent of CO_2 in the feed gas that "slips" through the absorber. This table indicates that system performance is most sensitive to the equilibrium constants and heats of reaction.

The first parameter varied was the H_2S equilibrium constant defined by equation (3.28) and fit to experimental data. This parameter was varied in two ways. First, the H_2S equilibrium constant was varied in both columns by multiplying it by a constant factor. Second, the constant was held constant at 40°C (absorber conditions) and varied in the stripper by adjusting the H_2S heat of reaction. As shown in Table 5.3, the H_2S leak is very sensitive to changes in the H_2S equilibrium constant in the stripper and the H_2S heat of reaction. The percent CO_2 slip is slightly sensitive to changing the H_2S equilibrium constant in the absorber because changing this constant varies the solution capacity. Figure 5.12 shows the effect of changing the H_2S equilibrium constant on system performance for these two cases with the liquid rate optimized at each point. Sensitivity of the

Table 5.3: Base Case Sensitivity of System Responses to Various Parameters.

$$\text{Sensitivity of response} = \frac{d[\ln(\text{response})]}{d[\ln(\text{parameter})]} = \frac{\Delta(\text{response})}{\Delta(\text{parameter})}\ \frac{\text{parameter}}{\text{response}}$$

	Sensitivity to Response		
Adjusted Parameter	H_2S Leak (ppm)	CO_2 Lean Loading	Percent CO_2 Slip
H_2S equilibrium constant in both columns	0.33	-0.96	0.01
H_2S equilibrium constant in only the stripper	1.72	-1.05	0.0
H_2S heat of reaction	-1.29	0.78	0.0
k_g	-0.27	0.0	0.0
k_l°	-0.48	0.14	-0.032
CO_2-MDEA rate constant	0.17	-0.60	-0.01

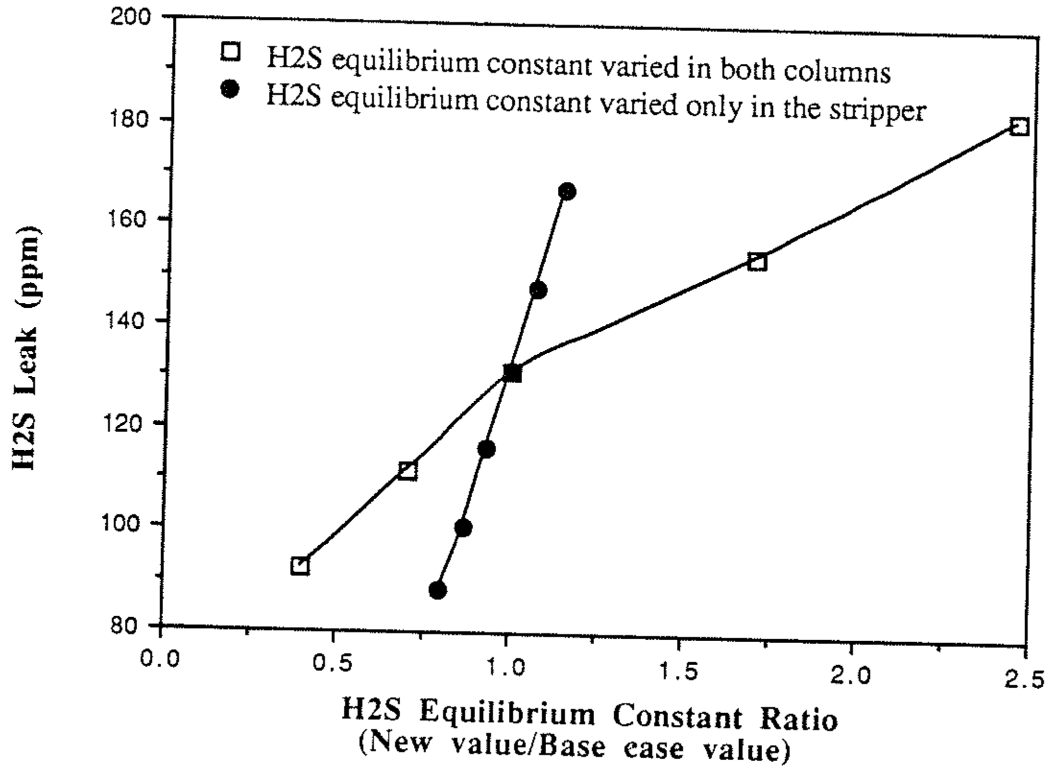

Figure 5.12: Effect of Varying the H_2S Chemical Equilibrium Constant on System Performance (1.1 atm absorber with 14 trays, 2.0 atm stripper with 18 trays, feed gas with 1% H_2S, 10% CO_2, 0.028 lb steam/SCF feed gas).

model results to values of the stripper equilibrium constant and heats of reaction. suggests that determination of these parameters at high temperatures is warranted.

The effect of changing the liquid and gas phase mass transfer coefficients was investigated by holding the interfacial area available for heat and mass transfer constant. The number of gas phase transfer units varied as the gas phase mass transfer coefficient varied. Table 5.3 indicates that the H_2S leak is sensitive to changes in both the gas and liquid phase mass transfer coefficients; however, percent CO_2 slip is sensitive to only values of the liquid phase coefficient. Figures 5.13 and 5.14 further illustrate this point. As shown in Table 5.2, the H_2S is partially liquid and partially gas phase controlled. As either the gas phase or liquid phase coefficient is increased, part of the mass transfer resistance is removed; therefore, H_2S can more easily approach total equilibrium and the H_2S leak is improved. Because the absorption of CO_2 is totally liquid phase controlled, changing the liquid phase coefficient significantly affects the selectivity while changes in the gas phase coefficient have virtually no effect. Similarly, as shown in Table 5.3, the CO_2 lean loading is unaffected by changes in k_g because CO_2 absorption is liquid phase controlled. Figure 5.13 illustrates that when adjusting the liquid transfer coefficient, either the H_2S leak or the amount of CO_2 absorbed must be sacrificed to improve the other; however, as illustrated in Figure 5.14, the gas phase coefficient can be increased to improve H_2S leak while maintaining the same selectivity. These results suggest a new column should be designed to give the highest gas phase coefficient while the liquid phase coefficient should be increased to the point of the desired performance or CO_2 removal.

Finally, the sensitivity of the results to the CO_2-MDEA rate constant was investigated. The rate constant was not expected to have a large effect on the H_2S leak because the CO_2 enhancement factor in the absorber is near 1.0; however, Table 5.3 and Figure 5.15 show that the H_2S leak is sensitive to values of this rate constant. The change in H_2S leak is due to the effect of CO_2 loading in the stripper. Table 5.3 shows that the CO_2 lean loading is very sensitive to the value of this rate constant. This sensitivity occurs because as the CO_2-MDEA rate constant is increased CO_2 is more easily stripped; therefore, the CO_2 lean loading is decreased. As discussed earlier for the case of reducing the stripper pressure, this

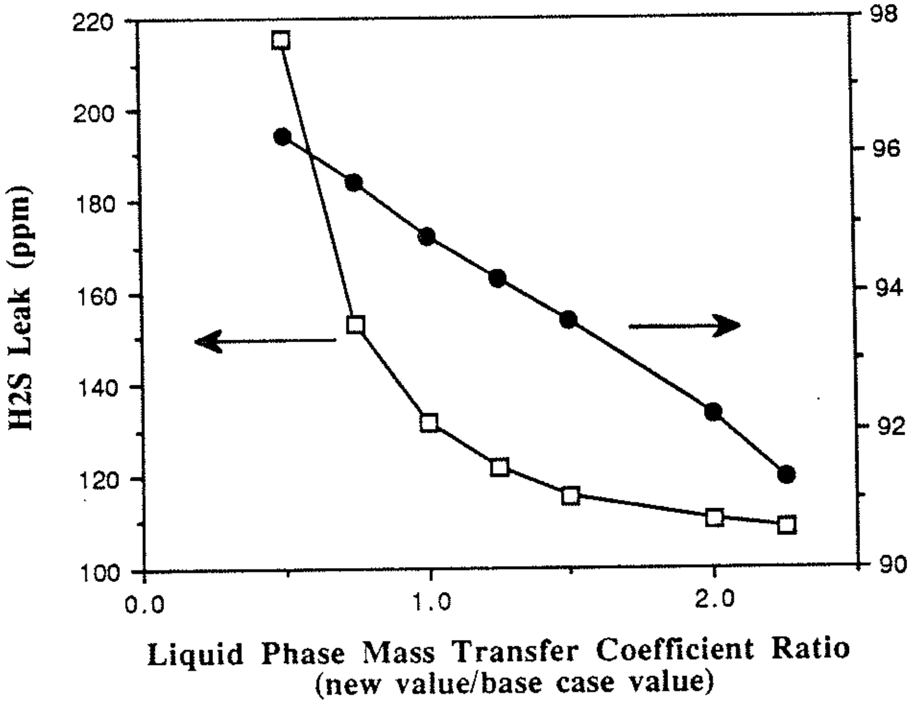

Figure 5.13: Effect of Changing the Liquid Phase Mass Transfer Coefficient on System Performance and Selectivity (1.1 atm absorber with 14 trays, 2.0 atm stripper with 18 trays, feed gas with 1% H_2S, 10% CO_2, 1.7 lb steam/gal solvent).

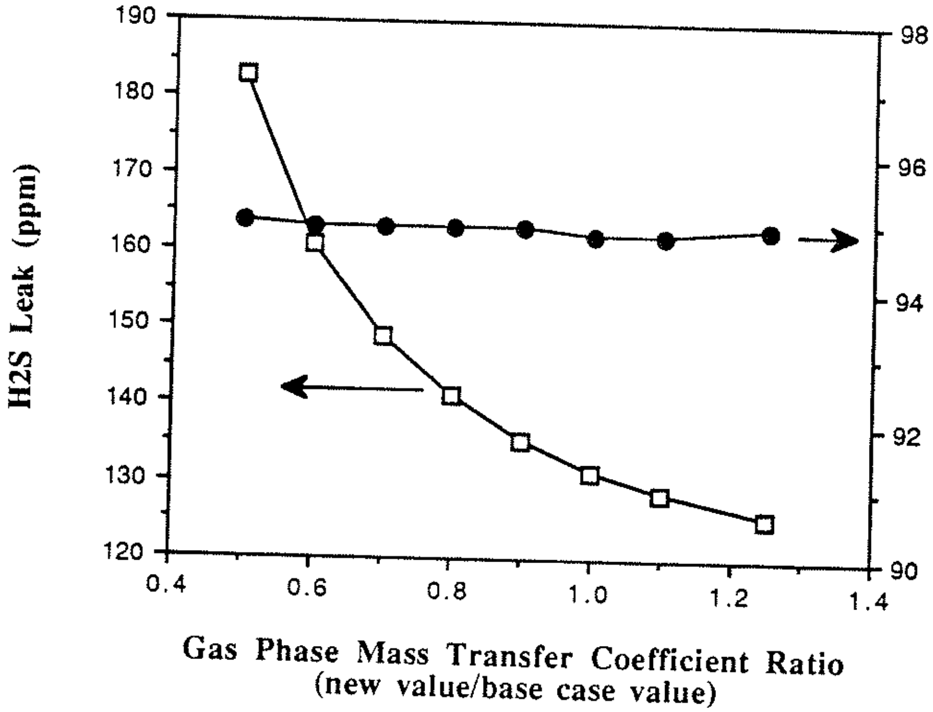

Figure 5.14: Effect of Changing the Gas Phase Mass Transfer Coefficient on System Performance and Selectivity (1.1 atm absorber with 14 trays, 2.0 atm stripper with 18 trays, feed gas with 1% H_2S, 10% CO_2, 1.7 lb steam/gal solvent).

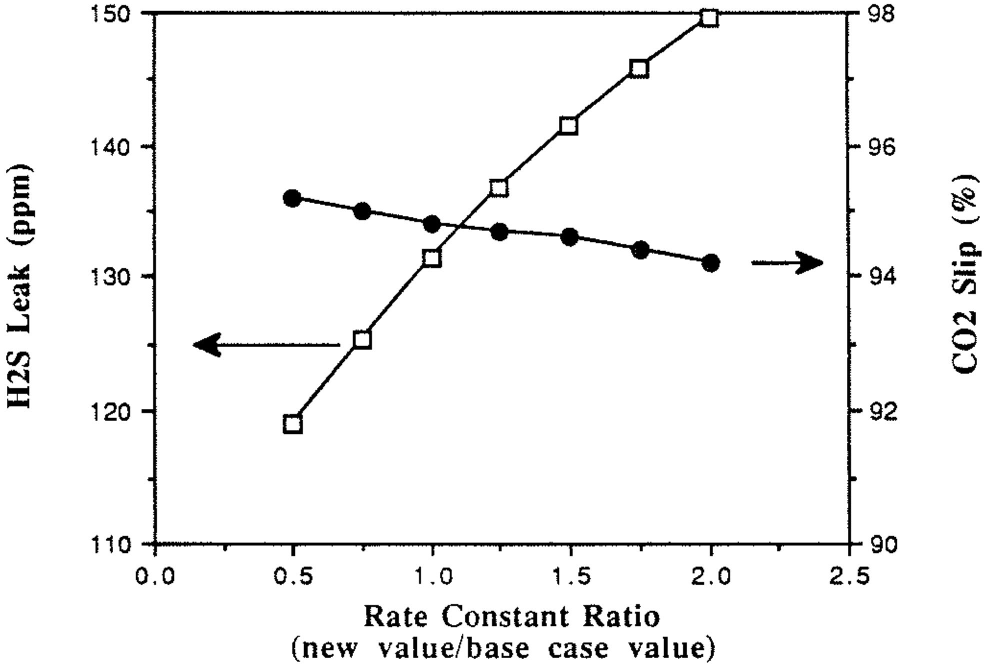

Figure 5.15: Effect of Changing the CO_2-MDEA Rate Constant on System Performance and Selectivity (.1 atm absorber with 14 trays, 2.0 atm stripper with 18 trays, feed gas with 1% H_2S, 10% CO_2, 1.7 lb steam/gal solvent).

decrease in CO_2 lean loading results in an improved H_2S leak. Table 5.4 compares the variation of CO_2 lean loading for the cases of reducing the stripper pressure and changing the CO_2-MDEA rate constant. Clearly, reducing the stripper pressure has the same effect on H_2S leak as varying the kinetic rate canstant. Percent CO_2 slip decreases slightly as the CO_2-MDEA rate constant is increased because CO_2 absorption is enhanced as the kinetic rate constant is increased.

5.2 Modeling with ASPEN PLUS™

The ASPEN PLUS™ model developed in Chapter 4 was used to perform equilibrium flash calculations and column modeling. The equilibrium flash calculations were done to verify that the physical properties and NRTL parameters supplied to ASPEN PLUS™ accurately represent the various amine systems. Because the rate-based column model RATEFRAC is currently unavailable, column modeling was attempted using the equilibrium-based model RADFRAC.

5.2.1 Equilibrium Calculations

Equilibrium curves for H_2S and CO_2 in the various amines were generated by performing bubble point calculations with an ASPEN PLUS™ flash model. Austgen (1989) provides an extensive set of experimental H_2S and CO_2 equilibrium data for MEA, DEA, MDEA, DGA, and mixed amines. For purposes of this work, a set of experimental data for each amine with H_2S and CO_2 was arbitrarily chosen and compared to the model predictions. This comparison is shown in Figures 5.16 through 5.26. These figures indicate overall good agreement between the experimental data and the model predictions over a wide temperature range for all amines with both H_2S and CO_2.

Table 5.4: Variation of CO_2 Lean Loading for Different Operating Conditions

Case	H_2S Leak (ppm)	CO_2 Lean Loading (mole CO_2/mole MDEA)
2 atm stripper with 25 trays, 10% CO_2 feed gas	98.2	0.00130
2 atm stripper with 25 trays, 2.5% CO_2 feed gas	61.8	0.000325
0.5 atm stripper with 25 trays, 10% CO_2 feed gas	4.0	0.0180
0.5 atm stripper with 25 trays, 2.5% CO_2 feed gas	25.3	0.00871
2 atm stripper with 18 trays, 10% CO_2 feed gas	131	0.00205
Increase the CO_2-MDEA rate constant by 100% using 18 stripper trays	150	0.00130
Decrease the CO_2-MDEA rate constant by 50% using 18 stripper trays	117	0.00291

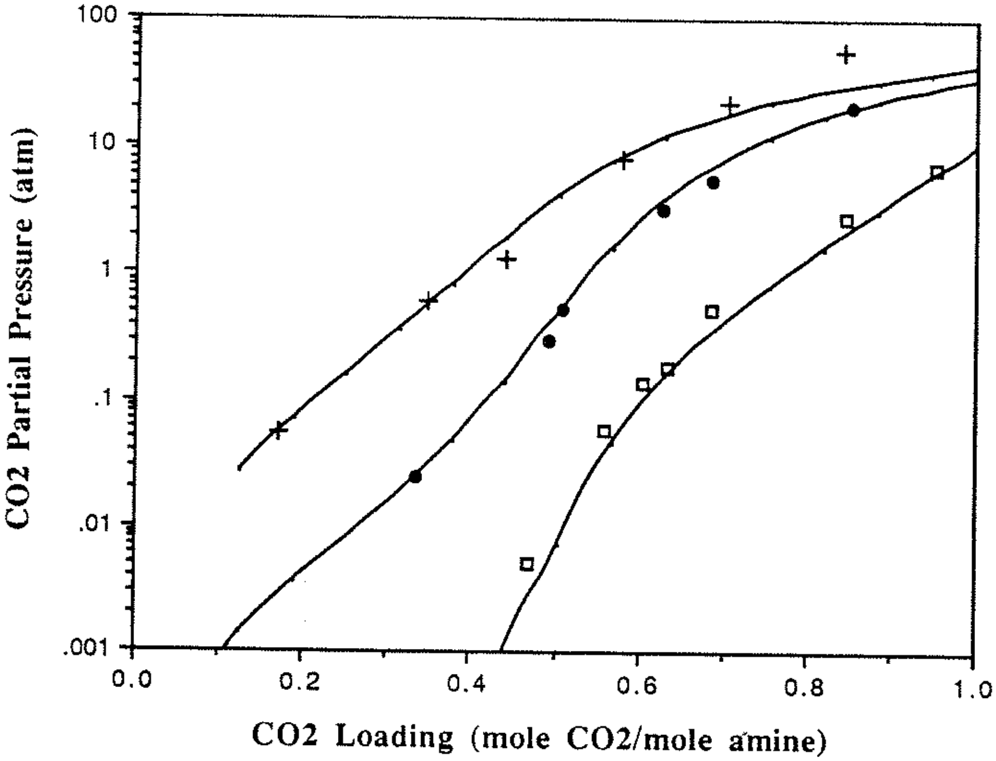

Figure 5.16: Comparison of Model Prediction to Experimental Data for CO_2 in 2.5M MEA Model prediction: (—). Experimental data from Lee et al. (1976a): (▫) - 25°C, (•) - 80°C, (+) - 120°C

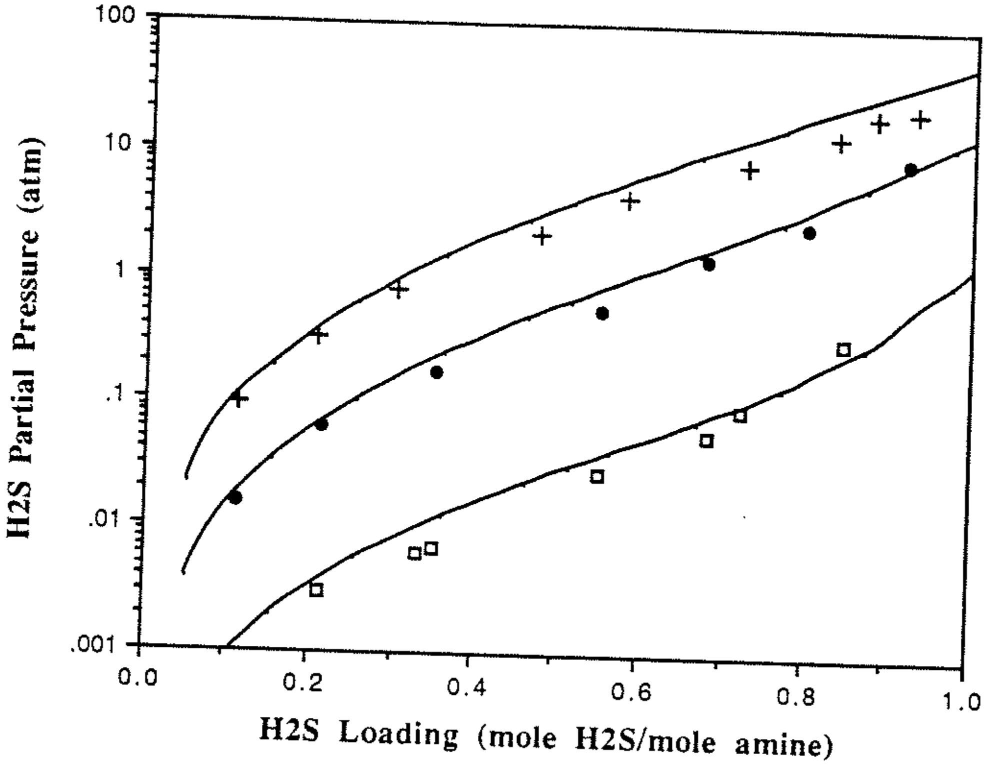

Figure 5.17: Comparison of Model Prediction to Experimental Data for H_2S in 5.0M MEA Model prediction: (—). Experimental data from Lee et al. (1976b): (▫) - 25°C, (•) - 80°C, (+) - 120°C

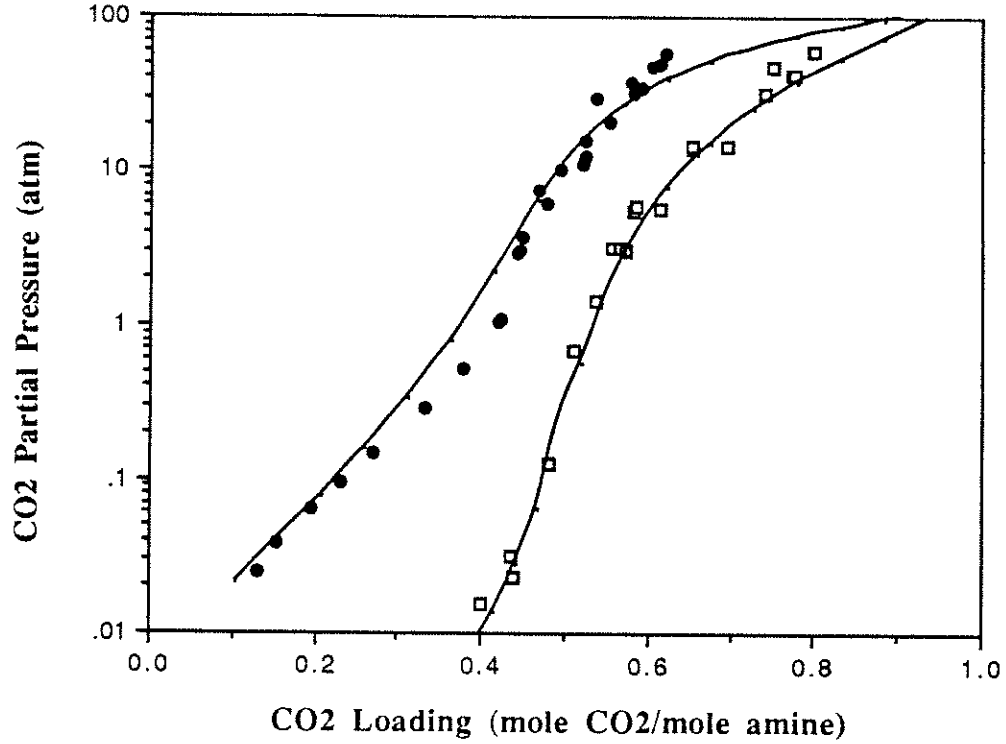

Figure 5.18: Comparison of Model Prediction to Experimental Data for CO_2 in 60 wt% DGA. Model prediction: (—). Experimental data from Martin et al. (1978): (▫) - 50°C, (•) - 100°C

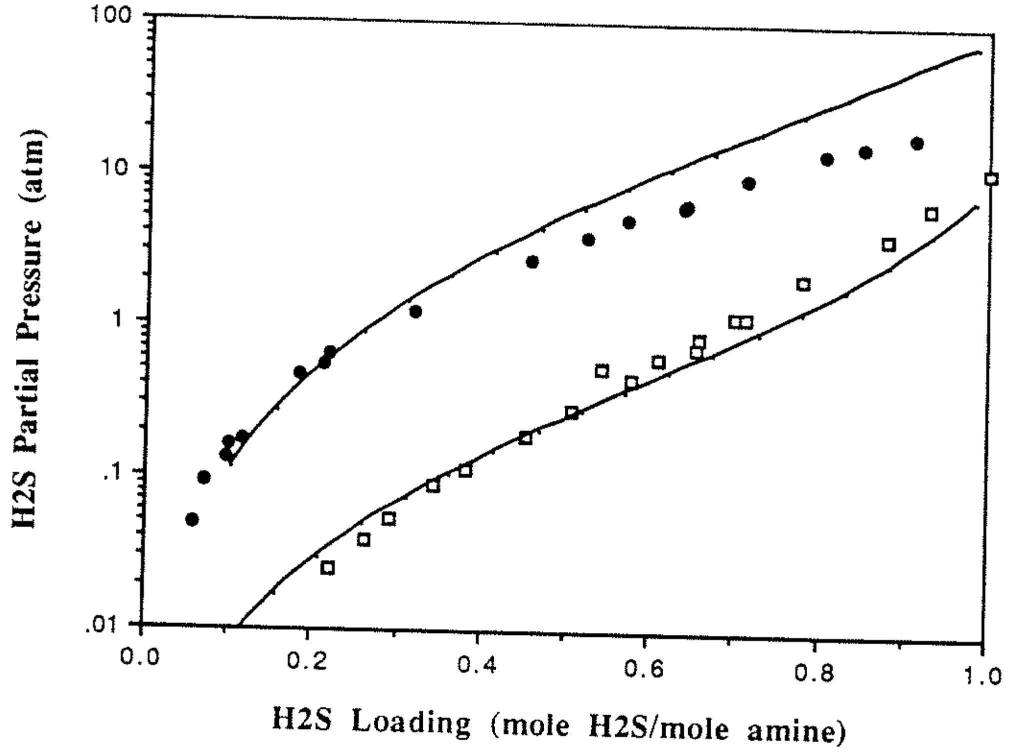

Figure 5.19: Comparison of Model Prediction to Experimental Data for H_2S in 60 wt% DGA. Model prediction: (—). Experimental data from Martin et al. (1978): (▫) - 50°C, (•) - 100°C

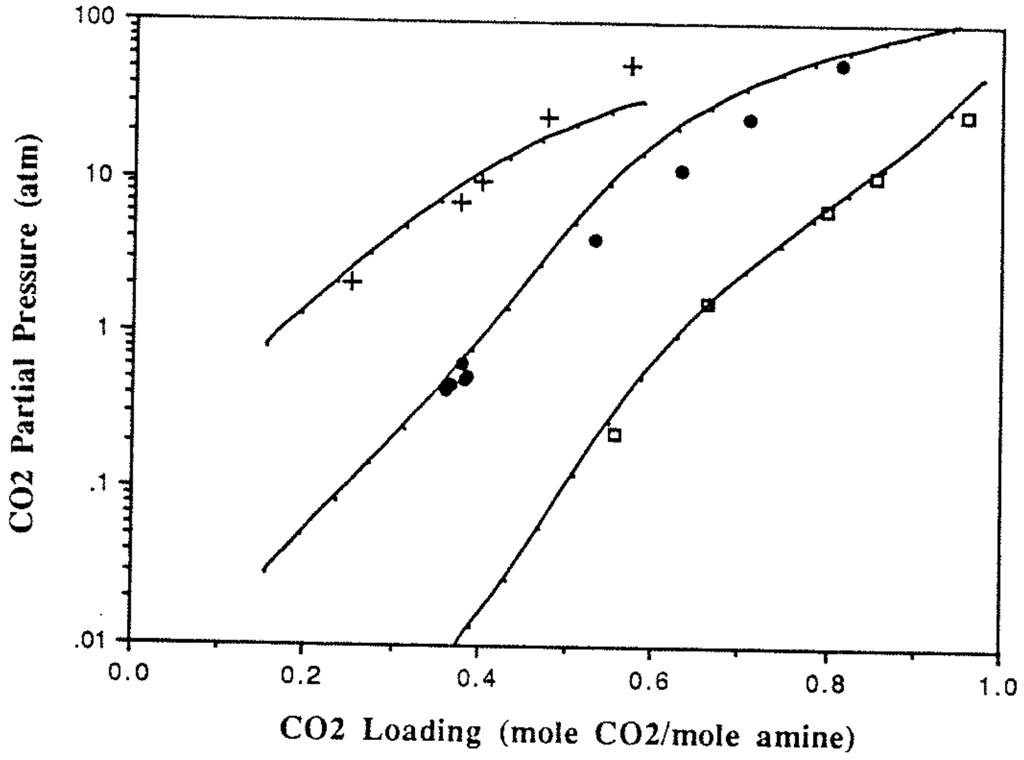

Figure 5.20: Comparison of Model Prediction to Experimental Data for CO_2 in 5.0M DEA. Model prediction: (—). Experimental data from Lee et al. (1972): (▫) - 25°C, (•) - 75°C, (+) - 120°C

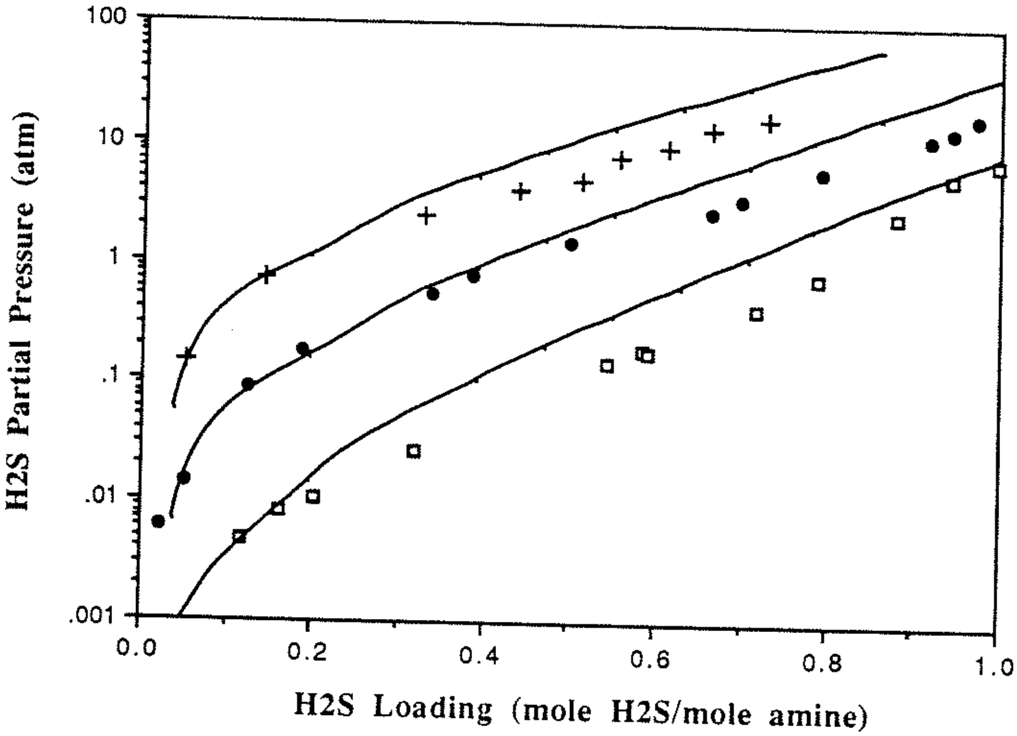

Figure 5.21: Comparison of Model Prediction to Experimental Data for H_2S in 5.0M DEA. Model prediction: (—). Experimental data from Lee et al. (1973): (▫) - 25°C, (•) - 75°C, (+) - 120°C

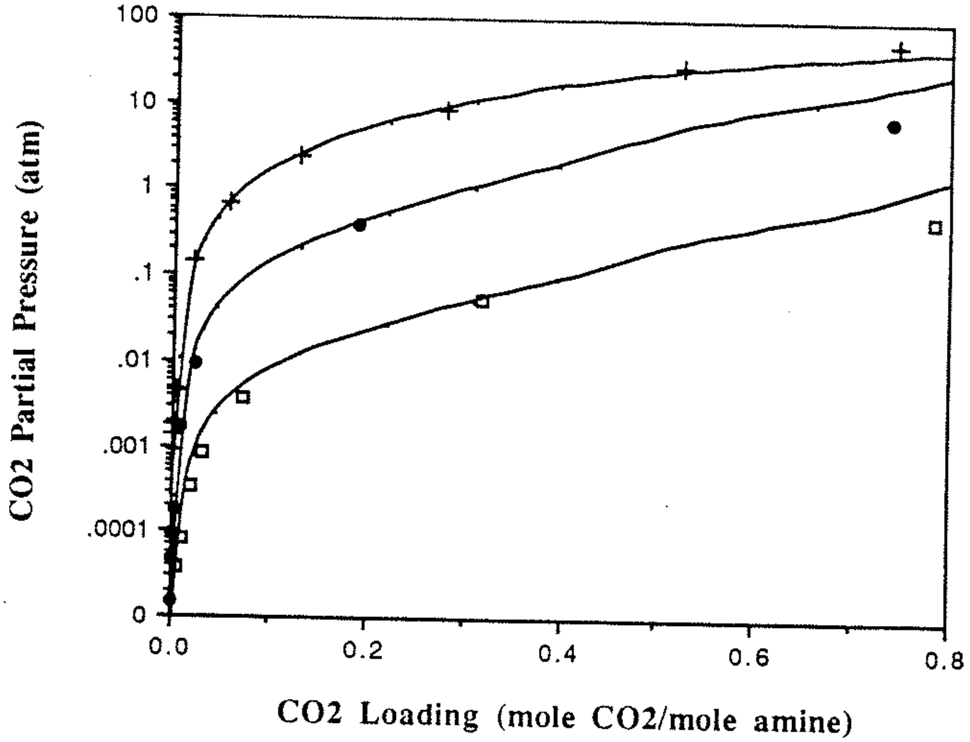

Figure 5.22: Comparison of Model Prediction to Experimental Data for CO_2 in 4.28M MDEA. Model prediction: (—). Experimental data from Jou et al. (1982): (□) - 25°C, (•) - 70°C, (+) - 120°C

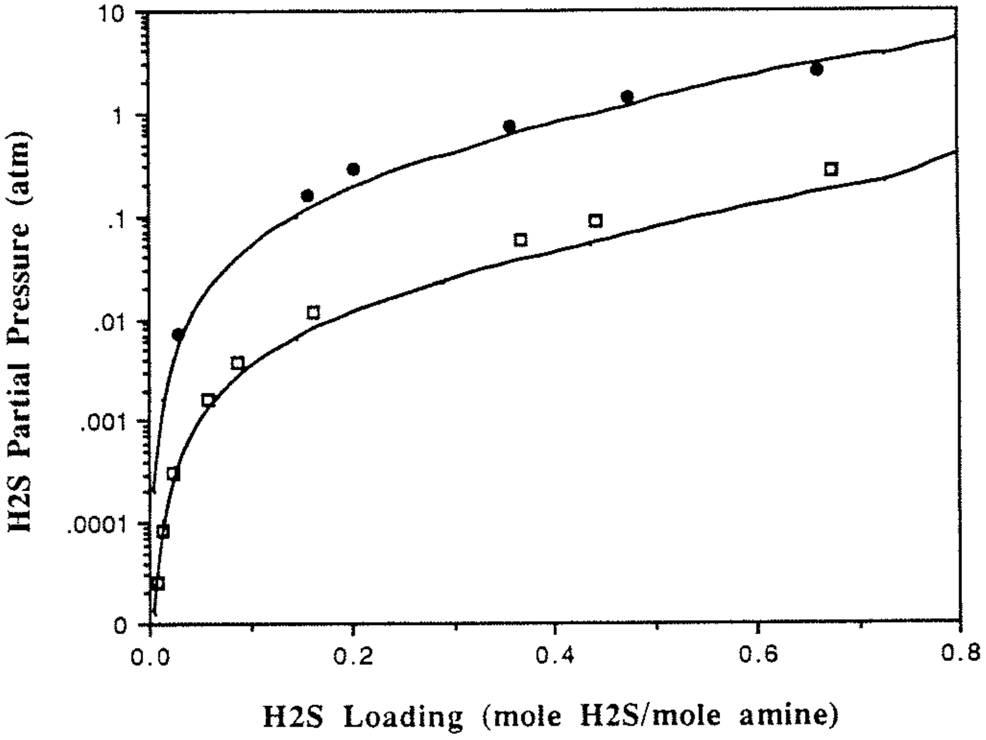

Figure 5.23: Comparison of Model Prediction to Experimental Data for H_2S in 2.0M MDEA . Model prediction: (—). Experimental data from Jou et al. (1982): (▫) - 40°C, (•) - 100°C

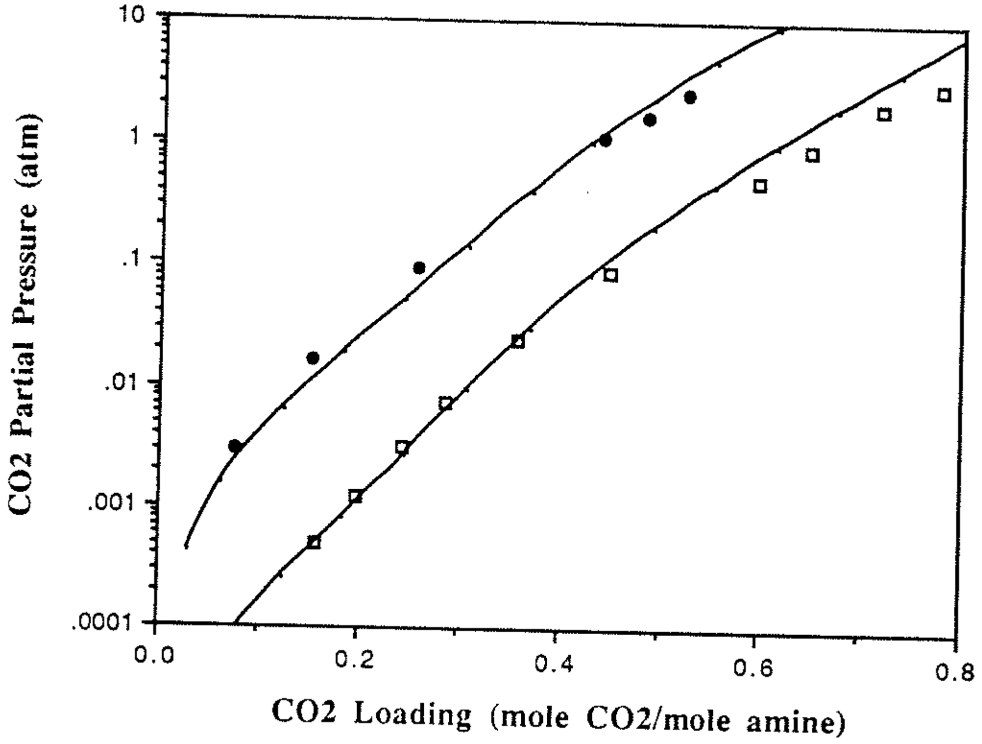

Figure 5.24: Comparison of Model Prediction to Experimental Data for CO_2 in 2.0M MEA - 2.0M MDEA. Model prediction: (—). Experimental data from Austgen (1989): (□) - 40°C, (•) - 80°C

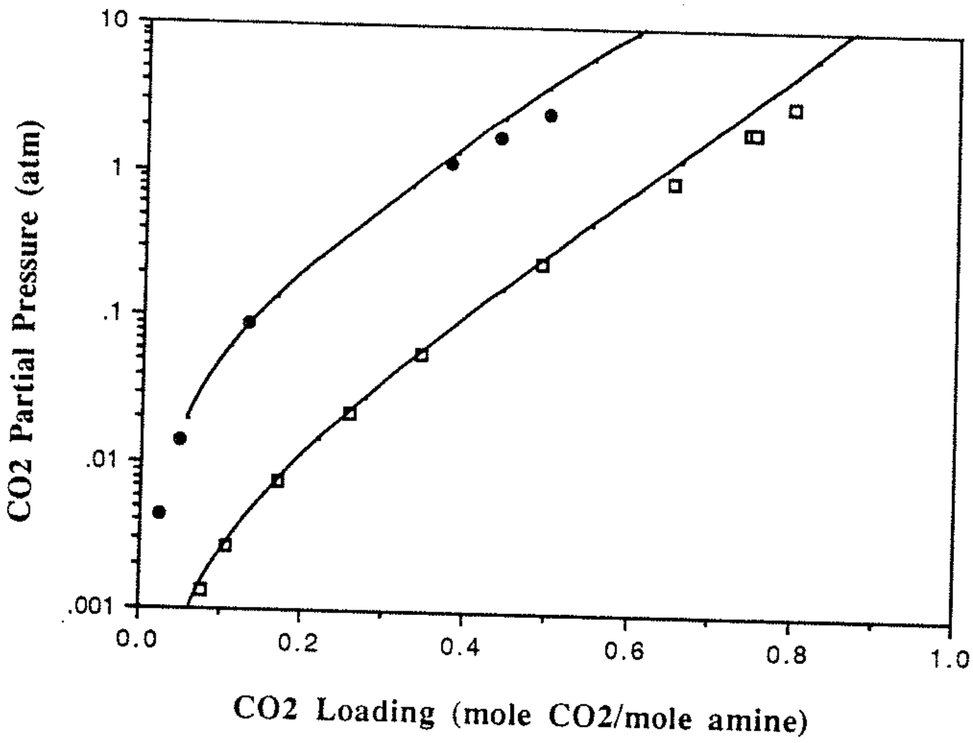

Figure 5.25: Comparison of Model Prediction to Experimental Data for CO_2 in 2.0M DEA - 2.0M MDEA. Model prediction: (—). Experimental data from Austgen (1989): (▫) - 40°C, (•) - 80°C

5.2.2 Column Modeling

As mentioned earlier, the rate-based column model developed by Aspen Technology is currently unavailable; therefore, detailed modeling similar to that done with the MDEA model was not done. The functionality of the kinetic routine developed in this work was tested using the equilibrium-based column model. Modeling of a simple, three stage absorber using MDEA was attempted. Unfortunately, this model was never able to converge for reasons discussed below; however, despite this setback, the kinetic routine worked and calculated reasonable reaction rates.

Three main calculations are performed in the kinetic subroutine to obtain the reaction rates. First, the liquid molar volume is calculated using an ASPEN PLUS™ supplied subroutine called VOLL. This subroutine returns reasonable values for the molar volume as well as activity coefficients. Second, because the apparent component approach is used, the apparent composition needs to be speciated by flashing the liquid phase. Finally, the reaction rates are calculated as described in Chapter 4. The ionic flow rates obtained from the flash calculation and the activity coefficients are used to calculate the component activities needed for the reaction rate expressions.

Originally, in order to speciate the liquid phase, an ASPEN PLUS™ subroutine called FLASH was used to perform a true component flash of the apparent composition. To obtain a true component flash, the variable NBOPST(4) is set equal to 1, FLASH is called, and then NBOPST(4) is immediately returned to a value of 0 to resume the apparent component approach. With this option, FLASH was used to calculate the activity coefficients and flow rates for all of the true components. For certain column conditions, FLASH returned reasonable values for the activity coefficients. However, FLASH never returned reasonable component compositions and often returned incorrect activity coefficients. For example in several cases the mole fraction of nitrogen in the liquid phase was calculated to be 0.5. The subroutine FLASH was also used in the apparent composition mode to try and obtain reasonable activity coefficients. Most of the time, reasonable values were returned; however, given the previous problems with the component flow rates, the calculations returned by FLASH were not trusted. Several conversations with the engineers at Aspen Technology resulted in no immediate answer as to why FLASH did not seem to be working properly.

To eliminate the problem of inaccurate liquid compositions, a subroutine was developed to speciate the liquid phase and avoid the use of FLASH. To speciate the liquid phase, eleven unknown component flow rates must be calculated (H_2O, amine, CO_2, H_2S, H_3O^+, protonated amine, OH^-, carbamate, HS^-, HCO_3^-, $CO_3^=$). The activity coefficients calculated by VOLL were used in this new flash routine to calculate equilibrium constants. Calculation of the true equilibrium constants for reactions (4.2) through (4.5) provide four of the equations to be solved. These equilibrium constants are calculated by dividing the expressions given in Table 4.8 by the appropriate activity coefficient ratio:

$$K_i = \frac{K_i^\infty}{\prod_{k=1}^{n} \gamma_k^{\nu_k}} \tag{5.6}$$

where K_i^∞ is the mole fraction based, infinite dilution equilibrium constant from Table 4.8, n is the number of components for reaction i, γ_k is the activity coefficient for component k, and ν_k is the stoichiometric coefficient for component k. The equilibrium constants for the dissociation of H_2CO_3 and RR'R"NCOOH are considered to be infinite.

The total apparent flow rate for each of the molecular components is passed into the kinetic subroutine for the current column conditions. These total rates represent the combined rates of both the physical and chemically combined forms of that component:

$$[H_2O]_{tot} = H_2O + OH^- + H_3O^+ \tag{5.7}$$

$$[H_2S]_{tot} = H_2S + HS^- \tag{5.8}$$

$$[RR'R''N]_{tot} = RR'R''N + RR'R''NH^+ \tag{5.9}$$

$$[CO_2]_{tot} = CO_2 \tag{5.10}$$

$$[H_2CO_3]_{tot} = HCO_3^- + CO_3^= \tag{5.11}$$

$$[RR'NCOOH]_{tot} = RR'NCOO^- \tag{5.12}$$

In the above equations, the subscript "tot" indicates the total, apparent component flow rate supplied by ASPEN PLUS™. Guessing the OH^- concentration and combining the equilibrium constants from equation (5.6) with equations (5.7) through (5.12) results in the speciation of the liquid. The guess for the OH^- concentration is then checked against the charge balance:

$$\sum_{i=1}^{nion} z_i \, [flow]_i = 0 \tag{5.13}$$

where nion is the number of ions in solution, z_i is the charge of ion i, and $[flow]_i$ is the flow rate of ion i. The flash routine uses the secant method to update the OH^- concentration until (5.13) is satisfied. This routine is essentially a reformulation of subroutine BULK used in the MDEA model described in Chapter 3.

After adding this flash subroutine, a column simulation would run for some time but then a mathematical error such as division by zero would occur. These errors are related to the convergence procedure within ASPEN PLUS™. ASPEN PLUS™ allows the user to supply initial temperature profiles, composition profiles, and total flow rate profiles to the column model. For the column being simulated, the total flow rate at the top stage could easily be estimated to be about 27 kmol/s, 17 kmol/s of liquid with the remainder gas. Despite supplying this initial total flow rate to stage one, the flow rate passed from stage one in the column to the kinetic subroutine was always extremely low, such as 1.5 kmol/s. Inevitably, as ASPEN PLUS™ tried to increase this flow rate, the calculated component flow rates or activity coefficients became unstable, and the program would have mathematical problems. The engineers at Aspen Technology have not satisfactorily answered the question of why the initial profiles provided in the input file are not being used.

Despite these problems, the kinetic subroutine appears to run adequately. Part of the problem is probably using an equilibrium-based column model primarily designed for reactive distillation to perform calculations for a system that involves mass transfer with chemical reaction. The use of the kinetic subroutine and modeling of this system will probably be better served with the rate-based model.

Chapter 6

Conclusions and Recommendations

6.1 Summary

Two process models for the simultaneous absorption and stripping of H_2S and CO_2 in alkanolamine solutions were developed. The first model simulates the MDEA system and is an extension of Hermes (1987). This rate-based model calculates mass and heat transfer on each stage and returns concentration and temperature profiles for each column. Although this model could be extended to other amine systems by incorporating the correct equilibrium and rate data, this task would be difficult because the model contains no general thermodynamic package for electrolytes. For the purpose of modeling other amine systems, especially mixed amine systems, the process simulator ASPEN PLUS™ was developed to simulate MEA, DGA, DEA, MDEA, and mixed amine systems. ASPEN PLUS™ was chosen because it contains a general thermodynamic package for electrolytes, a rate-based column model, and the ability to incorporate user subroutines for kinetic rate expressions.

6.2 Conclusions

1. The MDEA model is useful for exploring the effects of changing operating conditions and tower designs. For typical Claus tail gas conditions, the model predicts that a reasonable steam rate and solvent circulation rate gives a H_2S leak of 98 ppm. This leak is typical of such an industrial system. The absorber temperature bulge of about 3°C is also typical for a system using MDEA.

2. The results indicate that assuming an instantaneous CO_2 enhancement factor in the stripper can result in a large overestimation of the CO_2 flux.

3. System performance in an MDEA system can be improved by increasing the protonated amine concentration which linearizes the H_2S equilibrium. The model has shown that adding acid to the solvent improves performance to levels reported by Union Carbide (1984).

4. Lowering the stripper pressure improves system performance in two ways. The CO_2 lean loading is increased by lowering the stripper pressure which partially linearizes the H_2S equilibrium. In addition, lowering the stripper pressure increases the gas phase mass transfer coefficient and number of transfer units. Because H_2S is partially gas phase controlled, the increase in these parameters decreases the H_2S driving force throughout the stripper which results in a more efficient column.

5. Sensitivity analysis of the model results to various model parameters indicates that accurate values for equilibrium constants and heats of reactions at higher temperatures are needed. For the MDEA system, the gas phase mass transfer coefficient should be maximized to improve H_2S leak while the liquid phase coefficient should be adjusted to yield the desired selectivity.

6. ASPEN PLUS™ is a useful tool for modeling aqueous alkanolamine systems. This program satisfactorily represents the complicated equilibrium associated with these systems, including mixed amine systems.

7. Column modeling with an equilibrium-based model has shown difficulties in converging and obtaining reasonable initial profiles.

8. The kinetic subroutine developed for both equilibrium and rate-based modeling generates reasonable reaction rates and is sufficiently general to be used with MEA, DGA, DEA, MDEA, or a mixture of these amines.

6.3 Recommendations

The MDEA model could be improved in primarily two ways. First, a more rigorous and efficient numerical procedure for converging the columns would be beneficial. Currently, the model converges easily with good guesses; however, good guesses often have to be very close to the final answer, especially under tightly pinched conditions. A new method should be more rigorous to allow greater error in the initial guesses. Second, a gas phase equation of state should be incorporated to allow modeling of high pressure absorbers. Currently, the gas phase is assumed to be ideal, thus limiting the useful applications that can be modeled.

The ASPEN PLUS™ rate-based column model should be obtained as soon as possible. The kinetic subroutine is applicable to this model, and the acid gas-alkanolamine system is better represented using this approach. Continued consultation with the engineers at Aspen Technology should resolve the problems with column initialization and calculations using their subroutine FLASH. The enhancement factor approach discussed in Chapter 4 should be incorporated with the rate-based column model. This approach should save substantial computer time.

Appendix A

MDEA Model Code

The computer code used to perform MDEA modeling is listed below and is located in account CHHQ334 in the subdirectory MODEL. This code was used on the VAX/VMS system on node ORANGE (a 6000-410 CPU). The code is completely self sufficient; therefore, no other programs need to be linked with this program. The required input file for the program is INPUT.IN, and an example is shown is Appendix B. In addition, an optional input file, INITIAL.IN, can be used to store initial temperature profiles for the absorber and stripper. If this file is not used, initial profiles are generated internally.

The program generates four output files. The file OUT.OUT contains the detailed, stage-by-stage results for each column. The file TEMP.OUT contains the final temperature profiles for each column. This file can then be copied into INITIAL.IN to provide reasonable profiles for later simulations. The final two output files are PLOTS.OUT and PLOTC.OUT. These files contain the necessary data to make McCabe-Thiele plots for H_2S and CO_2, respectively. Generation of these files can be avoided with the use of a flag in the file INPUT.IN.

```
C
      PROGRAM ABSTR
C
C  THIS IS THE MAIN PROGRAM FOR THE ABSORBER/STRIPPER MODEL.  THE
C  MODEL CALCULATES THE PERFORMANCE OF THE ABSORBER, STRIPPER, OR
C  THE COMPLETE SYSTEM BASED ON THE INFORMATION ON THE STREAMS
C  INTO THE SYSTEM AND ON THE DESIGN OF THE SYSTEM.  THE MAIN
C  PROGRAM IS RESPONSIBLE FOR THE SYSTEM CONVERGENCE WHICH IS THE
C  CONVERGENCE OF THE AMOUNT (MOLES) OF H2S AND CO2 IN THE RICH
C  SOLUTION.  THE MAIN PROGRAM CALLS ONLY THE SUBROUTINE TCONV.
C
C
C SUBROUTINES AND FUNCTIONS:
C
C      1) TCONV -     DETERMINES TEMPERATURE CONVERGENCE FOR BOTH
C                     COLUMNS.  THIS ROUTINE CALLS ONLY TOWER.
C      2) TOWER -     COMBINES ALL OF THE INDIVIDUAL STAGES INTO A
C                     COMPLETE TOWER.  THIS ROUTINE INITIALLY CALLS
C                     DIFFUSE AND COEFF TO ESTABLISH THE DIFFUSIVITIES
C                     AND MASS TRANSFER PARAMETERS.  SECANT2 IS THEN
```

```
C                       CALLED TO DIRECT THE OVERALL CONVERGENCE OF
C                       INDIVIDUAL STAGES.
C      3) DIFFUSE -     CALCULATES THE DIFFUSION COEFFICIENTS FOR ALL OF
C                       THE COMPONENTS.  THESE ARE CHANGED WITH EACH
C                       STAGE.
C      4) COEFF -       CALCULATES THE MASS TRANSFER PARAMETERS AT THE
C                       BOTTOM OF EACH COLUMN AND THEN ASSUMES THE
C                       PARAMETERS ARE CONSTANT ON EVERY STAGE.
C      5) SECANT2 -     CALLS THE FUNCTION STAGE AND DIRECTS THE
C                       CONVERGENCE OF EACH STAGE.
C      6) STAGE -       PERFORMS THE MASS AND ENERGY BALANCES ON EACH
C                       STAGE. CALLS THE SUBROUTINE SECANT WITH THE
C                       FUNCTION BULK OR FACE.
C      7) SECANT -      CALLED BY THE FUNCTION STAGE TO DIRECT THE
C                       CONVERGENCE OF THE FUNCTIONS BULK AND FACE.
C      8) BULK -        PERFORMS THE BULK LIQUID SPECIATION CALCULATIONS
C      9) FACE -        PERFORMS THE CALCULATION OF THE LIQUID INTERFACE
C                       CONCENTRATIONS
C      10) RATE -       CALLED BY EITHER BULK OR FACE TO CALCULATE THE
C                       KINETIC RATE CONSTANTS AT THE CURRENT CONDITIONS.
C      11) EQ -         CALLED BY EITHER BULK OR FACE TO CALCULATE THE
C                       EQUILIBRIUM CONSTANTS AND HENRY'S CONSTANTS AT
C                       THE CURRENT CONDITIONS
C      12) DENSW -      A FUNCTION USED TO CALCULATE THE DENSITY OF WATER
C      13) DENSAM -     A FUNCTION USED TO CALCULATE THE DENSITY OF MDEA
C      14) PRINT -      A SUBROUTINE CALLED BY STAGE AT THE APPROPRIATE
C                       TIME TO PRINT THE RESULTS OF A RUN.
C      15) ERROR -      SUBROUTINE CALLED BY STAGE IF CERTAIN PROBLEM
C                       CONDITIONS OCCUR
C      OTHERS -         SEVERAL FUNCTIONS EXIST TO CALCULATE THE HEAT
C                       CAPACITY OF THE COMPONENTS
C
C  COMMON BLOCKS ARE USED TO TRANSFER MOST OF THE VARIABLE
C  VALUES BETWEEN SUBROUTINES.  THE COMMON BLOCKS ARE AS FOLLOWS:
C
C      1) FLAG -        CONTAINS FLAG VARIABLES AND OTHER INTEGER
C                       VARIABLES
C      2) DIFF -        CONTAINS THE DIFFUSIVITIES OF EACH SPECIES IN THE
C                       LIQUID PHASE, AN OVERALL LIQUID DIFFUSIVITY, AND AN
C                       OVERALL GAS DIFFUSIVITY
C      3) FLUX -        CONTAINS MASS TRANSFER PARAMETERS
C      4) DH -          CONTAINS THE HEATS OF REACTION AND VAPORIZATION
C      5) EK -          CONTAINS THE EQUILIBRIUM CONSTANTS AND HENRY'S
C                       CONSTANTS
C      6) LIN -         CONTAINS THE TOTAL MOLES OF EACH CHEMICAL IN THE
C                       LIQUID INTO A STAGE
C      7) LOUT -        CONTAINS THE TOTAL MOLES OF EACH CHEMICAL IN THE
C                       LIQUID OUT OF A STAGE
C      8) GIN -         CONTAINS THE MOLES OF EACH CHEMICAL IN THE GAS
C                       INTO A STAGE
C      9) GOUT -        CONTAINS THE MOLES OF EACH CHEMICAL IN THE GAS
C                       OUT OF A  STAGE
```

```
C        10) CONB -      CONTAINS THE BULK LIQUID CONCENTRATIONS OF EACH
C                        SPECIES
C        11) CONT -      CONTAINS THE TOTAL BULK LIQUID CONCENTRATION OF
C                        EACH CHEMICAL
C        12) CONI -      CONTAINS THE LIQUID CONCENTRATIONS OF EACH
C                        SPECIES AT THE INTERFACE
C        13) PI -        CONTAINS THE PARTIAL PRESSURES AT THE INTERFACE
C        14) PRESS -     CONTAINS THE OTHER PRESSURE VARIABLES NEEDED
C        15) TEMP -      CONTAINS THE TEMPERATURES OF THE STREAMS
C                        ASSOCIATED WITH A STAGE
C        16) ENHANC -    CONTAINS THE ENHANCEMENT FACTORS
C        17) TRAY -      CONTAINS PHYSICAL PARAMETERS TO DESCRIBE THE
C                        SPECIFIC TRAY CHARACTERISTICS
C
C  INPUT FILES:
C
C       INPUT.IN -       THIS FILE CONTAINS THE MINIMUM INFORMATION
C                        REQUIRED TO BEGIN A RUN.
C       INITIAL.IN -     THIS FILE IS USED TO READ IN AN INITIAL TEMPERATURE
C                        PROFILE FOR BOTH COLUMNS (OFTEN FROM A PREVIOUS
C                        RUN).  IF THIS FILE IS NOT USED, INITIAL PROFILES ARE
C                        GENERATED INTERNALLY.
C
C  OUTPUT FILES:
C
C       OUT.OUT -        CONTAINS THE DETAILED, STAGE-BY-STAGE RESULTS
C       TEMP.OUT -       CONTAINS THE TEMPERATURE PROFILES FOR BOTH
C                        COLUMNS
C       PLOTS.OUT -      CONTAINS THE MCCABE-THIELE INFORMATION FOR H2S
C       PLOTC.OUT -      CONTAINS THE MCCABE-THIELE INFORMATION FOR CO2
C
      IMPLICIT REAL*8 (A-H,O-Y)
      REAL*4  Z1, Z2
      REAL*8  GIA(4,50), GIS(4,50), LOA(5,50), LOS(5,50), TEMPA(50),
     &        TEMPS(50)
      REAL*8 NG,NGREB,LINH2S,LINCO2,LINH2O,LINAM,LINION,
     &       LINTOT,MKUPH2O
C
      CHARACTER RUNSUM*100
C
      COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
      COMMON /DH/ DHH2S,DHCO2,DHH2O,DHAM
      COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
      COMMON /LIN/ LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
      COMMON /GOUT/ GOUTH2S,GOUTCO2,GOUTH2O,GOUTNRT,GOUTTOT
      COMMON /TRAY/ ITRAY,F,HL,HFROTH
C
C CALL A VAX FUNCTION THAT WILL REPORT THE EXECUTION TIME
C
      Z1 = SECNDS(0.0)
C
```

```
      OPEN (UNIT=1,FILE='INPUT.IN',STATUS='UNKNOWN')
      OPEN (UNIT=3,FILE='OUT.OUT',STATUS='UNKNOWN')
      OPEN (UNIT=5,FILE='PLOTS.OUT',STATUS='UNKNOWN')
      OPEN (UNIT=6,FILE='PLOTC.OUT',STATUS='UNKNOWN')
      OPEN (UNIT=9,FILE='INITIAL.IN',STATUS='UNKNOWN')
      OPEN (UNIT=10,FILE='TEMP.OUT',STATUS='UNKNOWN')
C
C   A RUN NUMBER AND DESCRIPTION IS ASKED FOR.  THIS IS USED TO KEEP
C   TRACK OF THE VARIOUS RUNS THAT ARE MADE BY WRITING THIS
C   INFORMATION TO THE OUTPUT FILE 'OUT.OUT'.
C
      WRITE (*,*) 'INPUT THE RUN NUMBER'
      READ (*,*) IRUN
      WRITE (*,*) 'INPUT A BRIEF DESCRIPTION OF THIS RUN'
      READ (*,*) RUNSUM
      WRITE (3,1) 'RUN # ',IRUN,RUNSUM
 1    FORMAT (//,1X,A6,I3,/,A100/)
C
C   THE FOLLOWING DATA IS THE STANDARD INFORMATION THAT NEEDS TO BE
C   INPUT FOR EACH RUN.  EACH READ STATEMENT IS FOLLOWED BY A WRITE
C   STATEMENT IN ORDER TO WRITE THE INPUT INFORMATION TO THE OUTPUT
C   FILE 'OUT.OUT' FOR FUTURE REFERENCE.
C
      WRITE (3,*) 'THE FOLLOWING INPUT FILE WAS USED FOR THIS RUN:'
      WRITE (3,*) ' '
C
C   READ THE INPUT FOR THE ABSORBER FROM FILE 'INPUT.IN'.
C
C   READ: 1) NUMBER OF ACTUAL STAGES  2) MAX NO. OF TEMP CONVERGENCE
C   ITERATIONS       3) PRINT OPTION              4) REBOILER FLAG.
C   IF IMAXA IS EXCEEDED FOR A SYSTEM MODEL, TEMPERATURE
C   CONVERGENCE IS IGNORED AND EXECUTION CONTINUES.  IF IT IS EXCEEDED
C   FOR A SINGLE TOWER MODEL EXECUTION IS STOPPED.
C   THE PRINT OPTION TAKES THE FOLLOWING VALUES:
C        =0 PRINT EVERY STAGE CONVERGENCE
C        =1 PRINT EVERY TEMPERATURE PROFILE CONVERGENCE
C        =2 PRINT ONLY AFTER SYSTEM CONVERGENCE
C        =3 SAME AS 2 BUT ALSO PRINT PLOTS.OUT AND PLOTC.OUT
C   THE REBOILER FLAG TAKES THE FOLLOWING VALUES:
C        =0 NO REBOILER
C        =1 BOTTOM STAGE IS REBOILER
C
      READ (1,*) NLASTA,IMAXA,IPRINTA,IREBA
      WRITE (3,1001) NLASTA,IMAXA,IPRINTA,IREBA
C
C   READ:  1) TRAY TYPE (1=BUBBLE CAP, 2=SIEVE)
C          2) FRACTION APPROACH TO FLOOD
C          3) LIQUID HOLDUP ON EACH TRAY (CM)
C          4) EFFECTIVE FROTH HEIGHT ON EACH TRAY (CM) FOR SIEVE TRAYS
C          OR LIQUID SUBMERGENCE MEASURED AS HALF OF THE SLOT HEIGHT
C          TO THE TOP OF THE DISPERSION FOR BUBBLE CAP TRAYS
C
```

```
      READ (1,*) ITRAYA,FA,HLA,HFROTHA
      WRITE (3,1002) ITRAYA,FA,HLA,HFROTHA
C
C   READ: GAS INTO THE ABSORBER: H2S, CO2, H2O, INERT (MOLE/S)
C
      READ (1,*) GIA(1,1),GIA(2,1),GIA(3,1),GIA(4,1)
      WRITE (3,1000) GIA(1,1),GIA(2,1),GIA(3,1),GIA(4,1)
C
C   READ: LIQUID OUT OF THE ABSORBER: H2O, AMINE, ANION (MOLE/S)
C
      READ (1,*) LOA(3,1),LOA(4,1),LOA(5,1)
      WRITE (3,1000) LOA(3,1),LOA(4,1),LOA(5,1)
C
C   READ: GUESSES FOR THE RICH LIQUID LOADINGS OUT OF THE ABSORBER
C   (MOLE/S):  TWO GUESSES FOR H2S, TWO GUESSES FOR CO2
C
      READ (1,*) XS1,XS2,XC1,XC2
      WRITE (3,1000) XS1,XS2,XC1,XC2
C
C   READ:  1) PRESSURE AT THE BOTTOM OF THE ABSORBER (ATM)
C          2) PRESSURE DROP PER STAGE (ATM)
C
      READ (1,*) PBOTA,DPA
      WRITE (3,1000) PBOTA,DPA
C
C   READ:  TEMPERATURES (K): 1) GAS IN    2) LIQUID IN
C          3) GUESS FOR LIQUID OUT (IF =0 THE MODEL CALCULATES A GUESS)
C
      READ (1,*) TGIA,TEMPA(NLASTA),TBOTA
      WRITE (3,1000) TGIA,TEMPA(NLASTA),TBOTA
C
C   READ: HEATS OF RXN (CAL/MOLE): 1) H2S DISSOCIATION  2) H2CO3
C   DISSOCIATION   3) H2O VAPORIZATION  4) AMINE PROTONATION
C
      READ (1,*) DHH2SA,DHCO2A,DHH2OA,DHAMA
      WRITE (3,1000) DHH2SA,DHCO2A,DHH2OA,DHAMA
C
C   READ: STRIPPER INPUT.  SAME AS FOR THE ABSORBER ABOVE UNLESS
C   SPECIFIED.
C
      READ (1,*) NLASTS,IMAXS,IPRINTS,IREBS
      WRITE (3,1001) NLASTS,IMAXS,IPRINTS,IREBS
C
C   READ: 5) NUMBER OF GAS PHASE TRANSFER UNITS FOR THE REBOILER
C
      READ (1,*) ITRAYS,FSS,HLS,HFROTHS,NGREB
      READ (1,*) GIS(1,1),GIS(2,1),GIS(3,1),GIS(4,1)
      READ (1,*) PBOTS,DPS
      READ (1,*) TGIS,TEMPS(NLASTS),TBOTS
      READ (1,*) DHH2SS,DHCO2S,DHH2OS,DHAMS
C
      WRITE (3,1002) ITRAYS,FSS,HLS,HFROTHS,NGREB
```

```
      WRITE (3,1000) GIS(1,1),GIS(2,1),GIS(3,1),GIS(4,1)
      WRITE (3,1000) PBOTS,DPS
      WRITE (3,1000) TGIS,TEMPS(NLASTS),TBOTS
      WRITE (3,1000) DHH2SS,DHCO2S,DHH2OS,DHAMS
C
C  READ: 1) MAXIMUM NUMBER OF SYSTEM ITERATIONS  2) H2S DAMPING
C  FACTOR     3) CO2 DAMPING FACTOR          4) SYSTEM FLAG
C  IF JMAX IS EXCEEDED, THE USER CAN EITHER SUPPLY NEW GUESSES AND
C  CONTINUE WITH A NEW JMAX OR HAVE THE UNCONVERGED SYSTEM
C  WRITTEN AS OUTPUT AND STOP.
C  THE DAMPING FACTORS ARE USED TO HELP CONVERGENCE OF THE LOADING
C  VALUES AND CAN BE CHANGED INTERACTIVELY.
C  THE SYSTEM FLAG TAKES THE FOLLOWING VALUES:
C       =0 MODEL ONLY THE ABSORBER
C       =1 MODEL ONLY THE STRIPPER
C       =2 MODEL THE SYSTEM
C
      READ (1,*) JMAX, H2SDAMP, CO2DAMP, ISYS
      WRITE (1,1003) JMAX, H2SDAMP, CO2DAMP, ISYS
C
C  IF ONLY ONE TOWER IS TO BE MODELLED, INPUT THE LIQUID OUT OF THE
C  TOWER AND IGNORE THE VALUES GIVEN IN THE ABSORBER INPUT.
C
      IF (ISYS .EQ. 0) THEN
        READ (1,*) LOA(1,1),LOA(2,1),LOA(3,1),LOA(4,1),LOA(5,1)
        WRITE (3,1000) LOA(1,1),LOA(2,1),LOA(3,1),LOA(4,1),LOA(5,1)
      ENDIF
      IF (ISYS .EQ. 1) THEN
        READ (1,*) LOS(1,1),LOS(2,1),LOS(3,1),LOS(4,1),LOS(5,1)
        WRITE (3,1000) LOS(1,1),LOS(2,1),LOS(3,1),LOS(4,1),LOS(5,1)
      ENDIF
C
C  NOW ALL OF THE STANDARD INPUT HAS BEEN READ.  THE USER CAN NOW
C  USE THE PREVIOUSLY SAVED FILE 'INITIAL.IN' TO GET THE INITIAL
C  TEMPERATURE PROFILE.  IF THE USER DECIDES NOT TO USE THE
C  PREVIOUSLY SAVED FILE, THEN INITIALIZE THE TEMPERATURE PROFILE WITH
C  ZERO VALUES.
C
      WRITE (*,*) 'DO YOU WANT TO USE A PREVIOUSLY SAVED INITIAL
     &  TEMPERATURE PROFILE?'
      WRITE(*,*)  '(1=YES, 2=NO)'
      READ (*,*) IINPUT
C
      IF (IINPUT.EQ.1) THEN
        READ (9,*) TBOTA
        DO 250 I = 1,NLASTA-1
          READ (9,*) TEMPA(I)
250     CONTINUE
        READ (9,*) TBOTS
        DO 260 I = 1,NLASTS-1
          READ (9,*) TEMPS(I)
260     CONTINUE
```

```
          ELSE
            DO 300 M=1,NLASTA-1
              TEMPA(M)=0.
 300        CONTINUE
            DO 310 M=1,NLASTS-1
              TEMPS(M)=0.
 310        CONTINUE
          ENDIF
C
C   INITIALIZE THE ERROR FLAG, THE PRINT FLAG, THE SYSTEM ITERATION
C   COUNTER
C
          IERR=0
          IPR=0
          J=0
C
C   EXECUTION IS RETURNED HERE IF AN ERROR IS RETURNED TO THE MAIN
C   PROGRAM.  THE USER IS ASKED AT THE TERMINAL IF HE WANTS TO INPUT
C   NEW GUESSES FOR THE RICH SOLUTION LOADINGS AND WHAT THOSE
C   GUESSES ARE.  IF HE DOES NOT WANT TO INPUT NEW GUESSES, EXECUTION
C   IS STOPPED.  IF HE DOES, THE VALUES ARE READ AND SYSTEM
C   CONVERGENCE IS STARTED AGAIN. THE USER CAN ALSO CHANGE THE
C   DAMPING FACTORS.
C
 50       IF (IERR .GT. 0) THEN
            WRITE (*,*) 'DO YOU WANT TO INPUT NEW GUESSES? (Y=1/N=0)'
            READ (*,*) IQ
          IF (IQ .EQ. 0) THEN
            STOP
          ELSE
            WRITE (*,*) 'INPUT NEW GUESSES: 1) H2S 2) H2S 1) CO2 2) CO2'
            READ (*,*) XS1,XS2,XC1,XC2
            WRITE (*,*) 'DO YOU WANT TO CHANGE THE DAMPING FACTORS?'
            READ (*,*) IDAMP
          IF (IDAMP.EQ.1) THEN
              WRITE(*,*) 'INPUT THE DAMPING FACTORS (H2S, CO2)'
              READ (*,*) H2SDAMP, CO2DAMP
          ENDIF
            J=0
            IERR=0
          ENDIF
          ENDIF
C
C   SET THE INITIAL ERROR BETWEEN THE CALCULATED AND GUESSED LOADING
C   VALUES FOR H2S AND CO2.
C
          ERR = 1D10
C
C   BEGINNING OF THE SYSTEM ITERATION LOOP.
C
 30       J=J+1
C
```

```
C   THIS IS THE CODE WHICH DIRECTS SYSTEM CONVERGENCE.  FIRST, IF ONLY
C   ONE TOWER IS TO BE MODELLED GO TO 100. THIS IS WHERE TCONV IS
C   CALLED FOR EACH TOWER.  NEXT, IF THE MAXIMUM NUMBER OF SYSTEM
C   ITERATIONS HAS BEEN REACHED THE USER CAN EITHER CONTINUE OR HAVE
C   THE LAST GUESSES FOR THE LOADINGS WRITTEN AS OUTPUT.
C
        IF (ISYS .NE. 2) GOTO 100
        IF (J .GT. JMAX) THEN
          WRITE (*,*) 'SYSTEM DID NOT CONVERGE IN ',JMAX,' ITERATIONS.'
          WRITE (*,*) 'WOULD YOU LIKE TO CONTINUE? (1=YES)'
          READ (*,*) ICONT
        IF (ICONT.EQ.1) THEN
          WRITE(*,*) 'PLEASE INPUT THE NUMBER OF CONVERGENCE ITERATIONS'
          READ (*,*) JMAX
          IERR = 1
          GOTO 50
        ELSE
          WRITE (*,*) 'THE FINAL ITERATION WILL BE WRITTEN AS OUTPUT.'
          LOA(1,1) = XS2
          LOA(2,1) = XC2
          IFLAG = 4
          GOTO 100
        ENDIF
        ENDIF
C
C   NITIALIZE THE CO2 AND H2S LOADINGS FOR THIS ITERATION
C
        LOA(1,1)=XS2
        LOA(2,1)=XC2
        IFLAG=1
C
C   THIS BEGINS THE SYSTEM CALCULATION SECTION FOR GIVEN VALUES OF H2S
C   AND CO2 LOADING.  EXECUTION ALSO COMES HERE IF SYSTEM
C   CONVERGENCE IS OBTAINED AND EXECUTION IS DIRECTED HERE IF THE
C   MAXIMUM NUMBER OF ITERATIONS HAS BEEN REACHED.
C
 100    CONTINUE
C
C   IF ONLY THE STRIPPER IS TO BE MODELED GO TO THE STRIPPER PART OF
C   THIS SECTION.
C
        IF (ISYS .EQ. 1) GOTO 200
C
C   CALCULATE AN INITIAL TEMPERATURE PROFILE FOR THE ABSORBER.
C
        IF (TEMPA(NLASTA/2) .EQ. 0.) THEN
          XH2O=LOA(3,1)/(LOA(1,1)+LOA(2,1)+LOA(3,1)+LOA(4,1)+LOA(5,1))
          PH2O=PBOTA*GIA(3,1)/(GIA(1,1)+GIA(2,1)+GIA(3,1)+GIA(4,1))
            IF (TBOTA .EQ. 0.) THEN
              TBOTA=((1668.21/(7.96681-DLOG10(760.*PH2O/XH2O)))
     &          +273.-228.)
            ENDIF
```

```
          DT=TEMPA(NLASTA)-TBOTA
          DO 10 M=1,NLASTA-1
            TEMPA(M)=TBOTA+DT*DFLOAT(M)/DFLOAT(NLASTA)
 10       CONTINUE
        ENDIF
C
C   IF THE FLAGS INDICATE THAT THE SYSTEM HAS CONVERGED AND THAT
C   PRINTING IS DESIRED, SET THE PRINT FLAG.
C
        IF ( (IPRINT .GE. 2) .AND. (IFLAG .EQ. 4) ) THEN
          IPR=1
        ENDIF
C
C   SET THE VALUES NEEDED FOR THE ABSORBER CALCULATIONS TO THE
C   VARIABLE NAMES IN THE COMMON BLOCKS (TAKE THE "A" OF THE END OF
C   THE NAMES). THE COLUMN FLAG IS SET TO 1 TO INDICATE THE ABSORBER
C   CALCULATION IS BEING DONE.
C
        ICOLUMN = 1
        IREB=IREBA
        IPRINT=IPRINTA
        ITRAY = ITRAYA
        F = FA
        HL = HLA
        HFROTH = HFROTHA
        DHH2S=DHH2SA
        DHCO2=DHCO2A
        DHH2O=DHH2OA
        DHAM=DHAMA
        MKUPH2O=0.
C
C   CONVERGE THE TEMPERATURE PROFILE FOR THE ABSORBER.  CHECK FOR
C   AN ERROR.  PRINT TO THE TERMINAL THAT THE ABSORBER HAS BEEN
C   CONVERGED.  REINITIALIZE THE PRINT FLAG.  IF ONLY THE ABSORBER IS TO
C   BE MODELED, STOP.
C
        ICOEFF = 0
        CALL TCONV (GIA,LOA,TGIA,TEMPA,TBOTA,PBOTA,DPA,NLASTA,IMAXA,
     &                 MKUPH2O)
        IF (IERR .GT. 0) GOTO 50
        WRITE (*,*) 'ABSORBER'
        WRITE (*,*)
        IPR=0
        IF (ISYS .EQ. 0) STOP
C
C   THE LIQUID INTO THE ABSORBER IS THE LIQUID OUT OF THE STRIPPER.
C
        LOS(1,1)=LINH2S
        LOS(2,1)=LINCO2
        LOS(3,1)=LINH2O
        LOS(4,1)=LINAM
        LOS(5,1)=LINION
```

```
C
C   MAKEUP THE WATER LOST TO THE ABSORBER OFF GAS.  THIS IS ADDED TO
C   THE LIQUID INTO THE STRIPPER IN TOWER.
C
        MKUPH2O=GOUTH2O-GIA(3,1)
 200    CONTINUE
C
C   CALCULATE AN INITIAL TEMPERATURE PROFILE FOR THE STRIPPER.
C
        IF (TEMPS(NLASTS/2) .EQ. 0.) THEN
          XH2O=LOS(3,1)/(LOS(1,1)+LOS(2,1)+LOS(3,1)+LOS(4,1))
          PH2O=PBOTS*GIS(3,1)/(GIS(1,1)+GIS(2,1)+GIS(3,1)+GIS(4,1))
          IF (TBOTS .EQ. 0.) THEN
            TBOTS=((1668.21/(7.96681-DLOG10(760.*PH2O/XH2O)))
     &          +273.-228.)
          ENDIF
          DO 20 M=1,NLASTS-1
            TEMPS(M)=TBOTS-.6961*DEXP(2.2744*DFLOAT(M)/DFLOAT(NLASTS))
 20       CONTINUE
        ENDIF
C
C   IF THE FLAGS INDICATES THAT THE SYSTEM HAS CONVERGED AND THAT
C   PRINTING IS DESIRED, SET THE PRINT FLAG.
C
        IF ( (IPRINT .GE. 2) .AND. (IFLAG .EQ. 4) ) THEN
          IPR=1
        ENDIF
C
C   SET THE VALUES NEEDED FOR THE STRIPPER CALCULATIONS TO THE
C   VARIABLE NAMES IN THE COMMON BLOCKS (TAKE THE "S" OF THE END OF
C   THE NAMES).
C
        ICOLUMN = 2
        IREB=IREBS
        IPRINT=IPRINTS
        ITRAY = ITRAYS
        F = FSS
        HL = HLS
        HFROTH = HFROTHS
        DHH2S=DHH2SS
        DHCO2=DHCO2S
        DHH2O=DHH2OS
        DHAM=DHAMS
C
C   IF ONLY THE STRIPPER IS MODELLED THERE IS NO MAKEUP WATER.
C
        IF (ISYS .EQ. 1) THEN
          MKUPH2O=0.
        ENDIF
C
C   CONVERGE THE TEMPERATURE PROFILE FOR THE STRIPPER.  CHECK FOR AN
C   ERROR.  PRINT TO THE TERMINAL THAT THE STRIPPER HAS BEEN
```

```
C   CONVERGED. REINITIALIZE THE PRINT FLAG. IF ONLY THE STRIPPER IS TO
C   BE MODELED, STOP.
C
      ICOEFF = 0
      CALL TCONV (GIS,LOS,TGIS,TEMPS,TBOTS,PBOTS,DPS,NLASTS,IMAXS,
     &                MKUPH2O)
      IF (IERR .GT. 0) GOTO 50
      WRITE (*,*) 'STRIPPER'
      WRITE (*,*)
      IPR=0
      IF (ISYS .EQ. 1) STOP
C
C   CALCULATE THE ERRORS IN THE LOADING GUESSES FOR THIS SYSTEM
C   CALCULATION. IF THE ERRORS MEET THE CONVERGENCE CRITERION AND
C   THE SYSTEM HAS NOT ALREADY CONVERGED, THEN SET IFLAG AND RETURN
C   TO 100 SO THAT THE FINAL RESULTS CAN BE PRINTED.
C
      FS=LINH2S-LOA(1,1)
      FC=LINCO2-LOA(2,1)
      ERRS = DABS(FS/LOA(1,1))
      ERRC = DABS(FC/LOA(2,1))
C
C   WRITE THE GUESSES AND ERRORS ASSOCIATED WITH EACH SYSTEM
C   ITERATION TO THE SCREEN TO ASSIST IN FUTURE GUESSES.
C
      WRITE (*,101) LOA(1,1),FS,LOA(2,1),FC
101   FORMAT (/4(F13.9)/)
C
      IF (ERRS.LT.0.005.AND.ERRC.LT.0.005.AND.IFLAG.NE.4) THEN
        IFLAG = 4
        GOTO 100
      ENDIF
C
C   KEEP THE BEST VALUES FOR CO2 AND H2S LOADING FOR THE NEXT SYSTEM
C   ITERATION.
C
      IF ((ERRS + ERRC).LT.ERR) THEN
        XS1NEW = LOA(1,1)
        XC1NEW = LOA(2,1)
        ERR = ERRS + ERRC
      ENDIF
C
C   IF THE SYSTEM HAS NOT CONVERGED, NEW LOADING VALUES ARE
C   CALCULATED. A QUASI-NEWTON METHOD IS USED TO CONVERGE THE
C   SYSTEM AND UPDATE THE  GUESSES.  THE DAMPING FACTORS FOR H2S AND
C   CO2 ARE USED TO CONTROL THE  CHANGE IN THE NEW GUESS.  AFTER THE
C   THIRD SYSTEM CALCULATION, THE  GUESSES ARE UPDATED AND THE
C   PROCESS REPEATED UNTIL CONVERGENCE IS REACHED.
C
      IF (IFLAG .EQ. 1) THEN
        FS1 = FS
        FC1 = FC
```

```
        LOA(1,1) = XS2
        LOA(2,1) = XC1
        IFLAG = 2
        GOTO 100
      ELSE IF (IFLAG .EQ. 2) THEN
        FS2 = FS
        FC2 = FC
        LOA(1,1) = XS1
        LOA(2,1) = XC2
        IFLAG = 3
        GOTO 100
      ELSE IF (IFLAG .EQ. 3) THEN
        FS3 = FS
        FC3 = FC
        IF ((XC1 .EQ. 0.) .AND. (XC2 .EQ. 0.)) THEN
          XS3=XS2-(XS2-XS1)*FS1/(FS1-FS3)
          XC3=0.
        ELSE IF ((XS1 .EQ. 0.) .AND. (XS2 .EQ. 0.)) THEN
          XS3=0.
          XC3=XC2-(XC2-XC1)*FC1/(FC1-FC2)
        ELSE
          DFSXS=(FS1-FS3)/(XS2-XS1)
          DFSXC=(FS1-FS2)/(XC2-XC1)
          DFCXS=(FC1-FC3)/(XS2-XS1)
          DFCXC=(FC1-FC2)/(XC2-XC1)
          DUM=DFSXS*DFCXC-DFSXC*DFCXS
          DXS = (DFSXC*FC1-DFCXC*FS1)/DUM
          DXC = (DFCXS*FS1-DFSXS*FC1)/DUM
        IF (DABS(DXS)/XS2.GT.H2SDAMP) DXS = DABS(DXS)*H2SDAMP*XS2/DXS
        IF (DABS(DXC)/XC2.GT.CO2DAMP) DXC = DABS(DXC)*CO2DAMP*XC2/DXC
          XS3=XS2+DXS
          XC3=XC2+DXC
        ENDIF
        XS1 = XS1NEW
        XC1 = XC1NEW
        XS2=XS3
        XC2=XC3
        WRITE (*,*) XS3,XC3
        GOTO 30
      ELSE IF (IFLAG .EQ. 4 .AND. J .LE. JMAX) THEN
        WRITE (*,*) 'SYSTEM CONVERGED IN ',J,' ITERATIONS'
      ENDIF
C
      CLOSE (UNIT=1)
      CLOSE (UNIT=3)
      CLOSE (UNIT=5)
      CLOSE (UNIT=6)
      CLOSE (UNIT=9)
      CLOSE (UNIT=10)
C
C   WRITE THE EXECUTION TIME TO THE SCREEN
C
```

```
      Z2 = SECNDS(Z1)
      WRITE (*,*) 'EXECUTION TIME =',Z2
C
 1000 FORMAT (5(1X,F12.5))
 1001 FORMAT (4(1X,I2))
 1002 FORMAT (1X,I2,4(F12.5))
 1003 FORMAT (1X,I3,1X,F12.5,1X,F12.5,I2)
C
      STOP
      END
C
C***************************************************************
C
      SUBROUTINE TCONV (GI,LO,TGI,TEMP,TBOT,PBOT,DP,NLAST,ITERMAX,
     &                              MKUPH2O)
C
C  TCONV IS THE TEMPERATURE CONVERGENCE ROUTINE FOR A TOWER.  GIVEN
C  AN  INITIAL GUESS FOR THE TEMPERATURE PROFILE, WHICH CONSISTS OF
C  THE TEMPERATURE INTO EACH STAGE, TOWER IS SUCCESIVELY CALLED
C  UNTIL THAT  PROFILE HAS CONVERGED TO SOME LIMIT.  THE CONVERGENCE
C  IS ACHEIVED BY DIRECT SUBSTITUTION.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 GI(4,NLAST+1),LO(5,NLAST+1),TEMP(NLAST),T(50),MKUPH2O
C
      COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
C
C  SET THE CONVERGENCE FLAG.  THIS HELPS DETERMINE WHETHER PRINTING
C  IS DESIRED OR NOT. IF BOTH IPR AND ICONV = 1 THEN PRINT.
C
      ICONV = 0
C
C  CONVERGENCE IS ATTEMPTED UNTIL A MAXIMUM NUMBER OF ITERATIONS,
C  ITERMAX, HAS BEEN REACHED.
C
      DO 20 ITER=1,ITERMAX
C
C  IF EACH STAGE CONVERGENCE SHOULD BE PRINTED (IPRINT=0), SET THE
C  PRINT FLAG
C
      IF (IPRINT .EQ. 0) THEN
        IPR=1
        ICONV =1
      ENDIF
C
C  SUBSTITUTE THE CURRENT TEMPERATURES INTO STORAGE FOR
C  COMPARISON AFTER THE NEXT CONVERSION TO GET AN UPDATED VERSION.
C
      DO 50 L=1,NLAST-1
        T(L)=TEMP(L)
 50   CONTINUE
C
```

```
        CALL TOWER (GI,LO,TGI,TEMP,T,TBOT,PBOT,DP,NLAST,MKUPH2O,ICONV)
        IF (IERR .GT. 0) RETURN
C
C  IF THERE IS ONLY ONE STAGE, NO TEMPERATURE CONVERGENCE IS NEEDED.
C
        IF (NLAST .EQ. 1) GOTO 60
C
C  COMPARE THE CALCULATED TEMPERATURES FROM TOWER TO THE
C  CURRENT TEMPERATURE PROFILE TO SEE IF EACH ONE HAS MET THE
C  CONVERGENCE CRITERION.
C
        DO 30 K=1,NLAST-1
          IF (DABS(TEMP(K)-T(K)) .GT. 0.005) GOTO 20
 30     CONTINUE
        ICONV = 1
        GOTO 60
 20     CONTINUE
C
        WRITE (*,*) 'NO TEMPERATURE CONVERGENCE'
C
 60     CONTINUE
C
C  IF THE ENTIRE SYSTEM AS WELL AS THE TEMPERATURE PROFILE HAS
C  CONVERGED, THEN CALL TOWER ONE LAST TIME TO PRINT THE RESULTS.
C
        IF ( (IPR .EQ. 1) .AND. (IPRINT .GE. 2) ) THEN
          CALL TOWER (GI,LO,TGI,TEMP,T,TBOT,PBOT,DP,NLAST,MKUPH2O,ICONV)
          RETURN
        ENDIF
C
C  IF PRINTING IS DESIRED AFTER EACH TEMPERATURE CONVERGENCE, CHECK
C  TO SEE IF CONVERGENCE HAS BEEN MET AND THEN PRINT THE RESULTS.
C
        IF (IPRINT .EQ. 1) THEN
          IF (ICONV.EQ.0) THEN
            WRITE (3,*) 'NO TEMPERATURE CONVERGENCE'
            ICONV = 1
          ENDIF
          IPR=1
          CALL TOWER (GI,LO,TGI,TEMP,T,TBOT,PBOT,DP,NLAST,MKUPH2O,ICONV)
          RETURN
        ENDIF
C
        RETURN
        END
C
C*************************************************************
C
        SUBROUTINE TOWER (GI,LO,TGI,TEMP,T,TBOT,PBOT,DP,NLAST,
     &                    MKUPH2O,ICONV)
C
C  TOWER IS THE ROUTINE WHICH PUTS TOGETHER ALL OF THE CONVERGED
```

```
C   STAGES AS A COMPLETE TOWER SIMULATION.  ITS FUNCTION IS TO START AT
C   THE BOTTOM OF THE TOWER AND CONVERGE THE STAGES MOVING UP.  IT
C   ALSO CALLS THE PRINT ROUTINE WHEN DESIRED.
C
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 GI(4,NLAST+1),LO(5,NLAST+1),TEMP(NLAST),T(NLAST)
        REAL*8 LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT,MKUPH2O
        REAL*8 LOUTH2S,LOUTCO2,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
        REAL*8 NG, NGREB
C
        COMMON /GIN/ GINH2S,GINCO2,GINH2O,GINNRT,GINTOT
        COMMON /GOUT/ GOUTH2S,GOUTCO2,GOUTH2O,GOUTNRT,GOUTTOT
        COMMON /LIN/ LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
        COMMON /LOUT/LOUTH2S,LOUTCO2,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
        COMMON /TEMP/ TLOUT,TLIN,TGOUT,TGIN
        COMMON /PRESS/ PH2S,PCO2,P
        COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
        COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
        COMMON /FLUX/ FKL,FKG,NG,NGREB,AREA
        COMMON /CONT/ TAM,TH2S,TCO2,TION
C
        EXTERNAL STAGE
C
        TGIN=TGI
C
C   CONVERGE EACH STAGE OF THE TOWER BY CALLING SECANT2 WITHIN THIS
C   DO LOOP.
C
        DO 10 N=1,NLAST
C
C   FIND THE PRESSURE OF THIS STAGE ACCOUNTING FOR THE PRESSURE DROP.
C
        P=PBOT-DFLOAT(N-1)*DP
C
C   IF THIS IS THE FIRST TEMPERATURE CONVERGENCE ITERATION, USE THE GAS
C   INTO THE FIRST STAGE AS THE GUESS FOR THE GAS OUT.  A GUESS FOR THE
C   COMPOSITION OF THE GAS OUT IS NEEDED FOR STAGE.  AFTER THE FIRST
C   TEMPERATURE CONVERGENCE ITERATION, THE PROFILE OF THE GAS
C   COMPOSITION FROM THE PREVIOUS ITERATION IS USED FOR THE GUESSES.
C
        IF (ITER .EQ. 1) THEN
          DO 30 II=1,4
            GI(II,N+1)=GI(II,N)
 30       CONTINUE
        ENDIF
C
C   GET THE GAS IN, GAS OUT, AND LIQUID OUT FROM THE SAVED ARRAYS.  THE
C   LIQUID OUT AND GAS IN ARE KNOWN AND THE GAS OUT MUST BE GUESSED
C   BEFORE A STAGE CONVERGENCE IS STARTED.  THE TEMPERATURE OF THE
C   LIQUID IN IS ALSO KNOWN FROM ITS PROFILE.  THE PROFILE IS ACTUALLY
C   NOT KNOWN, BUT IS ASSUMED TO BE KNOWN FOR THE PURPOSE OF THE
C   TOWER CALCULATIONS BECAUSE THE TEMPERATURE PROFILE IS
```

```
C   CONVERGED EXTERNAL TO THESE CALCULATIONS.
C
      GINH2S=GI(1,N)
      GINCO2=GI(2,N)
      GINH2O=GI(3,N)
      GINNRT=GI(4,N)
      GINTOT=GINH2S+GINCO2+GINH2O+GINNRT
      GOUTH2S=GI(1,N+1)
      GOUTCO2=GI(2,N+1)
      GOUTH2O=GI(3,N+1)
      GOUTNRT=GI(4,N+1)
      GOUTTOT=GOUTH2S+GOUTCO2+GOUTH2O+GOUTNRT
      LOUTH2S=LO(1,N)
      LOUTCO2=LO(2,N)
      LOUTH2O=LO(3,N)
      LOUTAM=LO(4,N)
      LOUTION=LO(5,N)
      LOUTTOT=LOUTH2S+LOUTCO2+LOUTH2O+LOUTAM+LOUTION
      TLIN=TEMP(N)
C
C   THE TOTAL LIQUID CONCETRATION OF EACH SPECIES IS CALCULATED. THE
C   CONCENTRATIONS ARE IN UNITS OF MOLALITY (MOLES/KG WATER).
C
      WTH2O = LOUTH2O*0.018
      TH2S = LOUTH2S/WTH2O
      TCO2 = LOUTCO2/WTH2O
      TAM = LOUTAM/WTH2O
      TION = LOUTION/WTH2O
C
C   CALCULATE THE LIQUID DIFFUSIVITIES FOR THIS STAGE AND THEN THE MASS
C   TRANSFER PARAMETERS
C
      CALL DIFFUSE (TLIN)
      IF (ICOEFF.EQ.0) THEN
        ICOEFF = 1
        CALL COEFF ( TLIN, TGIN, P )
      ENDIF
C
C   THE SEACANT2 CONVERGENCE ROUTINE FOR STAGE NEEDS TWO INITIAL
C   GUESSES FOR THE TEMPERATURE OF THE LIQUID OUT OF THE STAGE.  ONE
C   GUESS IS FROM THE PROFILE, AND THE OTHER IS THAT VALUE PLUS AN
C   ARBITRARY SMALL AMOUNT.
C
      IF (N .EQ. 1) THEN
        XL=TBOT
      ELSE
        XL=TEMP(N-1)
      ENDIF
      XR=XL+.03
C
C   CONVERGE THE CURRENT STAGE.  CHECK FOR ERRORS.  IF THE TOWER HAS
C   A REBOILER AND THIS IS THE BOTTOM STAGE, THE WATER INTO THE
```

```
C   REBOILER IS EQUAL TO THE VALUE CALCULATED FOR THE MATERIAL
C   BALANCE IN STAGE PLUS THE STEAM IN, BECAUSE IT IS CONDENSED AT THE
C   TOP OF THE TOWER AND ADDED TO THE LIQUID.
C
        CALL SECANT2 (STAGE,XL,XR)
        IF (IERR .GT. 0) RETURN
        IF (IREB .EQ. 1) THEN
          IF (N .EQ. 1) THEN
            LINH2O=LINH2O+GINH2O
          ENDIF
          IF (N .EQ. NLAST) THEN
            LINH2O=LINH2O-GOUTH2O-MKUPH2O
            GOUTH2O=0.
          ENDIF
        ENDIF
C
C   IF THE PRINT FLAG IS SET, CALL THE PRINT ROUTINE.
C
        IF (IPR .EQ. 1 .AND. ICONV .EQ. 1)  CALL PRINT
C
C   THE GAS OUT OF THIS STAGE IS THE GAS INTO THE NEXT STAGE ABOVE IT.
C
        GI(1,N+1)=GOUTH2S
        GI(2,N+1)=GOUTCO2
        GI(3,N+1)=GOUTH2O
        GI(4,N+1)=GOUTNRT
        TGIN=TGOUT
C
C   THE LIQUID INTO THIS STAGE IS THE LIQUID OUT OF THE NEXT STAGE
C   ABOVE IT.
C
        LO(1,N+1)=LINH2S
        LO(2,N+1)=LINCO2
        LO(3,N+1)=LINH2O
        LO(4,N+1)=LINAM
        LO(5,N+1)=LINION
C
C   PUT THE CALCULATED TEMPERATURE INTO A TEMPORARY PROFILE TO BE
C   COMPARED WITH THE CURRENT TEMPERATURE PROFILE IN TCONV.
C
        IF (N .NE. 1) THEN
          TEMP(N-1)=TLOUT
        ELSE
          TBOT=TLOUT
        ENDIF
C
C   END OF DO LOOP.
C
 10     CONTINUE
C
        RETURN
        END
```

```
C
C*****************************************************************
C
      SUBROUTINE PRINT
C
C   THE PRINT ROUTINE IS CALLED BY TOWER FOR EACH STAGE WHEN PRINTING
C   IS DESIRED.  DATA IS TRANSFERRED TO FILE OUT.OUT.
C
         IMPLICIT REAL*8 (A-H,O-Z)
         REAL*8 LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT,LOUTH2S,
     &          LOUTCO2,LOUTH2O,LOUTAM,LOUTION,LOUTTOT,NG,NGREB,M
C
         COMMON /GIN/ GINH2S,GINCO2,GINH2O,GINNRT,GINTOT
         COMMON /EK/ HH2S,HCO2,EKAM,EKHCO3,EKH2S,EKCO2
         COMMON /GOUT/ GOUTH2S,GOUTCO2,GOUTH2O,GOUTNRT,GOUTTOT
         COMMON /LIN/ LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
         COMMON /LOUT/LOUTH2S,LOUTCO2,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
         COMMON /TEMP/ TLOUT,TLIN,TGOUT,TGIN
         COMMON /CONB/ OH,RNH,RN,HS,H2S,HCO3,CO3,CO2
         COMMON /CONT/ TAM,TH2S,TCO2,TION
         COMMON /CONI/ OHI,RNHI,RNI,HSI,H2SI,HCO3I,CO3I,CO2I,CO2IE
         COMMON /PI/ PH2SI,PCO2I,PH2OI,PNRTI
         COMMON /PRESS/ PH2S,PCO2,P
         COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
         COMMON /ENHANC/ EH2S,ECO2,M
         COMMON /FLUX/ FKL,FKG,NG,NGREB,AREA
C
C   WRITE THE TEMPERATURE PROFILES TO FILE 'TEMP.OUT' TO BE USED
C   FOR LATER RUNS IF DESIRED.
C
         WRITE (10,*) TLOUT
C
         WRITE (3,*) ' '
C
C   WRITE THE MASS TRANSFER PARAMETERS
C
         IF (N.EQ.1) THEN
           WRITE (3,*) 'GAS MASS TRANSFER COEFF = ',FKG
           WRITE (3,*) 'LIQ MASS TRANSFER COEFF = ',FKL
           WRITE (3,*) 'NUMBER GAS TRANSFER UNITS = ',NG
           WRITE (3,*) 'MASS TRANSFER AREA = ',AREA
           WRITE (3,*) 'THE CO2 HATTA NUMBER = ',DSQRT(M)
           WRITE (3,*) ' '
         ENDIF
C
C   STAGE NUMBER AND HEADINGS
C
         WRITE (3,100) N,'H2S','CO2','H2O','AMINE','OTHER',
     &                   'TOTAL','TEMP(K)'
C
C   GAS OUT OF THE STAGE (MOLE/S) AND TEMP
C
```

```
      IF (N .EQ. 1) THEN
        WRITE (3,101) 'GIN',GINH2S,GINCO2,GINH2O,'---',GINNRT,
     &        GINTOT,TGIN
      ENDIF
      WRITE (3,101) 'GOUT',GOUTH2S,GOUTCO2,GOUTH2O,'---',GOUTNRT,
     &      GOUTTOT,TGOUT
C
C  LIQUID INTO THE STAGE (MOLE/S) AND TEMP
C
      WRITE (3,102) 'LIN',LINH2S,LINCO2,LINH2O,LINAM,LINION,
     &       LINTOT,TLIN
      IF (N.EQ.1) THEN
        WRITE (3,102) 'LOUT',LOUTH2S,LOUTCO2,LOUTH2O,LOUTAM,
     &        LOUTION,LOUTTOT,TLOUT
      ENDIF
C
C  H2S AND CO2 BULK AND INTERFACE LIQUID CONCENTRATION (MOLE/KG H2O)
C
      WRITE (3,103) 'BCONC',H2S,CO2,'---',RN,'---','---'
      WRITE (3,103) 'ICONC',H2SI,CO2I,'---',RNI,'---','---'
C
C  AVERAGE (GAS IN AND GAS OUT) INTERFACIAL PARTIAL PRESSURES (ATM):
C
      WRITE (3,104) 'PRESS',PH2SI,PCO2I,PH2OI,'---',PNRTI,P
C
C  ENHANCEMENT FACTORS
C
      WRITE (3,105) 'EFACT',EH2S,ECO2
C
C  WHEN THE PRINT FLAG, IPRINT, EQUALS 3 OUTPUT THE NUMBERS FOR
C  MCCABE  THIELE PLOTS FOR H2S AND CO2.
C
      IF ( (IPRINT .EQ. 3) .AND. (GINTOT .GT. 0.) ) THEN
        WRITE (3,*) ' '
        WRITE (3,*) ' MCCABE-THIELE INFORMATION:'
        WRITE (3,*) ' '
        WRITE (3,110) 'TH2S = ',TH2S,'PPH2S = ',GINH2S/GINTOT*P,
     &         'EQ PPH2S = ',H2S*HH2S
        WRITE (3,110) 'TCO2 = ',TCO2,'PPCO2 = ',GINCO2/GINTOT*P,
     &         'EQ PPCO2 = ',CO2*HCO2
        WRITE (3,*)  'THE CO2 HATTA NUMBER = ',DSQRT(M)
C
        WRITE (5,110) 'TH2S = ',TH2S,'PPH2S = ',GINH2S/GINTOT*P,
     &         'EQ PPH2S = ',H2S*HH2S
        WRITE (6,110) 'TCO2 = ',TCO2,'PPCO2 = ',GINCO2/GINTOT*P,
     &         'EQ PPCO2 = ',CO2*HCO2

      ENDIF
C
 100  FORMAT (//3X,I2,7X,2(A3,7X),A3,7X,2(A5,5X),A5,4X,A7/)
 101  FORMAT (1X,A5,E11.4,1X,F8.4,2X,F8.4,7X,A3,2X,2(2X,F8.4),2X,F7.3)
 102  FORMAT (1X,A5,E11.4,1X,F8.4,2X,F8.4,2X,3(2X,F8.4),2X,F7.3)
```

```
 103     FORMAT (1X,A5,2(E10.3),5X,A3,6X,F8.4,5X,A3,7X,A3)
 104     FORMAT (1X,A5,E10.3,2(2X,F8.4),7X,A3,4X,F8.4,2X,F8.4)
 105     FORMAT (1X,A5,2X,F8.3,2X,F8.4)
 110     FORMAT (1X,3(A,E12.3,2X))
C
         RETURN
         END
C
C****************************************************************
C
         FUNCTION STAGE (T)
C
C   STAGE IS A FUNCTION USED TO DO MASS AND HEAT TRANSFER AND
C   BALANCE CALCULATIONS.  THERE IS A CONVERGENCE LOOP WITHIN STAGE
C   WHICH CONVERGES THE COMPOSITION OF THE GAS OUT OF THE STAGE FOR
C   A GIVEN TEMPERATURE OF THE LIQUID OUT.  THIS TEMPERATURE OF THE
C   LIQUID OUT IS NOT KNOWN BUT IS CONVERGED BY SECANT2 WHICH IS THE
C   CONVERGENCE ROUTINE FOR STAGE.  THE ERROR IN THE SUM OF THE
C   PARTIAL PRESSURES AT THE INTERFACE IS MINIMIZED BY MANIPULATING
C   THE TEMPERATURE OF THE LIQUID OUT OF THE STAGE.
C
C   THE MASS TRANSFER EQUATIONS ARE USED TO FIND THE COMPOSITION OF
C   THE GAS OUT (H2S AND CO2) OF THE STAGE, AND THE MATERIAL BALANCE
C   SPECIFIES THE COMPOSITION OF THE LIQUID IN. THE COMPOSITIONS OF THE
C   GAS IN AND LIQUID OUT ARE KNOWN COMING INTO THIS STAGE
C   CALCULATION BECAUSE THE STAGE BELOW THIS HAS BEEN CONVERGED OR
C   THIS IS THE BOTTOM STAGE.  THE ENTHALPY TRANSFER EQUATION IS USED
C   TO FIND THE TEMPERATURE OF THE GAS OUT OF THE STAGE, AND THE
C   ENTHALPY BALANCE SPECIFIES THE AMOUNT OF WATER TRANSFERRED FOR
C   THE STAGE.  AS ALREADY STATED A PRESSURE BALANCE FOR THE
C   INTERFACE SPECIFIES THE TEMPERATURE OF THE LIQUID OUT OF THE STAGE.
C   THE TEMPERATURE OF THE  GAS INTO THIS STAGE IS KNOWN, AND THE
C   TEMPERATURE OF THE LIQUID IN IS ASSUMED TO BE KNOWN FROM THE
C   CURRENT TEMPERATURE PROFILE FOR THE  TOWER.
C
         IMPLICIT REAL*8 (A-H,O-Z)
         REAL*8 LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
         REAL*8 LOUTH2S,LOUTCO2,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
         REAL*8 NG,NGREB,NTU,K
C
         COMMON /GIN/ GINH2S,GINCO2,GINH2O,GINNRT,GINTOT
         COMMON /GOUT/ GOUTH2S,GOUTCO2,GOUTH2O,GOUTNRT,GOUTTOT
         COMMON /LIN/ LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
         COMMON /LOUT/LOUTH2S,LOUTCO2,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
         COMMON /TEMP/ TLOUT,TLIN,TGOUT,TGIN
         COMMON  /PRESS/ PH2S,PCO2,P
         COMMON /FLUX/ FKL,FKG,NG,NGREB,AREA
         COMMON /CONB/ OH,RNH,RN,HS,H2S,HCO3,CO3,CO2
         COMMON /CONT/ TAM,TH2S,TCO2,TION
         COMMON /CONI/ OHI,RNHI,RNI,HSI,H2SI,HCO3I,CO3I,CO2I,CO2IE
         COMMON /EK/ HH2S,HCO2,EKAM,EKHCO3,EKH2S,EKCO2
         COMMON /DH/ DHH2S,DHCO2,DHH2O,DHAM
```

```
      COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
      COMMON /PI/ PH2SI,PCO2I,PH2OI,PNRTI
      COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
C
      EXTERNAL BULK,FACE
C
      TLOUT=T
C
C  GUESS THE CONCENTRATIONS OF THE IONIC SPECIES SO THAT AN INITIAL
C  GUESS FOR THE IONIC STRENGTH OF THE BULK SOLUTION CAN BE
C  CALCULATED  IN BULK.
C
      HS=TH2S
      HCO3=TCO2
      CO3=0.
      RNH=TH2S+TCO2
C
C  THE SECANT METHOD NEEDS TWO INITIAL GUESSES FOR THE POH OF THE
C  BULK SOLUTION.  SECANT CONVERGES BULK TO GIVE THE BULK LIQUID
C  CONCENTRATIONS.  IF ANY CONCENTRATION IS LESS THAN ZERO, THERE IS
C  AN ERROR, AND EXECUTION IS RETURNED.
C
      XL=3.
      XR=5.
      CALL SECANT (BULK,XL,XR)
      IF ( (OH .LT. 0.) .OR. (RNH .LT. 0.) .OR. (RN .LT. 0.) .OR.
     &   (HS .LT. 0.) .OR. (H2S .LT. 0.) .OR. (HCO3 .LT. 0.) .OR.
     &   (CO3 .LT. 0.) .OR. (CO2 .LT. 0.) ) THEN
C
        WRITE (*,*) ' '
        WRITE (*,*) 'OH = ',OH
        WRITE (*,*) 'RNH = ',RNH
        WRITE (*,*) 'RN = ',RN
        WRITE (*,*) 'HS = ',HS
        WRITE (*,*) 'H2S = ',H2S
        WRITE (*,*) 'HCO3 = ',HCO3
        WRITE (*,*) 'CO3 = ',CO3
        WRITE (*,*) 'CO2 = ',CO2
C
        IERR=1
        CALL ERROR
        RETURN
      ENDIF
C
C  PARTIAL PRESSURES OF THE GAS INTO THE STAGE ARE CALCULATED AND
C  THE VALUES ARE GIVEN TO THE VARIABLES IN THE COMMON BLOCK USED BY
C   FACE.
C
      PINH2S=GINH2S/GINTOT*P
      PINCO2=GINCO2/GINTOT*P
      PINNRT=GINNRT/GINTOT*P
      PH2S=PINH2S
```

```
      PCO2=PINCO2
C
C   GUESS THE CONCENTRATIONS OF THE IONIC SPECIES SO THAT AN INITIAL
C   GUESS FOR THE IONIC STRENGTH AT THE INTERFACE CAN BE CALCULATED
C   IN FACE.  GOOD GUESSES ARE THE BULK CONCENTRATIONS.
C
      HSI=HS
      HCO3I=HCO3
      CO3I=CO3
      RNHI=RNH
      RNI=RN
      OHI=OH
C
C   THE SECANT METHOD NEEDS TWO INITIAL GUESSES FOR THE POH AT THE
C   INERFACE.  ONE GUESS IS THE VALUE IN THE BULK SOLUTION.  THE OTHER
C   GUESS IS DIFFERENT FOR ABSORPTION AND STRIPPING.  FOR ABSORPTION,
C   THE POH IS GREATER AT THE INTERFACE THAN IN THE BULK. THE OPPOSITE
C   IS TRUE FOR STRIPPING.  SECANT CONVERGES FACE TO GIVE THE INTERFACE
C   CONCENTRATIONS.  IF ANY CONCENTRATION IS LESS THAN ZERO, THERE IS
C   AN ERROR, AND EXECUTION IS RETURNED.
C
      IF (PINH2S .GT. HH2S*H2S) THEN
        XL=-DLOG10(OH)
        XR=XL+.05
      ELSE
        XR=-DLOG10(OH)
        XL=XR-.1
      ENDIF
      CALL SECANT (FACE,XL,XR)
      IF ( (OHI .LT. 0.) .OR. (RNHI .LT. 0.) .OR. (RNI .LT. 0.) .OR.
     &   (HSI .LT. 0.) .OR. (H2SI .LT. 0.) .OR. (HCO3I .LT. 0.) .OR.
     &   (CO3I .LT. 0.) .OR. (CO2I .LT. 0.) .OR. (CO2IE .LT. 0.) ) THEN
C
        WRITE (*,*) ' '
        WRITE (*,*) 'OHI = ',OHI,' OH = ',OH
        WRITE (*,*) 'RNHI = ',RNHI,' RNH = ',RNH
        WRITE (*,*) 'RNI = ',RNI,' RN = ',RN
        WRITE (*,*) 'HSI = ',HSI,' HS = ',HS
        WRITE (*,*) 'H2SI = ',H2SI,' H2S = ',H2S
        WRITE (*,*) 'HCO3I = ',HCO3I,' HCO3 = ',HCO3
        WRITE (*,*) 'CO3I = ',CO3I,' CO3 = ',CO3
        WRITE (*,*) 'CO2I = ',CO2I,' CO2 = ',CO2
        WRITE (*,*) 'CO2IE = ',CO2IE
C
        IERR=2
        CALL ERROR
        RETURN
      ENDIF
C
C   CALCULATE THE PARTIAL PRESSURE AT THE INTERFACE AND THE PARTIAL
C   PRESSURE DRIVING FORCE FOR MASS TRANSFER OF H2S AND CO2
C   ASSOCIATED WITH THE GAS IN.
```

```
C
      PINSI=HH2S*H2SI
      PINCI=HCO2*CO2I
      DFINS=PINSI-PINH2S
      DFINC=PINCI-PINCO2
C
C   CALCULATE THE ENTHALPY OF THE KNOWN STREAMS (GAS IN AND LIQUID
C   OUT)
C
      CPGIN=GINH2S*CPH2S(TGIN,TLIN)+GINCO2*CPCO2(TGIN,TLIN)+
     &        GINH2O*CPH2O(TGIN,TLIN)+GINNRT*CPNRT(TGIN,TLIN)
      CPLOUT=(LOUTH2S*CH2S(TLOUT)+LOUTCO2*CCO2(TLOUT)+LOUTH2O*
     &         CH2O(TLOUT)+LOUTAM*CAM(TLOUT))*(TLOUT-TLIN)
C
C   CALCULATE THE THERMAL CONDUCTIVITY, DIFFUSIVITY, HEAT CAPACITY,
C   AND DENSITY IN THE GAS PHASE FOR USE IN THE MASS AND HEAT TRANSFER
C   ANC ABSORBER AND THAT OF WATER FOR THE STRIPPER.  THE VALUE IS
C   CALCULATED BY INTERPOLATION AT THE TEMPERATURE DESIRED FROM
C   DATA IN  INCROPERA AND DEWITT(1981). THE GAS PHASE DIFFUSIVITY IS
C   ASSUMED TO BE WATER IN NITROGEN FOR THE ABSORBER AND CO2 IN
C   WATER FOR THE STRIPPER.  VALUES ARE TAKEN FROM PERRY (1969) AND
C   ARE CORRECTED FOR TEMPERATURE AND PRESSURE.
C
      IF (ICOLUMN.EQ.2) THEN
        K=(5.88+(TGIN-380.)/20.*.36)*1.D-5
      ELSE
        K=(6.19+(TGIN-300.)/50.*.81)*1.D-5
      ENDIF
      IF (CPGIN .EQ. 0.) THEN
        CP=8.
      ELSE
        CP=CPGIN/(TGIN-TLIN)/GINTOT
      ENDIF
      RHO=P/.08206/TGIN/1000.
C
C   USE THE NUMBER OF TRANSFER UNITS FOR THE REBOILER OR A REGULAR
C   STAGE.
      IF ( (IREB .EQ. 1) .AND. (N .EQ. 1) ) THEN
        NTU=NGREB
      ELSE
        NTU=NG
      ENDIF
C
C   THE CHILTON AND COLBURN HEAT AND MASS TRANSFER ANALOGY IS USED
C   TO CALCULATE THE NUMBER OF GAS PHASE HEAT TRANSFER UNITS FROM
C   THE NUMBER OF MASS TRANSFER UNITS.
C
      HNTU=NTU*(K/DG/CP/RHO)**(2./3.)
C
C   INITIALIZE THE VARIABLES THAT MUST BE CONVERGED WITHIN STAGE.
C
      XH2S=GOUTH2S
```

```
      XCO2=GOUTCO2
      XH2O=GOUTH2O
      XNRT=PINNRT
C
C  INITIALIZE THE STAGE ITERATION COUNTER AND BEGIN THE ITERATION
C  LOOP.  WITHIN THE LOOP, IT IS AN ERROR IF THE ITERATIONS EXCEED
C  THE MAXIMUM AMOUNT ALLOWED.
C
      ISTAGE=0
 10   IF (ISTAGE .GT. 1000) THEN
C
        WRITE (*,*) ' '
        WRITE (*,*) 'ERRH2S = ',ERRH2S
        WRITE (*,*) 'ERRCO2 = ',ERRCO2
        WRITE (*,*) 'ERRH2O = ',ERRH2O
        WRITE (*,*) 'ERRNRT = ',ERRNRT
C
        IERR=3
        CALL ERROR
        RETURN
      ENDIF
      ISTAGE=ISTAGE+1
C
C  UPDATE THE GUESS FOR THE GAS OUT COMPOSITION AND THE INERT
C  INTERFACE PARTIAL PRESSURE (THE CONVERGENCE VARIABLES).
C
      GOUTH2S=XH2S
      GOUTCO2=XCO2
      GOUTH2O=XH2O
      GOUTTOT=GOUTH2S+GOUTCO2+GOUTH2O+GOUTNRT
      PNRTI=XNRT
C
C  PARTIAL PRESSURES OF THE GAS OUT OF THE STAGE ARE CALCULATED AND
C  THE VALUES ARE GIVEN TO THE VARIABLES IN THE COMMON BLOCK USED BY
C  FACE.
C
      POUTH2S=GOUTH2S/GOUTTOT*P
      POUTCO2=GOUTCO2/GOUTTOT*P
      POUTNRT=GOUTNRT/GOUTTOT*P
      PH2S=POUTH2S
      PCO2=POUTCO2
C
C  SECANT CONVERGES FACE TO GIVE THE INTERFACE CONCENTRATIONS.  IF
C  ANY CONCENTRATION IS LESS THAN ZERO, THERE IS AN ERROR, AND
C  EXECUTION IS RETURNED.  THESE INTERFACE CONCENTRATIONS ARE
C  ASSOCIATED WITH THE GAS OUT.
C
      CALL SECANT (FACE,XL,XR)
      IF ( (OHI .LT. 0.) .OR. (RNHI .LT. 0.) .OR. (RNI .LT. 0.) .OR.
     &     (HSI .LT. 0.) .OR. (H2SI .LT. 0.) .OR. (HCO3I .LT. 0.) .OR.
     &     CO3I .LT. 0.) .OR. (CO2I .LT. 0.) .OR. (CO2IE .LT. 0.) ) THEN
```

```
C
         WRITE (*,*) ' '
         WRITE (*,*) 'OHI = ',OHI,' OH = ',OH
         WRITE (*,*) 'RNHI = ',RNHI,' RNH = ',RNH
         WRITE (*,*) 'RNI = ',RNI,' RN = ',RN
         WRITE (*,*) 'HSI = ',HSI,' HS = ',HS
         WRITE (*,*) 'H2SI = ',H2SI,' H2S = ',H2S
         WRITE (*,*) 'HCO3I = ',HCO3I,' HCO3 = ',HCO3
         WRITE (*,*) 'CO3I = ',CO3I,' CO3 = ',CO3
         WRITE (*,*) 'CO2I = ',CO2I,' CO2 = ',CO2
         WRITE (*,*) 'CO2IE = ',CO2IE
C
         IERR=2
         CALL ERROR
         RETURN
       ENDIF
C
C   CALCULATE THE PARTIAL PRESSURE AT THE INTERFACE AND THE PARTIAL
C   PRESSURE DRIVING FORCE FOR MASS TRANSFER OF H2S AND CO2
C   ASSOCIATED WITH THE GAS OUT.  CHECK TO MAKE SURE THAT THE MASS
C   TRANSFER HAS NOT EXCEEDED EQUILIBRIUM.  IF IT HAS, THE PARTIAL
C   PRESSURE OF H2S OR CO2 IN THE GAS OUT IS EQUAL TO THE PARTIAL
C   PRESSURE AT THE INTERFACE ASSOCIATED WITH THE GAS OUT.
C
      POUTSI=HH2S*H2SI
      POUTCI=HCO2*CO2I
      IF ( ( (PINH2S .LT. PINSI) .AND. (POUTH2S .GT. POUTSI) ) .OR.
     &   ( (PINH2S .GT. PINSI) .AND. (POUTH2S .LT. POUTSI) ) ) THEN
        POUTH2S=POUTSI
      ENDIF
      IF ( ( (PINCO2 .LT. PINCI) .AND. (POUTCO2 .GT. POUTCI) ) .OR.
     &   ( (PINCO2 .GT. PINCI) .AND. (POUTCO2 .LT. POUTCI) ) ) THEN
        POUTCO2=POUTCI
      ENDIF
      DFOUTS=POUTSI-POUTH2S
      DFOUTC=POUTCI-POUTCO2
C
C   CALCULATE THE DRIVING FORCE FOR MASS TRANSFER OF H2S AND CO2 AS
C   A LOG MEAN AVERAGE OF THE DRIVING FORCES ASSOCIATED WITH THE GAS
C   IN AND GAS OUT.  IF THE NUMBERS ARE SUCH THAT THE LOG MEAN
C   CALCULATION  WOULD CAUSE AN ARITHMETIC ERROR (SUCH AS DIVIDING BY
C   ZERO), USE AN ARITHMETIC AVERAGE DRIVING FORCE.
C
      IF (POUTH2S .EQ. PINH2S) THEN
        DFAVGS=(DFINS+DFOUTS)/2.
      ELSE
      IF ( (DFINS .EQ. DFOUTS).OR.(DFINS .EQ. 0.).OR.
     &    (DFOUTS .EQ. 0.).OR.((DFINS .GT. 0.).AND.(DFOUTS .LT. 0.))
     &    .OR.((DFINS .LT. 0.).AND.(DFOUTS .GT. 0.)) ) THEN
        DFAVGS=(DFINS+DFOUTS)/2.
      ELSE
        DFAVGS=(DFINS-DFOUTS)/DLOG(DFINS/DFOUTS)
```

```
        ENDIF
        ENDIF
        IF ( (DFINC .EQ. DFOUTC).OR.(DFINC .EQ. 0.).OR.
     &    (DFOUTC .EQ. 0.).OR.((DFINC .GT. 0.).AND.(DFOUTC .LT. 0.))
     &    .OR. ((DFINC .LT. 0.) .AND. (DFOUTC .GT. 0.)) ) THEN
          DFAVGC=(DFINC+DFOUTC)/2.
        ELSE
          DFAVGC=(DFINC-DFOUTC)/DLOG(DFINC/DFOUTC)
        ENDIF
C
C   CALCULATE AN AVERAGE PARTIAL PRESSURE FOR H2S, CO2, AND THE
C   INERT TO BE USED IN THE COMPENSATION FOR BULK TRANSFER IN THE
C   MASS TRANSFER EQUATIONS.
C
        PAVGH2S=(PINH2S+PINSI+POUTH2S+POUTSI)/4.
        PAVGCO2=(PINCO2+PINCI+POUTCO2+POUTCI)/4.
        PAVGNRT=(PINNRT+2.*PNRTI+POUTNRT)/4.
C
C   CALCULATE THE AMOUNT (MOLES) OF H2S AND CO2 IN THE GAS OUT BY
C   MASS TRANSFER EQUATIONS FOR THE GAS PHASE WITH BULK TRANSFER
C   INCLUDED.
C
        GOUTH2S=GINH2S+PAVGH2S/P*(GOUTTOT-GINTOT)+FKG*AREA*DFAVGS
        GOUTCO2=GINCO2+PAVGCO2/P*(GOUTTOT-GINTOT)+FKG*AREA*DFAVGC
C
C   IF THERE IS INERT IN THE GAS (THE ABSORBER), CALCULATE THE PARTIAL
C   PRESSURE OF INERT AT THE INTERFACE BY SOLVING THE INERT MASS
C   TRANSFER EQUATION SET EQUAL TO ZERO.  BECAUSE IT IS NOT SOLUBLE
C   THERE IS NO TRANSFER FOR THE INERT.  IF THE TOTAL MOLES OF GAS IN
C   AND GAS OUT ARE EQUAL, THE PARTIAL PRESSURE OF INERT IN THE GAS IN
C   AND GAS OUT ARE EQUAL AND EQUAL TO THE PARTIAL PRESSURE OF
C   INERT AT THE INTERFACE.
C
        IF (PAVGNRT .EQ. 0.) THEN
          PNRTI=0.
        ELSE
        IF (GINTOT .EQ. GOUTTOT) THEN
          PNRTI=PINNRT
        ELSE
          DUM=DEXP(P/PAVGNRT/(GINTOT-GOUTTOT)*FKG*AREA*
     &          (POUTNRT-PINNRT))
          PNRTI=(PINNRT-DUM*POUTNRT)/(1.-DUM)
        ENDIF
        ENDIF
C
C   CALCULATE THE TEMPERATURE OF THE GAS OUT BY ENTHALPY TRANFER.
C   THE ENTHALPY TRANSFER RELATIONSHIP IS SIMPLIFIED BY ASSUMING THAT
C   THE TOTAL MOLES OF GAS IN AND GAS OUT ARE EQUAL.
C
        TGOUT=TLOUT+(TGIN-TLOUT)*DEXP(-HNTU)
C
C   CALCULATE THE AMOUNT OF WATER IN THE GAS OUT BY AN ENTHALPY
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```
C   BALANCE.
        DUM=(CPGIN-CPLOUT-GOUTH2S*CPH2S(TGOUT,TLIN)-GOUTCO2*
     &     CPCO2(TGOUT,TLIN)-GOUTNRT*CPNRT(TGOUT,TLIN)+(DHH2S+DHAM)*
     &     (GINH2S-GOUTH2S)+(DHCO2+DHAM)*(GINCO2-GOUTCO2))
        GOUTH2O=(DUM+DHH2O*GINH2O)/(DHH2O+CPH2O(TGOUT,TLIN))
C
        GOUTTOT=GOUTH2S+GOUTCO2+GOUTH2O+GOUTNRT
C
C   IF A FLOWRATE LESS THAN ZERO HAS BEEN CALCULATED, THEN SET IT
C   EQUAL TO ZERO.
C
        IF (GOUTH2S .LT. 0.) THEN
          GOUTH2S=0.
        ENDIF
        IF (GOUTCO2 .LT. 0.) THEN
          GOUTCO2=0.
        ENDIF
        IF (GOUTH2O .LT. 0.) THEN
          GOUTH2O=0.
        ENDIF
C
C   MATERIAL BALANCE EQUATIONS ARE USED TO CALCULATE THE
C   COMPOSITION OF THE LIQUID INTO THE STAGE.
C
        LINH2S=LOUTH2S+GOUTH2S-GINH2S
        LINCO2=LOUTCO2+GOUTCO2-GINCO2
        LINH2O=LOUTH2O+GOUTH2O-GINH2O
        LINAM=LOUTAM
        LINION=LOUTION
C
C   THE PROGRAM TENDS TO BLOWUP WHEN THE H2S LOADING STARTS GETTING
C   LARGE.  THEREFORE, AN ERROR IS REPORTED IF THE LOADING IS GREATER
C   THAN ONE.  IF THE MODEL IS TO BE USED AT CONDITIONS OF H2S LOADINGS
C   AROUND ONE, THIS PROBLEM WILL HAVE TO BE SOLVED.  SO FAR H2S
C   LOADINGS HAVE REACHED ONE IN THE STRIPPER ONLY BECAUSE OF BAD
C   GUESSES FOR THE RICH LOADING VALUES IN THE INPUT TO THE PROGRAM.
C
        IF (LINH2S/LINAM .GT. 1.) THEN
C
          WRITE (*,*) 'STAGE = ',N
          WRITE (*,*) 'LINH2S = ',LINH2S
          WRITE (*,*) 'LINAM = ',LINAM
C
          IERR=5
          CALL ERROR
          RETURN
        ENDIF
C
C   IF A FLOWRATE LESS THAN ZERO HAS BEEN CALCULATED FOR THE LIQUID
C   IN, THEN SET IT EQUAL TO A SMALL AMOUNT AND CORRECT THE MATERIAL
C   BALANCE.
C
```

```
      IF (LINH2S .LT. 0.) THEN
        WRITE (*,*) 'LINH2S < 0 AT STAGE ',N
        LINH2S = 1D-6
      ENDIF
      IF (LINCO2 .LT. 0.) THEN
        WRITE (*,*) 'LINCO2 < 0 AT STAGE ',N
        LINCO2 = 1D-6
      ENDIF
      IF (LINH2O .LT. 0.) THEN
        IERR = 8
        CALL ERROR
        RETURN
      ENDIF
C
      LINTOT = LINH2S + LINCO2 + LINH2O + LINION + LINAM
C
C   IF THIS IS THE FIRST ITERATION WITHIN THE STAGE CONVERGENCE LOOP,
C   INITIALIZE THE VARIABLES USED IN THE CONVERGENCE AND DO ANOTHER
C   ITERATION BY RETURNING TO THE BEGINNING OF THE LOOP. THIS MUST BE
C   DONE BECAUSE THE SECANT METHOD USED TO CONVERGE THE VARIABLES
C   IN THIS LOOP REQUIRES TWO INITIAL GUESSES. WHAT THIS AMOUNTS TO IS
C   USING DIRECT SUBSTITUTION FOR THE FIRST ITERATION AND A SECANT
C   METHOD FOR THE REST.
C
      IF (ISTAGE .EQ. 1) THEN
        FOLDH2S=GOUTH2S-XH2S
        FOLDCO2=GOUTCO2-XCO2
        FOLDH2O=GOUTH2O-XH2O
        FOLDNRT=PNRTI-XNRT
        DELH2S=GOUTH2S-XH2S
        DELCO2=GOUTCO2-XCO2
        DELH2O=GOUTH2O-XH2O
        DELNRT=PNRTI-XNRT
        XH2S=GOUTH2S
        XCO2=GOUTCO2
        XH2O=GOUTH2O
        XNRT=PNRTI
        GOTO 10
      ENDIF
C
C   CALCULATE THE FUNCTIONS WHICH ARE TO BE MINIMIZED BY THE SECANT
C   METHOD. THESE FUNCTIONS ARE SIMPLY DIFFERENCES BETWEEN THE
C   CALCULATED VALUES AND THE GUESS FROM THE LAST ITERATION.
      FH2S=GOUTH2S-XH2S
      FCO2=GOUTCO2-XCO2
      FH2O=GOUTH2O-XH2O
      FNRT=PNRTI-XNRT
C
C   USE THE SECANT METHOD TO CALCULATE THE NEW GUESSES OF THE
C   VARIABLES  TO BE CONVERGED FOR THE NEXT ITERATION, UNLESS IT WOULD
C   CAUSE A DIVISION BY ZERO, THEN USE DIRECT SUBTITUTION.
C
```

```
          IF (FH2S .EQ. FOLDH2S) THEN
            DELH2S=GOUTH2S-XH2S
          ELSE
            DELH2S=-DELH2S*FH2S/(FH2S-FOLDH2S)
          ENDIF
          IF (FCO2 .EQ. FOLDCO2) THEN
            DELCO2=GOUTCO2-XCO2
          ELSE
            DELCO2=-DELCO2*FCO2/(FCO2-FOLDCO2)
          ENDIF
          IF (FH2O .EQ. FOLDH2O) THEN
            DELH2O=GOUTH2O-XH2O
          ELSE
            DELH2O=-DELH2O*FH2O/(FH2O-FOLDH2O)
          ENDIF
          IF (FNRT .EQ. FOLDNRT) THEN
            DELNRT=PNRTI-XNRT
          ELSE
            DELNRT=-DELNRT*FNRT/(FNRT-FOLDNRT)
          ENDIF
          XH2S=XH2S+DELH2S
          XCO2=XCO2+DELCO2
          XH2O=XH2O+DELH2O
          XNRT=XNRT+DELNRT
C
C   THE NEW GUESSES CANNOT BE LESS THAN ZERO.
C
          IF (XH2S .LT. 0.) THEN
            XH2S=0.
          ENDIF
          IF (XCO2 .LT. 0.) THEN
            XCO2=0.
          ENDIF
          IF (XH2O .LT. 0.) THEN
            XH2O=0.
          ENDIF
          IF (XNRT .LT. 0.) THEN
            XNRT=0.
          ENDIF
C
C   THE ERROR IN THE VARIABLES TO BE CONVERGED MUST BE CALCULATED TO
C   CHECK FOR CONVERGENCE.  THE ERROR IS A PERCENT CHANGE, UNLESS
C   THIS CAUSES A DIVISION BY ZERO, THEN IT IS AN ABSOLUTE CHANGE.
C
          IF (XH2S .EQ. 0.) THEN
            ERRH2S=DABS(DELH2S)
          ELSE
            ERRH2S=DABS(DELH2S/XH2S)
          ENDIF
          IF (XCO2 .EQ. 0.) THEN
            ERRCO2=DABS(DELCO2)
          ELSE
```

```
          ERRCO2=DABS(DELCO2/XCO2)
        ENDIF
        IF (XH2O .EQ. 0.) THEN
          ERRH2O=DABS(DELH2O)
        ELSE
          ERRH2O=DABS(DELH2O/XH2O)
        ENDIF
        IF (XNRT .EQ. 0.) THEN
          ERRNRT=DABS(DELNRT)
        ELSE
          ERRNRT=DABS(DELNRT/XNRT)
        ENDIF
C
C   IF ANY OF THE ERRORS IS NOT WITHIN THE CONVERGENCE LIMIT, DO
C   ANOTHER ITERATION.
C
        IF ( (ERRH2S .GT. .001) .OR. (ERRCO2 .GT. .001) .OR.
     &    (ERRH2O .GT. .001) .OR. (ERRNRT .GT. .001) ) THEN
          FOLDH2S=FH2S
          FOLDCO2=FCO2
          FOLDH2O=FH2O
          FOLDNRT=FNRT
          GOTO 10
        ENDIF
C
C   NOW THAT THE CONVERGENCE LOOP WITHIN STAGE IS FINISHED, THE ERROR
C   IN THE SUM OF THE PARTIAL PRESSURES AT THE INTERFACE IS CALCULATED
C   FOR USE BY SECANT2 TO CONVERGE THE TEMPERATURE OF THE LIQUID OUT
C   WHICH OCCURS EXTERNAL TO THIS FUNCTION.  THE PARTIAL PRESSURES OF
C   H2S AND CO2 AT THE INTERFACE IS AN ARITHMETIC AVERAGE VALUE OF THE
C   GAS IN AND GAS OUT INTERFACIAL VALUES WHICH WERE CALCULATED IN
C   THE LOOP ABOVE.  THE VALUE FOR THE INERT WAS ALSO CALCULATED IN
C   THE LOOP ABOVE.  THE PARTIAL PRESSURE OF WATER AT THE INTERFACE IS
C   CALCULATED BY ASSUMING THAT IT IS IN EQUILIBRIUM WITH THE LIQUID
C   INTERFACE AND USING RAOULT'S LAW.  THE ANTOINE EQUATION FOR THE
C   VAPOR PRESSURE OF WATER IS FROM FELDER AND ROUSSEAU (P.214).
C
        PH2SI=(PINSI+POUTSI)/2.
        PCO2I=(PINCI+POUTCI)/2.
        P0H2O=(10.**(7.96681-1668.21/(TLOUT+228.-273.)))/760.
        XH2OI=1.0/0.018/(1/0.018+OHI+RNHI+RNI+HSI+H2SI+HCO3I+CO3I+CO2I)
        PH2OI=P0H2O*XH2OI
        STAGE=P-PH2SI-PCO2I-PH2OI-PNRTI
C
C
        RETURN
        END
C
C***************************************************************
C
        FUNCTION CPH2S (TEMP,TEMPR)
C
```

```
C   CALCULATES THE ENTHALPY CHANGE FOR H2S GOING FROM TEMP TO
C   TEMPR.  DATA FROM FELDER AND ROUSSEAU.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      T=TEMP-273.
      TR=TEMPR-273.
      CPH2S=(33.51*(T-TR)+1.547D-2/2.*(T**2-TR**2)+.3012D-5/3.*
     &     (T**3-TR**3)-3.292D-9/4.*(T**4-TR**4))/4.1842
C
      RETURN
      END
C
C*****************************************************************
C
      FUNCTION CPCO2 (TEMP,TEMPR)
C
C   CALCULATES THE ENTHALPY CHANGE FOR CO2 GOING FROM TEMP TO
C   TEMPR. DATA FROM FELDER AND ROUSSEAU.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      T=TEMP-273.
      TR=TEMPR-273.
      CPCO2=(36.11*(T-TR)+4.233D-2/2.*(T**2-TR**2)-2.887D-5/3.*
     &     (T**3-TR**3)+7.464D-9/4.*(T**4-TR**4))/4.1842
C
      RETURN
      END
C
C*****************************************************************
C
      FUNCTION CPH2O (TEMP,TEMPR)
C
C   CALCULATES THE ENTHALPY CHANGE FOR WATER VAPOR GOING FROM
C   TEMP TO TEMPR.  DATA FROM FELDER AND ROUSSEAU.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      T=TEMP-273.
      TR=TEMPR-273.
      CPH2O=(33.46*(T-TR)+.688D-2/2.*(T**2-TR**2)+.7604D-5/3.*
     &     (T**3-TR**3)-3.593D-9/4.*(T**4-TR**4))/4.1842
C
      RETURN
      END
C
C*****************************************************************
C
      FUNCTION CPNRT (TEMP,TEMPR)
C
C   CALCULATES THE ENTHALPY CHANGE FOR INERT GAS (N2) GOING FROM
C   TEMP TO TEMPR.  DATA FROM FELDER AND ROUSSEAU.
C
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      T=TEMP-273.
      TR=TEMPR-273.
      CPNRT=(29.0*(T-TR)+.2199D-2/2.*(T**2-TR**2)+.5723D-5/3.*
     &     (T**3-TR**3)-2.871D-9/4.*(T**4-TR**4))/4.1842
C
      RETURN
      END
C
C******************************************************************
C
      FUNCTION CH2S(T)
C
C   THE HEAT CAPACITY OF H2S IN THE LIQUID IS ESTIMATED AS THAT OF H2O.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CH2S=18.
C
      RETURN
      END
C
C******************************************************************
C
      FUNCTION CCO2(T)
C
C   THE HEAT CAPACITY OF CO2 IN THE LIQUID IS ESTIMATED AS THAT OF H2O.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CCO2=18.
C
      RETURN
      END
C
C******************************************************************
C
      FUNCTION CH2O(T)
C
C   THE HEAT CAPACITY OF LIQUID WATER.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CH2O=18.
C
      RETURN
      END
C
C******************************************************************
C
      FUNCTION CAM(T)
C
C   THE HEAT CAPACITY OF MDEA IS ESTIMATED FROM THE HEAT CAPACITY OF
C   DEA FROM KOHL AND RIESENFELD (P.72).
C
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      CAM=91.63
C
      RETURN
      END
C
C************************************************************
C
      SUBROUTINE ERROR
C
C  THIS ERROR ROUTINE IS CALLED IF A SPECIFIED ERROR OCCURS.  A
C  MESSAGE IS PRINTED TO THE TERMINAL AND EXECUTION IS RETURNED.
C  AFTER THE ERROR IS DETECTED EXECUTION IS RETURNED THROUGH EVERY
C  SUBROUTINE BACK TO THE MAIN PROGRAM.  AN INTEGER SPECIFIES WHICH
C  ERROR HAS OCCURRED.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
C
      IF (IERR .EQ. 1) THEN
        WRITE (*,*) 'PROBLEM IN BULK SOLUTION'
      ENDIF
C
      IF (IERR .EQ. 2) THEN
        WRITE (*,*) 'PROBLEM IN INTERFACE SOLUTION'
      ENDIF
C
      IF (IERR .EQ. 3) THEN
        WRITE (*,*) 'STAGE DOES NOT CONVERGE'
      ENDIF
C
      IF (IERR .EQ. 5) THEN
        WRITE (*,*) 'H2S LOADING TOO HIGH'
      ENDIF
C
      IF (IERR .EQ. 6) THEN
        WRITE (*,*) 'LINH2S < 0 AT STAGE ',N
      ENDIF
C
      IF (IERR .EQ. 7) THEN
        WRITE (*,*) 'LINCO2 < 0 AT STAGE ',N
      ENDIF
C
      IF (IERR .EQ. 8) THEN
        WRITE (*,*) 'LINH2O < 0 AT STAGE ',N
      ENDIF
C
      RETURN
      END
C
C************************************************************
C
      SUBROUTINE SECANT (FUNCT,XL,XR)
```

```
C
C   SECANT IS THE CONVERGENCE ROUTINE FOR BULK AND FACE.  OBVIOUSLY,
C   IT IS BASED ON THE SECANT METHOD; THEREFORE, TWO INITIAL GUESSES
C   (XL AND XR) ARE NEEDED TO START THE METHOD.  THE VALUE F IS
C   MINIMIZED BY MANIPULATING X.  THE CONVERGENCE CRITERION IS BASED
C   ON THE CHANGE IN X.
C
        IMPLICIT REAL*8 (A-H,O-Z)
        XOLD=XL
        X=XR
C
        DELTA=X-XOLD
        FOLD=FUNCT(XOLD)
C
C   BEGINNING OF THE LOOP
C
 10     F=FUNCT(X)
        DELTA=-DELTA*F/(F-FOLD)
        X=X+DELTA
C
C   IF THE CONVERGENCE CRITERION IS NOT MET GO BACK TO THE BEGGINING
C   OF THE LOOP.
C
        IF (DABS(DELTA) .GT. .0005) THEN
          FOLD=F
          GOTO 10
        ENDIF
C
        RETURN
        END
C
C*****************************************************************
C
        SUBROUTINE SECANT2 (FUNCT,XL,XR)
C
C   SECANT2 IS EXACTLY THE SAME ROUTINE AS SECANT, BUT IS USED FOR
C   CONVERGENCE OF STAGE.  SECANT COULD NOT BE USED TO CONVERGE
C   STAGE ALSO BECAUSE STAGE CALLS SECANT.  THIS ROUTINE ALSO CHECKS
C   ERROR CONDITIONS COMING OUT OF STAGE.  IF THERE IS AN ERROR,
C   EXECUTION RETURNS.
C
        IMPLICIT REAL*8 (A-H,O-Z)
        COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
C
        XOLD=XL
        X=XR
C
        DELTA=X-XOLD
        FOLD=FUNCT(XOLD)
C
        IF (IERR .GT. 0) RETURN
C
```

```
 10     F=FUNCT(X)
        IF (IERR .GT. 0) RETURN
        DELTA=-DELTA*F/(F-FOLD)
        X=X+DELTA
C
        IF (DABS(DELTA) .GT. .005) THEN
          FOLD=F
          GOTO 10
        ENDIF
C
        RETURN
        END
C
C**************************************************************
C
        FUNCTION BULK (POH)
C
C   BULK IS A FUNCTION USED TO CALCULATE THE BULK LIQUID
C   CONCENTRATIONS. THE EQUILIBRIUM EQUATIONS DESCRIBING THE BULK
C   LIQUID ARE SOLVED SEQUENTIALLY GIVEN A GUESS FOR THE HYDROXIDE
C   CONCENTRATION AND VARIABLE BULK IS THE ERROR IN THE BULK CHARGE
C   BALANCE WHICH IS MINIMIZED BY THE SUBROUTINE SECANT BY
C   MANIPULATING THE POH IN THE BULK SOLUTION.  THERE IS A CONVERGENCE
C   LOOP WITHIN BULK BECAUSE THE  EQUILIBRIUM CONSTANTS ARE A
C   FUNCTION OF IONIC STRENGTH WHICH IS NOT KNOWN UNTIL THE BULK
C   CONCENTRATIONS ARE KNOWN.
C
        IMPLICIT REAL*8 (A-H,O-Z)
        COMMON /EK/ HH2S,HCO2,EKAM,EKHCO3,EKH2S,EKCO2
        COMMON /CONB/ OH,RNH,RN,HS,H2S,HCO3,CO3,CO2
        COMMON /CONT/ TAM,TH2S,TCO2,TION
        COMMON /TEMP/ TLOUT,TLIN,TGOUT,TGIN
C
        T=TLOUT
        OH=10.**(-POH)
        BULKOLD=0.
C
C   THIS IS THE BEGINNING OF THE CONVERGENCE LOOP WITHIN BULK.
C
 10     SUMION=.5*(OH+RNH+HS+HCO3+4.*CO3+TION)
        IF (SUMION .LT. 0.0) SUMION = -SUMION
        IF (SUMION .GT. 50) SUMION = 6.0
C
C   CALCULATE THE EQUILIBRIUM CONSTANTS AT THE BULK LIQUID
C   CONDITIONS.
C
        CALL EQ (T,SUMION,TAM)
C
C   CALCULATE THE BULK LIQUID CONCENTRATIONS SEQUENTIALLY GIVEN THE
C   GUESS FOR THE HYDROXIDE CONCENTRATION.
C
        RNH=EKAM*TAM/(OH+EKAM)
```

```
      RN=RNH*OH/EKAM
      HS=EKH2S*RN*TH2S/(RNH+EKH2S*RN)
      H2S=HS*RNH/EKH2S/RN
      CO3=TCO2/(1.+1./(EKHCO3*OH*(1.-RNH/(EKCO2*RN+RNH))))
      CO2=RNH*(TCO2-CO3)/(EKCO2*RN+RNH)
      HCO3=TCO2-CO3-CO2
      BULK=OH+HS+HCO3+2.*CO3-RNH+TION
C
C  IF THE CONVERGENCE CRITERION IS NOT MET GO BACK TO THE BEGINNING
C  OF  THE LOOP.
C
      IF (DABS((BULK-BULKOLD)/BULK) .GT. .0005) THEN
        BULKOLD=BULK
        GOTO 10
      ENDIF
C
C
      RETURN
      END
C
C*****************************************************************
C
      FUNCTION FACE (POH)
C
C  FACE IS A FUNCTION USED TO CALCULATE THE INTERFACIAL LIQUID
C  CONCENTRATIONS.  THE SYSTEM OF EQUATIONS DESCRIBING THE INTERFACE
C  ARE SOLVED SEQUENTIALLY GIVEN A GUESS FOR THE HYDROXIDE
C  CONCENTRATION.  THE VARIABLE FACE IS THE ERROR IN ONE OF THESE
C  EQUATIONS WHICH IS MINIMIZED BY THE SUBROUTINE SECANT BY
C  MANIPULATING THE POH AT THE INTERFACE.  THERE ARE NINE EQUATIONS
C  AND NINE UNKNOWNS, EIGHT SPECIES AND AN EQUILIBRIUM VALUE FOR
C  FREE CO2 AS WELL AS THE ACTUAL VALUE BECAUSE CO2 IS NOT IN
C  EQULIBRIUM AT THE INTERFACE.  THE NINE EQUATIONS INCLUDE FOUR
C  EQULIBRIUM RELATIONSHIPS, A CHARGE FLUX BALANCE, AN AMINE FLUX
C  CONSERVATION, TWO EQUATIONS MATCHING THE LIQUID AND GAS PHASE
C  FLUX OF H2S AND CO2, AND ANOTHER FLUX EQUATION FOR CO2 BASED ON
C  THE ENHANCEMENT FACTOR.  THERE IS A CONVERGENCE LOOP WITHIN FACE
C  BECAUSE THE EQUILIBRIUM CONSTANTS ARE A FUNCTION OF IONIC
C  STRENGTH WHICH IS NOT KNOWN UNTIL THE INTERFACE CONCENTRATIONS
C  ARE KNOWN.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 M, NG, NGREB
C
C  USE A DATA STATEMENT TO INPUT THE ARBITRARY CONSTANT C3 IN THE
C  CO2  ENHANCEMENT FACTOR EXPRESSION.
C
      DATA  C3  /1.5/
C
      COMMON /EK/ HH2S,HCO2,EKAM,EKHCO3,EKH2S,EKCO2
      COMMON /CONI/ OHI,RNHI,RNI,HSI,H2SI,HCO3I,CO3I,CO2I,CO2IE
      COMMON /CONB/ OH,RNH,RN,HS,H2S,HCO3,CO3,CO2
```

```
      COMMON /CONT/ TAM,TH2S,TCO2,TION
      COMMON /PRESS/ PH2S,PCO2,P
      COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
      COMMON /FLUX/ FKL,FKG,NG,NGREB,AREA
      COMMON /TEMP/ TLOUT,TLIN,TGOUT,TGIN
      COMMON /ENHANC/ EH2S,ECO2,M
C
      T=TLOUT
      FACEOLD=0.
      OHI=10.**(-POH)
C
C   THE FOLLOWING IS A CONVERSION FACTOR TO CHANGE THE
C   CONCENTRATIONS FROM UNITS OF MOLE/KG H2O TO MOLARITY TO ENSURE
C   UNIT CONSISTENCY WITH THE OTHER PARAMETERS FKL AND FKG.
C
      CONVERT = DENSAM(T)/(0.044*TCO2 + 0.034*TH2S + 0.119*TAM + 1.0)
C
C   THIS IS THE BEGINNING OF THE CONVERGENCE LOOP WITHIN FACE.
C
 10   SUMION=.5*(OHI+RNHI+HSI+HCO3I+4.*CO3I+TION)
      IF (SUMION .LT. 0.) SUMION=-SUMION
      IF (SUMION .GT. 10) SUMION = 6.0
      TAMI=RNHI+RNI
C
C   CALCULATE THE EQUILIBRIUM AND RATE CONSTANTS AT THE CONDITIONS
C   OF THE INTERFACE.
C
      CALL EQ (T,SUMION,TAMI)
      CALL RATE (T,SUMION,CONVERT,RKAM,RKOH)
C
C   CALCULATE THE INTERFACE CONCENTRATIONS SEQUENTIALLY GIVEN THE
C   GUESS  FOR THE HYDROXIDE CONCENTRATION.
C
      RNHI=(DRN*RN+DRNH*RNH)/(DRNH+DRN*OHI/EKAM)
      RNI=RNHI*OHI/EKAM
      HSI=(FKL*(DSQRT(DH2S/DCO2)*H2S+DSQRT(DHS/DCO2)*HS)+
     &   FKG*PH2S/CONVERT)/(FKG*HH2S*RNHI/EKH2S/RNI/CONVERT+FKL*
     &   (DSQRT(DH2S/DCO2)*RNHI/EKH2S/RNI+DSQRT(DHS/DCO2)))
      H2SI=HSI*RNHI/EKH2S/RNI
C
C   THIS "IF" STATEMENT DIRECTS DIFFERENT EQUATIONS TO BE USED IF THERE
C   IS OR IS NOT CO2 IN THE SOLUTION.  IF THERE IS NO CO2 IN THE
C   SOLUTION, THE ERROR EQUATION IS THE CHARGE FLUX BALANCE.  IF THERE
C   IS CO2 IN THE SOLUTION, THE ERROR EQUATION IS THE DIFFERENCE
C   BETWEEN THE CO2 ENHANCEMENT FACTOR FLUX AND THE CO2 GAS PHASE
C   FLUX.
C
      IF (TCO2 .EQ. 0.) THEN
        HCO3I=0.
        CO3I=0.
        CO2I=0.
        CO2IE=0.
```

```
        ECO2=0.
        FACE=DHS*(HS-HSI)+DOH*(OH-OHI)+DHCO3*(HCO3-HCO3I)+
     &       2.*DCO3*(CO3-CO3I)-DRNH*(RNH-RNHI)
      ELSE
        HCO3I=(DHS*(HS-HSI)+DOH*(OH-OHI)+DHCO3*HCO3+2.*DCO3*CO3+
     &        DRNH*(RNHI-RNH))/(DHCO3+2.*DCO3*OHI*EKHCO3)
        CO3I=HCO3I*OHI*EKHCO3
        CO2IE=HCO3I*RNHI/EKCO2/RNI
        CO2I=(FKL*(CO2+DSQRT(DHCO3/DCO2)*(HCO3-HCO3I)+
     &        DSQRT(DCO3/DCO2)*(CO3-CO3I))+FKG*PCO2/CONVERT)/
     &        (FKG*HCO2/CONVERT+FKL)
        THETA=(CO2IE-CO2)/(CO2I-CO2)
        M=DCO2/FKL**2*(RKAM*RNI+RKOH*OHI)*CONVERT
        ECO2=DSQRT(1.+M)*(1.+THETA/(1.-C3)*(C3-M/(1.-C3**2+
     &       M)))+C3*THETA/(1.-C3)*(M/(1.-C3**2+M)-1.)
        FACE=ECO2*FKL*(CO2-CO2I)*CONVERT-FKG*(HCO2*CO2I-PCO2)
      ENDIF
C
C   THE H2S ENHANCEMENT FACTOR IS NOT USED IN THE EQUATIONS, BUT IT IS
C   CALCULATED FOR THE OUTPUT FROM THE MODEL.
C
      IF ( (H2S .NE. 0.) .OR. (H2SI .NE. 0.) ) THEN
        EH2S=1.+DHS/DH2S*(HS-HSI)/(H2S-H2SI)
      ENDIF
C
C   IF THE CONVERGENCE CRITERION IS NOT MET GO BACK TO THE BEGINNING
C   OF THE LOOP.
C
      IF (DABS((FACE-FACEOLD)/FACE) .GT. .0005) THEN
        FACEOLD=FACE
        GOTO 10
      ENDIF
C
      RETURN
      END
C
C*******************************************************************
C
      SUBROUTINE RATE (T,SUMION,CONVERT,RKAM,RKOH)
C
C  RATE SUPPLIES THE REACTION RATE CONSTANTS FOR THE TWO REACTION
C  MECHANISMS FOR CO2 AT THE SPECIFIED TEMPERATURE AND IONIC
C  STRENGTH.  THEY ARE NEEDED FOR CALCULATION OF THE ENHANCEMENT
C  FACTOR FOR CO2. THE EXPRESSION FOR THE HYDROXIDE REACTION IS FROM
C  ASTARITA (1983), AND THAT OF THE AMINE REACTION IS FROM LITTEL ET
C  AL.(1990).  UNITS ARE LITER/MOLE/SEC.
C
C  RKOH    CO2  +  OH  =  HCO3
C  RKAM    CO2  +  R3N  =  HCO3  +  R3NH
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      RKOH=10.**(13.635-2895./T+SUMION*CONVERT*.08)
      RKAM=1.34E9*DEXP(-5771.0/T)
C
      RETURN
      END
C
C*************************************************************
C
      SUBROUTINE EQ (T,SUMION,AMMOL)
C
C  EQ CALCULATES VALUES OF THE EQULIBRIUM CONSTANTS AND HENRY'S
C  LAW CONSTANTS AT THE TEMPERATURE (!K), IONIC STRENGTH (MOLALITY),
C  AND AMINE CONCENTRATION (MOLALITY) DESIRED.  THE VALUES ARE
C  TRANSFERRED IN THE COMMON BLOCK /EK/
C
C  EKH2S    H2S(AQ) + R3N = HS + R3NH
C  EKCO2    CO2(AQ) + R3N = HCO3 + R3NH
C  EKHCO3    HCO3 + OH = CO3
C  EKAM     R3N = R3NH + OH
C  EKW      H2O = H + OH
C  HH2S     H2S(AQ) = H2S(G)
C  HCO2     CO2(AQ) = CO2(G)
C
C  VARIABLES:
C      EKW -       WATER DISSOCIATION CONSTANT. FIT FROM DATA IN THE CRC
C                  HANDBOOK OF CHEMISTRY AND PHYSICS (MOLES/L)^2
C      EKHCO3 -    INFINITE DILUTION BICARBONATE DISSOCIATION CONSTANT
C                  FROM EDWARDS (1978) WITH SOME CONVERSION FACTORS
C                  BECAUSE THE REACTIONS WERE DEFINED DIFFEENTLY (KG
C                  H2O/MOLE)
C      EKAM -      INFINITE DILUTION AMINE PROTONATION CONSTANT FIT TO
C                  DATA FROM SCHWABE (1959) WITH SOME CONVERSION
C                  FACTORS BECAUSE THE REACTIONS WERE DEFINED
C                  DIFFERENTLY AND THE HEAT OF RXN EXTRACTED SO IT CAN
C                  BE CHANGED (MOLE/KG H2O)
C      EKCO2 -     CO2 EQUILIBRIUM CONSTANT FIT TO AN EMPIRICAL EQUATION
C                  WITH SIX ADJUSTABLE PARAMETERS USING EQUILIBRIUM
C                  DATA FROM JOU
C      EKH2S -     SAME AS EKCO2 BUT FOR H2S
C
C      HH2S -      H2S HENRY'S CONSTANT FOR INFINITE DILUTION IN H2O FROM
C                  EDWARDS (1978) (ATM-KG H2O/MOLE)
C      HCO2I -     CO2 HENRY'S CONSTANT FOR INFINITE DILUTION IN H2O FROM
C                  EDWARDS (1978) (ATM-KG H2O/MOLE).
C      HCO2IM -    SAME AS HCO2I BUT WITH UNITS (ATM-L/MOLE)
C      HCO2M -     CO2 HENRY'S CONSTANT AS A FUNCTION OF TEMP, WT%
C                  MDEA, AND ION CONCENTRATION WITH UNITS OF MOLARITY
C                  (ATM-L/MOLE). ION CONCENTRATION IS INDICATED BY THE
C                  AMOUNT OF PROTONATED AMINE.  DATA WAS TAKEN BY
C                  TOMAN TO GET THIS CORRELATION.
C      HCO2 -      SAME AS HCO2M BUT WITH UNITS (ATM-KG H2O/MOLE).  THIS
C                  VALUE IS USED ELSEWHERE IN THE PROGRAM.
```

```
C
C      RNHM -    TOTAL PROTONATED AMINE CONCENTRATION IN MOLARITY
C                (MOLE/L).
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /EK/ HH2S,HCO2,EKAM,EKHCO3,EKH2S,EKCO2
      COMMON /DH/ DHH2S,DHCO2,DHH2O,DHAM
      COMMON /CONT/ TAM,TH2S,TCO2,TION
      COMMON /CONB/ OH,RNH,RN,HS,H2S,HCO3,CO3,CO2
C
C  THE FOLLOWING DATA STATEMENTS CONTAIN THE PARAMETERS THAT WERE
C  ADJUSTED TO FIT THE EQUILIBRIUM CONSTANTS FOR H2S AND CO2.  THE
C  FIRST DATA STATEMENT IS FOR H2S AND THE SECOND FOR CO2.
C
      DATA AH,BH,CH,DH,DDH,EH /-17.281,-0.119,-.50602,19.39,.01,-4895.7/
      DATA AC,BC,CC,DC,DDC,EC /2.9611,0.3932,-2.1779,0.1082,1.,-7036.05/
C
      EKW=10.**(285.521-11987.6/T+.0616564*T-48.737*DLOG(T))
C
      EKHCO3 =DEXP(-12431.7/T - 35.4819*DLOG(T) + 220.067)*(DENSW(T)**2)
     &       /EKW
C
      PKA=8.523
      DHTERM=DHAM/1.987/298.**2
      EKAM=EKW/DEXP(-PKA*DLOG(10.D0)+DHTERM*(T-298.))/DENSW(T)
C
      HH2S = DEXP(-13236.8/T - 55.0551*DLOG(T) + 0.0595651*T + 342.595)
      EKH2S = 101.325*HH2S/DEXP(AH + BH*SUMION + CH*DSQRT(SUMION) +
     &       DH*AMMOL**DDH + EH*(1./T-1./298.))
C
C  CALCULATE THE INFINTE DILUTION VALUE TO GET THE TEMPERATURE
C  DEPENDENCE
C
      HCO2I = DEXP(-6789.04/T - 11.4519*DLOG(T) - 0.010454*T + 94.4914)
      HCO2IM = HCO2I/DENSW(T)
C
C  HCO2M IS CURRENTLY SET FOR 50 WT% MDEA.  FOR OTHER COMPOSITIONS,
C  SIMPLY  SUBSTITUTE THE 50.0 WITH THE NEW WT%.
C
      RNHM = RNH*DENSAM(T)/(0.044*TCO2 + 0.034*TH2S + 0.119*TAM + 1.0)
      HCO2M = 10.0**(DLOG10(HCO2IM + 0.032361*(50.0) +
     &            0.0035283*(50.0D0)**2) + 0.09*RNHM)
      HCO2 = HCO2M*DENSAM(T)/(0.044*TCO2 + 0.034*TH2S + 0.119*TAM + 1.)
      EKCO2 = 101.325*HCO2/DEXP(AC + BC*SUMION + CC*DSQRT(SUMION) +
     &       DC*AMMOL**DDC + EC*(1./T-1./298.))
C
      RETURN
      END
C
C*****************************************************************
C
      SUBROUTINE DIFFUSE (T)
```

```
C
C   THIS SUBROUTINE CALCULATES THE DIFFUSIVITIES FOR THE VARIOUS
C   SPECIES AS A FUNCTION OF VISCOSITY.  VISCOSITY IN TURN IS A FUNCTION
C   OF TEMPERATURE AND CO2 LOADING.
C
C   VISCOSITIES:
C
C   THE EQUATION FOR WATER VISCOSITY WAS FIT TO DATA IN THE CRC
C   HANDBOOK OF CHEMISTRY AND PHYSICS.  THE EQUATION FOR UNLOADED
C   SOLUTION VISCOSITY  COMES FROM GLASSCOCK (1990) WHICH WAS DERIVED
C   FROM AL-GHAWAS (1988) DATA.
C   THE EQUATION FOR LOADED SOLUTION VISCOSITY WAS FIT TO DATA FROM
C   TOMAN (1990) TO OBTAIN THE SLOPE 0.7527.  THE FACTOR (298/T)**2 WAS
C   ARBITRARILY USED TO REDUCE THE DEPENDENCE OF VISCOSITY ON
C   LOADING AT HIGHER TEMPERATURES.  THIS EFFECT IS NOT A PROVEN ONE
C   BUT TOMAN FELT THAT IT WOULD PROBABLY OCCUR.
C
C   DIFFUSIVITIES:
C
C   THE UNLOADED SOLUTION DIFFUSIVITY FOR CO2 CAME FROM ANALOGY TO
C   THE WORK OF TOMCEJ (1989) ALONG WITH DATA FROM AL-GHAWAS (1988).
C   THE LOADED  SOLUTION DIFFUSIVITIES ARE FOUND USING THE MODIFIED
C   STOKES-EINSTEIN  RELATIONSHIP.  THE VALUE 8.08D-8 IS THE DIFFUSIVITY
C   (DM^2/S) OF MDEA AT 25 C IN H2O ASSUMING THAT THE MDEA VALUE IS
C   EQUAL TO THE DEA VALUE   (I.E. THE VALUE IS FOR DEA FOUND FROM
C   VERSTEEG (1988)).  THE VALUE   1.77D-7 IS THE DIFFUSIVITY (DM^2/S) OF H2S
C   AT 16 C IN H2O FOUND IN   THE CRC HANDBOOK OF CHEMISTRY AND
C   PHYSICS.
C
C   THE DIFFUSIVITIES OF THE IONS ARE ARBITRARILY SET EQUAL TO THAT OF
C   MDEA.
C
C   VARIABLES:
C
C      D[COMPONENT] -  RESPECTIVE COMPONENT DIFFUSIVITY FOR LOADED
C                      SOLUTION (DM^2/S)
C      DCO2ULD -       UNLOADED SOLUTION CO2 DIFFUSIVITY (M^2/S)
C      VISH2O -        WATER VISCOSITY (CP)
C      VISLD -         LOADED SOLUTION VISCOSITY (CP)
C      VISULD -        UNLOADED SOLUTION VISCOSITY (CP)
C      CO2LDG -        CO2 LOADING (MOLE/MOLE)
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /CONT/ TAM,TH2S,TCO2,TION
      COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
C
      VISULD = DEXP(-34.51 + 7434.0/T + 0.03951*T)
      CO2LDG = TCO2/TAM
      VISLD = DEXP(VISULD + 0.7527*((298.0/T)**2)*CO2LDG)
      DCO2ULD = 1.1*T*DEXP(-30.7509 - 0.7785*DLOG(VISULD/1000.0))
C
      DCO2 = 100.0*DCO2ULD*(VISULD/VISLD)**0.6
```

```
C
      TEMP = T - 273.0
      VISH2O = DEXP(0.55479 - 0.028401*TEMP + 1.04D-4*TEMP**2)
C
      DH2S = 1.77D-7*T/289.0*(VISH2O/VISLD)**0.6
      DRN = 8.08D-8*T/298.0*(VISH2O/VISLD)**0.6
      DRNH = DRN
      DHS = DRN
      DHCO3 = DRN
      DCO3 = DRN
      DOH = DRN
C
      RETURN
      END
C
C END OF SUBROUTINE DIFFUSE
C
C *****************************************************************
C
      SUBROUTINE COEFF ( TLIN, TGIN, P )
C
C  THIS SUBROUTINE CALCULATES THE MASS TRANSFER COEFFICIENTS AND
C  THE NUMBER OF MASS TRNSFER UNITS.  CURRENTLY, THE EXPRESSIONS
C  ARE FOR SIEVE TRAYS OR BUBBLE CAP TRAYS THAT ARE SPACED BY 24
C  INCHES.  THE TRAY SPACING PLAYS A PART IN THE CALCULATION OF
C  THE GAS VELOCITY BECAUSE THE FLOOD VELOCITY IS CALCULATED USING A
C  CORRELATION IN PERRY'S HANDBOOK BASED ON 24 INCH TRAYS.
C
C  THE CORRELATION FOR SIEVE TRAYS IS FROM CHAN AND FAIR (1983).  THE
C  CORRELATION FOR BUBBLE CAP TRAYS IS FROM SHARMA (1969).
C
C  INPUTS (FOUND IN COMMON BLOCK):
C
C     F -         FRACTION FLOOD, THAT IS RATIO OF GAS TO FLOOD VELOCITY
C     HL -        LIQUID HOLDUP ON EACH TRAY (CM)
C     HFROTH -    EFFECTIVE FROTH HEIGHT ON EACH TRAY (CM)
C
C  VARIABLES:
C
C     DG -          ESTIMATE OF OVERALL GAS DIFFUSION COEFFICIENT. FOR
C                   THE ABSORBER, ASSUMED TO BE H2O DIFFUSING IN N2.  FOR
C                   THE STRIPPER, ASSUMED TO BE CO2 DIFFUSING IN H2O. THE
C                   ESTIMATES WERE FOUND USING A METHOD BY FULLER
C                   (1966).(CM^2/S)
C     FKGA -        GAS PHASE MASS TRANSFER COEFFICIENT WITH UNITS (M/S)
C                   MULTIPLIED BY THE AREA AVAILABLE FOR MASS TRANSFER
C                   WITH  UNITS (M^2/M^3). (1/S)
C     GMW -         GAS MOLECULAR WEIGHT (KG/KMOLE)
C     GDENS -       GAS DENSITY (KG/M^3)
C     GVEL -        GAS VELOCITY THRU ACTIVE AREA OF TRAY. UNITS (M/S)
C                   FOR SIEVE TRAYS AND (CM/S) FOR BUBBLE CAP TRAYS
C     FVA -         FACTOR DEFINED BY CHAN AND FAIR
```

```
C       DL -          ESTIMATE OF OVERALL LIQUID DIFFUSION COEFFICIENT
C                     (CM^2/S)
C       FKLA -        SAME AS FKG BUT FOR THE LIQUID (M/S)
C       AREAVOL -     INTERFACIAL AREA AVAILABLE FOR MASS TRANSFER IN
C                     M^2/M^3 FROTH.  THE CORRELATION SHOULD NOT BE USED
C                     FOR FVA GREATER THAN 4.0.  THE CORRELATION CAME
C                     FROM A GRAPH IN BISIO (1985).
C       AREAPFA -     INTERFACIAL AREA AVAILABLE FOR MASS TRANSFER IN
C                     DM^2/CM^2 FLOOR AREA.
C       PHI -         EFFECTIVE FROTH DENSITY
C       TV -          AVERAGE VAPOR RESIDENCE TIME (S)
C       NG -          NUMBER OF GAS PHASE MASS TRANSFER UNITS
C       FKG -         GAS PHASE MASS TRANSFER COEFFICIENT
C                     (MOLE/DM^2/S/ATM)
C       FKL -         LIQUID PHASE MASS TRANSFER COEFFICIENT (DM/S).  THIS
C                     COEFFICIENT IS BASED ON THE CO2 DIFFUSIVITY;
C                     THEREFORE, IT IS THE CO2 LIQUID PHASE MASS TRANSFER
C                     COEFFICIENT.  OTHER  COMPONENT COEFFICIENTS ARE
C                     FOUND BY RATIOING THE SQUARE ROOT OF DIFFUSIVITIES.
C       AREA -        ACTUAL AREA FOR MASS TRANSFER IN DM^2
C
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8  NG, NGREB
C
        COMMON /TRAY/ ITRAY,F,HL,HFROTH
        COMMON /FLUX/ FKL,FKG,NG,NGREB,AREA
        COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
        COMMON /GIN/ GINH2S,GINCO2,GINH2O,GINNRT,GINTOT
        COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
C
        IF (ICOLUMN.EQ.1) THEN
          DG = 1.233D-5*TGIN**1.75/P
        ELSE
          DG = 9.851D-6*TGIN**1.75/P
        ENDIF
C
        DL = DCO2*100.0

        GMW = (34.0*GINH2S + 44.0*GINCO2 + 18.0*GINH2O +
     &        28.0*GINNRT)/GINTOT
        GDENS = P*GMW/TGIN/0.08205
C
C   CHECK TRAY TYPE AND CALCULATE THE APPROPRIATE COEFFICIENTS
C
        IF (ITRAY.EQ.1) THEN
          GVEL = 10.7*F*DSQRT((1000.0*DENSAM(TLIN) - GDENS)/GDENS)
          FKG = 0.0467*(GVEL)**0.25*DSQRT(DG)/DSQRT(HFROTH)
          FKL = 1.3*(GVEL)**0.25*DSQRT(DL)/DSQRT(HFROTH)
          AREAPFA = 0.00535*DSQRT(GVEL)*HFROTH**0.83
          AREA = AREAPFA*GINTOT*GMW*1000.0/GDENS/GVEL
          NG = FKG*AREA*P/GINTOT
        ELSE
```

```
          GVEL = 0.107*F*DSQRT((1000.0*DENSAM(TLIN) - GDENS)/GDENS)
          FVA = GVEL*DSQRT(GDENS)
          FKGA = DSQRT(DG)*(1030.0*F - 867.0*F**2)/DSQRT(HL)
          FKLA = (0.40*FVA + 0.17)*197.0*DSQRT(DL)
C
C   NOW THE MASS TRANSFER COEFFICIENTS NEED TO BE PUT INTO DIFFERENT
C   UNITS TO BE CONSISTENT WITH THE OTHER VALUES IN FUNCTION FACE.
C   FKG NEEDS TO BE IN UNITS (MOLE/DM^2/S/ATM) AND FKL IN UNITS OF
C   (DM/S).  THEREFORE:
C
          AREAVOL = 0.75794 + 311.55*FVA - 94.321*FVA**2 + 9.8741*FVA**3
          FKG = FKGA/AREAVOL*10.0/0.08205/TGIN
          FKL = FKLA/AREAVOL*10.0
C
C   CALULATE THE ACTUAL AREA (DM^2) AVAILABLE.  THIS IS FOUND BY
C   MULTIPLYING THE AREA PER VOLUME (AREAVOL) TIMES THE LIQUID VOLUME
C   ON EACH TRAY.
C
          AREA = AREAVOL*HFROTH*GINTOT*0.08205*TGIN/P/1000.0/GVEL
          PHI = HL/HFROTH
          TV = (1 - PHI)*HL/100.0/PHI/GVEL
          NG = FKGA*TV
        ENDIF
C
        RETURN
        END
C
C END OF SUBROUTINE COEFF
C
C ******************************************************************
C
        FUNCTION DENSW (TEMP)
C
C   THE DENSITY OF WATER IS CALCULATED IN KG/L FROM AN EXPRESSION
C   FROM THE CRC HANDBOOK OF CHEMISTRY AND PHYSICS (P. F-6).  THE
C   TEMPERATURE IS INPUT IN !K AND CONVERTED TO !C.
C
        IMPLICIT REAL*8 (A-H,O-Z)
        T=TEMP-273.
        DENSW=(999.83952+16.945176*T-7.9870401D-3*T**2-46.170461D-6*
     & T**3+105.56302D-9*T**4-280.54253D-12*T**5)/(1.+16.87985D-3*
     & T)/1000.
C
        RETURN
        END
C
C END OF FUNCTION DENSW
C
C ******************************************************************
C
        FUNCTION DENSAM (TEMP)
C
```

```
C   THIS FUNCTION CALCULATES THE DENSITY FOR 50 WT% MDEA SOLUTIONS AS
C   A FUNCTION OF TEMPERATURE AND CO2 LOADING.  THE EQUATION WAS
C   DEVELOPED FROM THE DATA OF TOMAN (1989).
C
C   VARIABLES:
C       DENSAM -    50 WT% MDEA SOLUTION DENSITY (KG/L)
C       CO2WTP -    WT% CO2 IN SOLUTION
C       T -         TEMPERATURE IN CELCIUS
C
        IMPLICIT REAL*8 (A-H,O-Z)
        COMMON /CONT/ TAM,TH2S,TCO2,TION
C
        T = TEMP - 273.0
        CO2WTP = 100.0*44.0*TCO2/
     &        (44.0*TCO2 + 34.0*TH2S + 119.0*TAM + 1000.0)
C
        DENSAM = 1.0580 - 6.2606D-4*T + 0.009998*CO2WTP
C
        RETURN
        END
```

Appendix B

MDEA Base Case Input File and Tabulated Model Results

MDEA Base Case Input File

Absorber:

Line 1 - number of absorber stages, number of absorber temperature iterations, print flag (0 = print every stage convergence, 1 = print every temperature profile convergence, 2 = print only after system convergence, 3 = same as 2 but also print the M^{c}Cabe-Thiele information), absorber reboiler flag (0 = no reboiler, 1 = bottom stage is reboiler)

20, 30, 3, 0

Line 2 - tray type flag (1 = bubble cap, 2 = sieve), fractional approach to vapor flood velocity, liquid depth on each tray (cm), froth height on each tray (cm)

1, 0.7, 7.82, 17.0

Line 3 - absorber feed gas component flow rates (mole/s): H_2S, CO_2, H_2O, N_2

0.1, 1.0, 0.6, 8.3

Line 4 - amine solution flow rates (mole/s): H_2O, MDEA, acid anion

13.8889, 2.1008, 0.0

Line 5 - guesses for rich solution loadings out of the absorber (mole/s): $(H_2S)_1$, $(H_2S)_2$, $(CO_2)_1$, $(CO_2)_2$

0.108, 0.1075, 0.068, 0.0685

Line 6 - absorber bottom pressure (atm), pressure drop per stage (atm)
1.1, 0.007

Line 7 - absorber feed gas temperature (K), absorber inlet liquid temperature (K), estimate of absorber outlet liquid temperature (K)
313.0, 313.0, 314.5

Line 8 - absorber heats of reaction (cal/mole): H_2S dissociation, CO_2 dissociation, MDEA protonation, and H_2O vaporization
2089, 6364, 10325, 7889

<u>Stripper</u>:

Line 9 - number of stripper stages, number of stripper temperature iterations, print flag (see Line 1), stripper reboiler flag (see Line 1)
25, 15, 3, 1

Line 10 - tray type flag (see Line 2), fractional approach to vapor flood velocity, liquid depth on each tray (cm), froth height on each tray (cm), number of mass transfer units in the reboiler
1, 0.7, 7.82, 15.0, 2.0

Line 11 - stripper feed gas component flow rates (mole/s): H_2S, CO_2, H_2O, N_2
0.0, 0.0, 5.5, 0.0

Line 12 - stripper bottom pressure (atm), pressure drop per stage (atm)
2.0, 0.007

Line 13 - stripper feed gas temperature (K), stripper inlet liquid temperature (K), estimate of stripper outlet liquid temperature (K)
400.0, 385.0, 0.0

Line 14 - stripper heats of reaction (cal/mole): H_2S dissociation, CO_2 dissociation, MDEA protonation, and H_2O vaporization
2089, 6364, 9461, 7889

General:

Line 15 - max number of system iterations, H_2S damping factor, CO_2 damping factor, system flag (0=absorber, 1=stripper, 2=both columns)
3, 0.01, 0.01, 2

Line 16 - column outlet liquid component flow rates if only the absorber or stripper is modeled (mole/s): H_2S, CO_2, H_2O, MDEA, anion
0.0, 0.0, 0.0, 0.0, 0.0

Note: The damping factors are used to control the size of the change in the H_2S and CO_2 rich loadings generated by the secant method. In many cases, the numerical method calculates large changes in the rich loading values; therefore, if this change is too large, the damping factors limit the change to a smaller value. The use of damping factors is especially helpful under tightly pinched conditions in either column. If the system does not converge in the maximum number of iterations, the user can continue the calculations by interactively resetting the number of iterations, the rich loading guesses, and the damping factors.

Tabulated Results

The tabulated modeling results are listed on the following pages. All of these results are for 50 wt% MDEA using the model developed in Chapter 3. Component flow rates for these results can be found in the blue lab data book labeled "Data Book #2". The run numbers listed in the following tables correspond to run numbers found in the lab book.

Vary the Liquid Rate and Steam Rate

(Run #109, 119, 120)

Steam Rate (mole/s)	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
4.5	0.022	0.014185191	135.1
	0.021	0.013540409	134
	0.02	0.012895628	136
	0.023	0.014829972	136.1
	0.025	0.016119535	138.9
	0.03	0.019343442	150.9
	0.035	0.022567349	184.2
5.5 (base case)	0.025	0.016119535	98.8
	0.024	0.015474753	98.5
	0.023	0.014829972	98.9
	0.022	0.014185191	98.2
	0.021	0.013540409	97.8
	0.02	0.012895628	99.3
	0.027	0.017409098	100.1
	0.03	0.019343442	103.7
	0.035	0.022567349	124.7
	0.04	0.025791256	156.1
6.5	0.022	0.014185191	77.8
	0.023	0.014829972	77.3
	0.025	0.016119535	77.1
	0.027	0.017409098	77.1
	0.03	0.019343442	78.4
	0.035	0.022567349	92.9
	0.04	0.025791256	115
	0.021	0.013540409	77.5
	0.02	0.012895628	78.9

Effect of Acid Addition on System Performance

(Run #109-118)

Acid Rate (mole/s)	Acid Rate (equiv/L)	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
0	0	0.025	0.016119535	98.8
	0	0.024	0.015474753	98.5
	0	0.023	0.014829972	98.9
	0	0.022	0.014185191	98.2
	0	0.021	0.013540409	98.7
	0	0.02	0.012895628	99.3
	0	0.027	0.017409098	100.1
	0	0.03	0.019343442	103.7
	0	0.035	0.022567349	124.7
	0	0.04	0.025791256	156.1
0.01	0.0414	0.025	0.016119535	81.5
	0.043125	0.024	0.015474753	79.1
	0.045	0.023	0.014829972	76.4
	0.047045455	0.022	0.014185191	73.4
	0.049285714	0.021	0.013540409	71
	0.039807692	0.026	0.016764316	83.5
0.03	0.119423077	0.026	0.016764316	47.5
	0.1242	0.025	0.016119535	42.4
	0.129375	0.024	0.015474753	37.2
	0.135	0.023	0.014829972	32.2
	0.141136364	0.022	0.014185191	28.3
	0.147857143	0.021	0.013540409	28.5

Acid Rate (mole/s)	Acid Rate (equiv/L)	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
0.05	0.235227273	0.022	0.014185191	23.6
	0.225	0.023	0.014829972	13.4
	0.215625	0.024	0.015474753	12.5
	0.207	0.025	0.016119535	14.9
0.07	0.278653846	0.026	0.016764316	7.3
	0.268333333	0.027	0.017409098	8.7
	0.2898	0.025	0.016119535	8.4
0.1	0.345	0.03	0.019343442	5.7
0.15	0.443571429	0.035	0.022567349	5.7
	0.437323944	0.0355	0.02288974	6.5
0.2	0.5175	0.04	0.025791256	8.1
	0.504878049	0.041	0.026436037	10.4
	0.530769231	0.039	0.025146474	6.3
0.25	0.575	0.045	0.029015163	12.6
	0.601744186	0.043	0.0277256	8.2
0	0	0.022	0.014185191	98.2
0.01	0.047045455	0.022	0.014185191	74.2
0.03	0.141136364	0.022	0.014185191	28.8
0.05	0.235227273	0.022	0.014185191	24.9
0.051	0.239931818	0.022	0.014185191	26.4
0.052	0.244636364	0.022	0.014185191	28.3

Effect of Stripper Pressure Reduction on System Performance with 10% CO_2 Feed Gas

(Run #109,121-123)

Pressure (atm)	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
2	0.025	0.016119535	98.8
	0.024	0.015474753	98.5
	0.023	0.014829972	98.9
	0.022	0.014185191	98.2
	0.021	0.013540409	98.7
	0.02	0.012895628	99.3
	0.027	0.017409098	100.1
	0.03	0.019343442	103.7
	0.035	0.022567349	124.7
	0.04	0.025791256	156.1
1.5	0.022	0.014185191	64.6
	0.023	0.014829972	65.8
	0.021	0.013540409	62.6
1	0.022	0.014185191	24.4
	0.021	0.013540409	22.3
	0.02	0.012895628	22.1
0.5	0.022	0.014185191	3.8

Effect of Stripper Pressure Reduction on System Performance with 2.5% CO_2 Feed Gas

(Run #124-126)

Pressure (atm)	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
2	0.022	0.014185191	68.1
	0.021	0.013540409	65.8
	0.019	0.012250846	61.8
1	0.022	0.014185191	53
	0.02	0.012895628	47.4
0.5	0.022	0.014185191	25.3

Change the Number of Stages to 14 Absorber and 18 Stripper Stages

(Run #128)

Steam Rate (mole/s)	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
5.5	0.022	0.014185191	133.9
	0.023	0.014829972	132
	0.024	0.015474753	131.4
	0.025	0.016119535	131.4
	0.026	0.016764316	132.7
	0.028	0.018053879	135.6
	0.03	0.019343442	140.6
	0.035	0.022567349	163.9
	0.02	0.012895628	155.6
	0.021	0.013540409	139.2

Effect of Stripper Stages on System Performance for a 2 atm Stripper and 14 Stage Absorber

(Run #128-137)

Stripper Stages	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
10	0.022	0.014185191	227.1
	0.023	0.014829972	223.6
14	0.022	0.014185191	159.7
	0.023	0.014829972	157.8
15	0.024	0.015474753	149.4
	0.025	0.016119535	149.6
	0.023	0.014829972	149.2
16	0.025	0.016119535	142.3
	0.026	0.016764316	143.4
	0.024	0.015474753	142.5
17	0.022	0.014185191	138.5
	0.023	0.014829972	136.7
	0.024	0.015474753	136.2
18	0.022	0.014185191	133.9
19	0.024	0.015474753	127.3
	0.025	0.016119535	127.9

Stripper Stages	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
20	0.023	0.014829972	124.9
	0.022	0.014185191	126.5
	0.024	0.015474753	124
	0.025	0.016119535	123.7
21	0.025	0.016119535	120.9
	0.026	0.016764316	121.7
	0.024	0.015474753	121.1
22	0.024	0.015474753	118.4
	0.025	0.016119535	117.9
23	0.025	0.016119535	115.8

Change the MDEA Equilibrium Constant Using 14 Absorber and 18 Stripper Stages

(Run #138-141)

$$\text{Ratio of EKAM} = \frac{\text{New EKAM}}{\text{Base Case EKAM}}$$

Ratio of EKAM	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)	H2S Selectivity	CO2 % Slip
1	0.025	0.0161195	131.4	1.91	94.8
2	0.022	0.0141851	145.6	2.09	95.3
	0.023	0.0148299	142.5	2.02	95.1
	0.024	0.0154747	141.5	1.96	95
	0.025	0.0161195	140.9	1.91	94.9
	0.027	0.0174090	141.9	1.85	94.7
	0.026	0.0167643	140.9	1.88	94.8
3	0.026	0.0167643	145.8	1.87	94.7
	0.028	0.0180538	147.8	1.82	94.6
	0.025	0.0161195	145.8	1.91	94.8
0.5	0.025	0.0161195	124	1.91	94.8
	0.026	0.0167643	124.8	1.9	94.8
	0.024	0.0154747	123	1.97	95
	0.022	0.0141851	124.5	2.11	95.3
0.3	0.023	0.0148299	118.5	2.04	95.2
	0.024	0.0154747	118.7	1.98	95
	0.025	0.0161195	119.3		

Change the Liquid Phase Mass Transfer Coefficient Using 14 Absorber and 18 Stripper Stages

(Run #145-152)

$$\text{Ratio of } k_l = \frac{\text{New } k_l}{\text{Base Case } k_l}$$

Ratio of k_l	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)	H2S Selectivity	CO2 % Slip
1	0.025	0.0161195	131.4	1.91	94.8
2	0.025	0.0161195	110	1.26	92.2
	0.026	0.0167643	109.9	1.23	92
2.25	0.026	0.0167643	108.7	1.14	91.3
	0.028	0.0180539	109.3	1.1	91
1.5	0.025	0.0161195	115.7	1.54	93.6
	0.026	0.0167643	116.1	1.51	93.4
1.25	0.026	0.0167643	122	1.67	94.1
	0.025	0.0161195	121.5	1.71	94.2
0.75	0.025	0.0161195	152.9	2.24	95.6
	0.024	0.0154748	152.9	2.27	95.7
0.5	0.024	0.0154748	216.8	2.67	96.3
	0.025	0.0161195	215.4	2.61	96.3
0.25	0.025	0.0161195	721.6	2.99	96.9
	0.026	0.0167643	688.9	2.96	96.9
	0.034	0.0219226	609.2	2.79	96.6

Change the Gas Phase Mass Transfer Coefficient Using 14 Absorber and 18 Stripper Stages

(Run #153-160)

$$\text{Ratio of } k_g = \frac{\text{New } k_g}{\text{Base Case } k_g}$$

Ratio of kg	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)	H2S Selectivity	CO2 % Slip
1	0.025	0.0161195	131.4	1.91	94.8
1.1	0.025	0.0161195	128.4	1.91	94.8
	0.026	0.0167643	129.7	1.89	94.8
1.25	0.024	0.0154747	124.5	1.95	94.9
	0.025	0.0161195	125.6	1.92	94.9
0.9	0.025	0.0161195	135.5	1.92	94.9
	0.026	0.0167643	136.3	1.89	94.8
0.8	0.025	0.0161195	141.1	1.93	94.9
	0.024	0.0154747	141.4	1.98	95
0.7	0.024	0.0154747	150.9	1.99	95
	0.025	0.0161195	148.7	1.94	94.9
	0.026	0.0167643	148.3	1.9	94.8
0.6	0.025	0.0161195	160.8	1.94	94.9
0.5	0.025	0.0161195	182.9	1.95	95
	0.026	0.0167643	179.1	1.91	94.9
	0.028	0.0180538	175.7	1.85	94.7
0.25	0.03	0.0193434	372.4	1.85	94.8
	0.031	0.0199882	365.5	1.84	94.8
	0.035	0.0225673	359.5	1.81	94.7

Change the CO_2-MDEA Rate Constant Using
14 Absorber and 18 Stripper Stages
(Run #161-166)

$$\text{Ratio of } k_{MDEA} = \frac{\text{New rate constant}}{\text{Base case rate constant}}$$

Ratio of k_{MDEA}	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)	H2S Selectivity	CO2 % Slip
1	0.025	0.0161195	131.4	1.91	94.8
1.25	0.025	0.0161195	136.8	1.86	94.7
	0.026	0.0167643	137.7	1.84	94.6
1.5	0.025	0.0161195	141.6	1.82	94.6
	0.026	0.0167643	141.8	1.79	94.5
1.75	0.026	0.0167643	145.9	1.74	94.3
	0.025	0.0161195	145.9	1.77	94.4
2	0.026	0.0167643	149.7	1.7	94.2
	0.027	0.0174091	149.6	1.68	94.1
0.75	0.025	0.0161195	125.4	1.97	95
	0.026	0.0167643	127.1	1.95	94.9
	0.024	0.0154748	125.7	2.02	95.1
0.5	0.024	0.0154748	117.7	2.09	95.3
	0.025	0.0161195	119	2.06	95.2
	0.023	0.01483	117	2.16	95.4
	0.022	0.0141852	117.8	2.25	95.6
0.25	0.022	0.0141852	106.1	2.32	95.7

Effect of Stripper Stages on System Performance with a 1 atm Stripper and 20 Absorber Stages

(Run #168-174)

Number of Stripper Stages	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
25	0.021	0.013540409	22.3
24	0.02	0.012895628	23
	0.021	0.013540409	22.9
23	0.022	0.014185191	25.9
	0.02	0.012895628	23.9
	0.021	0.013540409	23.7
22	0.02	0.012895628	24.7
	0.021	0.013540409	24.6
21	0.021	0.013540409	25.7
	0.02	0.012895628	26
20	0.021	0.013540409	26.6
	0.022	0.014185191	28.3
19	0.021	0.013540409	27.7

Effect of Stripper Stages on System Performance with a 1 atm Stripper and 14 Absorber Stages

(Run #175-178)

Number of Stripper Stages	H2O Rate (kg/mole feed gas)	Liquid Rate (gal/SCF)	H2S Leak (ppm)
18	0.025	0.016119535	52.4
	0.026	0.016764316	55.3
	0.023	0.014829972	50
	0.022	0.014185191	49.5
	0.021	0.013540409	52.8
17	0.022	0.014185191	51.7
	0.023	0.014829972	51.3
16	0.023	0.014829972	53.8
	0.022	0.014185191	54.6
15	0.023	0.014829972	56.9
	0.024	0.015474753	57.9

Effect of Varying the H_2S Equilibrium Constant in Both Columns

(Run #179-182)

Ratio of EKH2S	H2O Rate (kg/mole feed gas)	H2S Leak (ppm)	H2S Selectivity	CO2 % Slip
1	0.025	131.4	1.91	94.8
2.45	0.025	238.1	1.86	94.7
	0.026	246.3	1.84	94.7
	0.024	231.5	1.87	94.8
	0.023	224.4	1.91	94.9
	0.021	212.53	1.95	95
	0.018	194.13	2.05	95.2
	0.016	182.5	2.14	95.4
1.7	0.025	183.8	1.87	94.8
	0.024	179.2	1.89	94.8
	0.023	175.2	1.92	94.9
	0.021	168.4	1.98	95
	0.019	160.9	2.06	95.2
	0.017	154.6	2.2	95.5
	0.015	155	2.41	95.9
0.7	0.025	154	2.08	95.3
	0.023	281.2	2.19	95.6
	0.027	121	1.98	95
	0.029	112.8	1.88	94.7
	0.031	111.5	1.8	94.5
	0.032	113.7	1.8	94.5
0.4	0.032	303.5	1.96	95.1
	0.035	119.9	1.88	94.7
	0.037	93.9	1.82	94.6
	0.04	95.4	1.79	94.5
	0.038	92.2	1.8	94.5

Effect of Changing the H_2S Heat of Reaction

(Run #183-187)

EKH2S ratio in the stripper	H2S heat of reaction	H2O Rate (kg/mole feed gas)	H2S Leak (ppm)	H2S Selectivity	CO2 % Slip
1	2089	0.025	131.4	1.91	94.8
0.93	2290	0.025	116.3	1.92	94.8
		0.026	116.8	1.89	94.8
		0.024	115.8	1.97	95
0.87	2500	0.023	102	2.02	95.1
		0.025	100.9	1.91	94.8
		0.026	102	1.89	94.8
0.8	2700	0.024	89.1	1.96	95
		0.025	88.5	1.91	94.8
		0.026	89.6	1.89	94.8
1.07	1900	0.026	149.3	1.89	94.8
		0.025	148	1.92	94.9
		0.024	147.5	1.96	95
1.15	1700	0.024	166.6	1.97	95
		0.025	167.2	1.92	94.9
		0.023	167	2.03	95.1

Appendix C

Subroutines and Files for ASPEN PLUS™

A description of the ASPEN PLUS™ files found in account CHHQ322, an example input file for using RADFRAC, and the kinetic subroutine are listed below. All of the ASPEN PLUS™ files are located in account CHHQ322 in the subdirectory CAREY. The input files use inserts stored in the user library PROPS.ILB to obtain the physical properties needed. Information about inserts and user libraries is found in the ASPEN PLUS™ *System Maintenance Guide.*

File descriptions:

AREA.FOR -	Contains the user subroutine used to calculate the interfacial area for heat and mass transfer.
COEFF.FOR -	Contains the user subroutine used to calculate the mass transfer coefficients for both the liquid and the gas.
DEA.INP -	This file is the working file for the CO_2-H_2S-DEA system. This file is constantly edited to perform different ASPEN PLUS runs for this system.
DEAMDEA.INP -	This file is the working file for the CO_2-H_2S-DEA-MDEA system. This file is constantly edited to perform different ASPEN PLUS runs for this system. This file is the iput file shown below.
DEAMIX.INS -	File was used as the source file to create the user insert "DEAMIX". This insert contains all of the necessary data to make a DEA-MDEA run including the NRTL parameters.
DEAPR.INS -	File was used as the source file to create the user insert "DEAPR". This insert contains all of the necessary data to make a DEA run including the NRTL parameters.
DGAMDEA.INP -	Same as DEAMDEA.INP but for DGA.
DGAMIX.INS -	Same as DEAMIX.INS but for DGA.
DGAPR.INS -	Same as DEAPR.INS but for DGA.

FLASH.INP - This file contains the input language needed to perform a two phase flash calculation. This file can be appended to any of the system files (e.g. DEAMDEA.INP) to perform flashes.

KINETICS.FOR - Contains the user subroutine used to perform the rate calculations for the formation of bicarbonate and carbamate. This can be used with RADFRAC or RATEFRAC.

MDEA.INP - This file is the working file for the CO_2-H_2S-MDEA system. This file is constantly edited to perform different ASPEN PLUS runs for this system.

MDEACO2.INP - This file is used to perform a bubble point calculation for CO_2 and MDEA. This file was used to predict the VLE for this system and compare the predictions to experimental data.

MDEAH2S.INP - This file is the same as MDEACO2.INP but for H_2S.

MDEAPR.INS - Same as DEAPR.INS but for MDEA.

MEA.INP - This file is the working file for the CO_2-H_2S-MEA system. This file is constantly edited to perform different ASPEN PLUS runs for this system.

MEAMDEA.INP - This file is the working file for the CO_2-H_2S-MEA-MDEA system. This file is constantly edited to perform different ASPEN PLUS runs for this system.

MEAMIX.INS - Same as DEAMIX.INS but for MEA-MDEA.

MEAPR.INS - Same as DEAPR.IND but for MEA.

NRTL.INS - This file contains all of the NRTL parameters for MEA, DEA, MDEA, DGA, and mixed amine combinations. This can be used as a source file to create a library.

PROPS.INS - This file contains all of the needed properties not in the data banks including Henry's constant for CO2 and H2S, properties for MDEA, DEA, and DGA, properties for all protonated amines and carbamates, and the Rackett parameters.

PROPS.ILB - This file is the user library containing all of the inserts listed above. This library is referred to in every ASPEN run in order to obtain the needed properties.

RTFRAC.INP - This file contains the input blocks needed to use RATEFRAC. This file can be appended to any of the system files above in order to run this model.

Sample input file for the DEA, MDEA, or DEA-MDEA system:

```
;
TITLE      'MDEA-DEA SYSTEM'
DESCRIPTION 'THIS FILE IS USED TO MODEL THE MDEA OR DEA SYSTEMS
         INDEPENDENTLY OR AS A MIXED AMINE SYSTEM DEA-MDEA.'
;
;      LIMIT THE EXECUTION TIME AND DEFINE ANY REPORT OPTIONS
;
HISTORY
 MSG-LEVEL SIM-LEVEL=6 SYS-LEVEL=6 CONV-LEVEL=8
SYS-OPTIONS TRACE=YES
RUN-CONTROL MAX-TIME=1000
;
;       SPECIFY THE UNITS
;
IN-UNITS  SI TEMPERATURE=C PRESSURE=ATM
OUT-UNITS SI TEMPERATURE=C PRESSURE=ATM
;
;       ENTER THE NEEDED COMPONENTS.  THE COMPONENTS SHOULD
;       ALWAYS BE ENTERED IN THE ORDER SHOWN.  ADDITIONAL MOLECULAR
;       COMPONENTS SHOULD BE ENTERED AFTER THE LAST STANDARD
;       MOLECULAR COMPONENT (CARB).  FOR EXAMPLE N2.  ADDITIONAL
;       CATIONS SHOULD BE ENTERED AFTER THE LAST STANDARD CATION
;       AND THE SAME FOR ANIONS.
;
COMPONENTS    H2O  H2O / MDEA / DEA / CO2  CO2 / H2S  H2S / H2CO3 H2CO3 /
              CARB  NH2COO- / N2  N2 / H3O+  H3O+/ MDEAH+ / DEAH+ /
              OH-  OH- / R2NCOO- NH2COO- / HCO3-  HCO3- / HS-  HS- /
              CO3--  CO3-2 / S--  S-2
HENRY-COMPS   LIST1  CO2  H2S
;
;       SPECIFY THE APPROPRIATE DATABANKS AND PROPERTY SET.  ALSO
;       INCLUDE THE APPROPRIATE INSERT.
;
DATABANKS    AQUEOUS
PROPERTIES   SYSOP15M     HENRY-COMPS=LIST1  CHEMISTRY=MDEADEA  &
          TRUE-COMPS=NO
INSERT * DEAMIX
;
;       ENTER THE NECESSARY PROPERTIES FOR THE COMPONENTS H2CO3
;       AND RR'R"NCOOH.  THE PROPERTIES FOR RR'R"NCOOH HAVE BEEN SET
;       EQUAL TO THOSE OF THE ION CARBAMATE; THEREFORE, ONLY THE
;       MW AND IONIC CHARGE NEED TO BE CHANGED.  STANDARD PROPERTY
;       VALUES FOR IONIC SPECIES ARE USED FOR H2CO3.
```

```
;
PROP-DATA
 PROP-LIST        MW / CHARGE
   PVAL  CARB  149.15 / 0.0
 PROP-LIST  CPIG
   PVAL  H2CO3  2.08E4 0.0 0.0 0.0 0.0 0.0 0.0 2000 3.3256E4 21.29 1.5
 PROP-LIST  PLXANT
   PVAL  H2CO3  -1E35 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2000
;
;      SPECIFY THE REACTIONS OCCURING FOR THE DEA-MDEA SYSTEM
;
CHEMISTRY  MDEADEA
   PARAM  MOLAL=0
;
   STOIC      1    MDEAH+  -1 / H2O  -1 / MDEA  1 / H3O+  1
   K-STOIC     1     -9.4165      -4234.98   0.0       0.0
;
   STOIC      2    HCO3-   -1 / H2O  -1 / CO3-- 1 / H3O+  1
   K-STOIC     2     216.049      -12431.70  -35.4819  0.0
;
   STOIC      3    H2S    -1 / H2O  -1 / HS-   1 / H3O+  1
   K-STOIC     3     214.582      -12995.4   -33.5471  0.0
;
   STOIC      4    H2O     -2 / OH-   1 / H3O+  1
   K-STOIC     4     132.899     -13445.9   -22.4773   0.0
;
   STOIC      5    DEAH+   -1 / H2O  -1 / DEA   1 / H3O+  1
   K-STOIC     5     -6.7936      -5927.65   0.0       0.0
;
   DISS     H2CO3   H2O  -1 / HCO3- 1 / H3O+ 1
;
   DISS     CARB    H2O  -1 / R2NCOO- 1 / H3O+ 1
;
;  STOIC      2    CO2     -1 / H2O  -2 / HCO3- 1 / H3O+  1
;  K-STOIC     2     231.465      -12092.10  -36.7816  0.0
;
;  STOIC      7    R2NCOO- -1 / H2O  -1 / DEA 1 / HCO3- 1
;  K-STOIC     7     4.5146       -3417.34   0.0       0.0
;
STREAM  AFG     TEMP=40      PRES=1.0
   MOLE-FLOW    H2O  0.6  / CO2  1.0  / H2S  0.1 / N2  8.3 /
                MDEA 0.0 / DEA 0.0 / H2CO3 0.0 / CARB 0.0
STREAM  ALF     TEMP=40      PRES=1.0
   MOLE-FLOW    H2O  15.0  /  MDEA   2.2689 /  CO2  0.0  / N2 0.0 /
                H2S  0.0    / DEA  0.0 / H2CO3 0.0 / CARB 0.0
;
;      DEFINE THE FLOWSHEET CONNECTIVITY
;
FLOWSHEET
   BLOCK  ABS   IN=AFG ALF  OUT=AGP ALP
;
;      DEFINE THE RATE-CONTROLLED REACTIONS FOR THE COLUMN RADFRAC
```

```
;
REACTIONS AMINE
    PARAM  SUBROUTINE=KINET  NINT=20 NREAL=20 KBASIS=MOLEFRAC
    REAC-DATA 1 KINETIC / 2 KINETIC / 3 EQUIL / 4 EQUIL / 5 EQUIL /
        6 EQUIL / 7 EQUIL
    STOIC  1  CO2  -1 / H2O  -1 / H2CO3 1
    STOIC  2  CO2  -1 / DEA  -1 / CARB  1
;
    STOIC      3    MDEAH+  -1 / H2O  -1 / MDEA  1 / H3O+  1
    K-STOIC    3     -9.4165      -4234.98   0.0       0.0
;
    STOIC      4    HCO3-   -1 / H2O  -1 / CO3-- 1 / H3O+  1
    K-STOIC    4     216.049      -12431.70  -35.4819  0.0
;
    STOIC      5    H2S     -1 / H2O  -1 / HS-   1 / H3O+  1
    K-STOIC    5     214.582      -12995.4   -33.5471  0.0
;
    STOIC      6    H2O     -2 / OH-   1 / H3O+  1
    K-STOIC    6     132.899      -13445.9   -22.4773   0.0
;
    STOIC      7    DEAH+   -1 / H2O  -1 / DEA   1 / H3O+  1
    K-STOIC    7     -6.7936      -5927.65   0.0       0.0
;
    DISS     H2CO3   H2O  -1 / HCO3- 1 / H3O+ 1
;
    DISS     CARB    H2O  -1 / R2NCOO- 1 / H3O+ 1
;
;       THE INT AND REAL VARIBALES ARE USED TO PASS VALUES TO THE
;       KINETIC SUBROUTINE.  INT PASSES THE SYSTEM FLAG, THE NUMBER
;       OF MOLECULAR COMPONENTS PRESENT, THE NUMBER OF CATIONS
;       PRESENT, THE CHARGES OF EACH OF THE CATIONS, THE NUMBER OF
;       ANIONS, THE CHARGE OF EACH ANION.  REAL PASSES THE VARIOUS
;       KINETIC CONSTANTS.  SEE THE KINETIC SUBROUTINE TO KNOW WHICH
;       ORDER THESE CONSTANTS ARE INPUT.
;
    INT   4 8 3 1 1 1 5 -1 -1 -1 -1 -2
    REAL  2668.2  3710  0.0  0.0  2.617D10  8107  17.122  -2895  0.0  &
      14.477  -2152  0.0  3.144D9  9314  5.625D8  -105  5.098D6  11000
;
;      INPUT THE ABSORBER BLOCK
;
BLOCK  ABS  RADFRAC
    PARAM     NSTAGE=3  ALGORITHM=NONIDEAL EFF=MURPHREE
    FEEDS    AFG  4  ABOVE-STAGE / ALF  1  ABOVE-STAGE
    PRODUCTS  AGP  1   V / ALP  3  L
    P-SPEC    3  1.1
    COL-SPECS MOLE-RDV=1  Q1=0 QN=0 DP-STAGE=0.007
    REAC-STAGES 1 3 AMINE
    RES-TIME  1 3 LTIME=1  VTIME=1.5
    T-EST     1 32 / 2 25 / 3 19
;   COMP-EFF  1 CO2 0.01 / 2 CO2 0.01 / 3 CO2 0.01
;         1 H2S 0.61 / 2 H2S 0.61 / 3 H2S 0.61
```

```
;    X-EST     1 CO2 0.005 / 1 H2S 0.0063 / 1 H2O 0.86 /
;              2 CO2 0.0052  / 2 H2S 0.007  / 2 H2O 0.8 /
;              3 CO2 0.0053   / 3 H2S 0.015 / 3 H2O 0.78
;    Y-EST     1 CO2 0.02  / 1 H2S 0.001 / 1 H2O 0.067 / 1 N2 0.9 /
;              2 CO2 0.05  / 2 H2S 0.005  / 2 H2O 0.064 / 2 N2 0.87 /
;              3 CO2 0.1     / 3 H2S 0.009  / 3 H2O 0.062 / 3 N2 0.82
     L-EST     1 13.8 / 2 14.0 / 3 14.2
     V-EST     1 10.2 / 2 10.1 / 3 10.0
```

The kinetic subroutine and flash subroutine:

```
C
C        THIS SUBROUTINE IS THE USER SUBROUTINE USED TO
C        CALCULATE THE REACTION RATES.  THE CALL SEQUENCE
C        IS FOUND IN THE NOTES AND INTERFACES MANUAL.  THIS
C        ROUTINE USES ASPEN'S FLASH ROUTINE TO CALCULATE THE
C        ACTIVITY COEFFICIENTS AND A USER FLASH TO SPECIATE
C        THE LIQUID PHASE.  THIS WAS DONE BECAUSE ASPEN'S
C        FLASH WAS RETURNING FLOW RATES OF ZERO FOR ALL SPECIES.
C
      SUBROUTINE KINET ( N     , NC    , NR    , NRL    , NRV    , T     ,
     1                   TLIQ  , TVAP  , P     , VF     , F      , X     ,
     2                   Y     , IDX   , NBOPST, KDIAG  , STOIC  , IHLBAS,
     3                   HLDLIQ, TIMLIQ, IHVBAS, HLDVAP, TIMVAP, NINT  ,
     4                   INT   , NREAL , REAL  , RATES )
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 MDEA, MDEAH, MEA, MEAH
C
C       INSERT THE DIMENSIONS FOR THE KINET CALL.  THESE
C       DIMENSIONS ARE FOUND IN THE NOTES AND INTERFACES MANUAL.
C
      DIMENSION  X(NC), Y(NC), IDX(NC), NBOPST(6), STOIC(NC,NR),
     1      INT(NINT), REAL(NREAL), RATES(NC)
C
C       INSERT THE DIMENSIONS FOR ASPEN'S FLASH.  WHEN USING THE
C       ASPEN FLASH THE COMMON BLOCKS STWKWK AND STWORK MUST
C       BE INCLUDED.  DIMENSION VALUES ARE IN THE NOTES AND
C       INTERFACES MANUAL.
C
      DIMENSION  SVEC(30), IDXSUB(1), ITYPE(1), RETN(1), IRETN(1),
     1      INDEX(1), SUBSTR(1), XX(100)
      EQUIVALENCE (INDEX(1), RESLTS(1))
C
C       INSERT THE DIMENSIONS FOR THE USER VARIABLES.  THE VALUE
C       OF 20 WAS ARBITRARILY CHOSEN.  IF OTHER MOLECULES OR
C       IONS ARE USED, THIS MIGHT NEED TO BE INCREASED.
C
      DIMENSION  CONC(20), ICHARG(20), ACT(20), FLOW(20)
```

```
C
C     THE COMMON BLOCK GAMMA IS ASPEN'S AND RETURNS THE NATURAL
C     LOG OF THE ACTIVITY COEFFICIENTS.  THE OTHER COMMON BLOCKS
C      ARE USER BLOCKS OR ARE FOR ASPEN'S FLASH.
C
      COMMON /GAMMA/ GAMMA(1)
      COMMON /USREK/  EKW   , EKMDEA, EKDEA , EKMEA , EKDGA , EKCO2 ,
     1          EKH2S , EKCARB, EKHCO3
      COMMON /USRFLG/   ISYS  , IMOL  , ICAT  , IAN
      COMMON /USRFLO/ TOTFLO(20)
      COMMON /USRACT/ ACTCOF(20)
C
      COMMON /STWKWK/ NCPM  , NCPCS , NCPNC , NTRIAL, IDUM3(2),
     1          TCALC , PCALC , VCALC , QCALC , BETCAL  ,
     2          RDUM(21), RESLTS(1)
C
      COMMON /STWORK/ NRETN , NIRETN, NHXF  , NHYF  , NWYF  ,
     1          NSTW  , KK1   , KK2   , KZ1   , KZ2   ,
     2          KA1   , KA2   , KRET  , KRSC  , MF    ,
     3          MX    , MX1   , MX2   , MY    , MCS   ,
     4          MNC   , MHXF  , MHYF  , MWY   , MRETN ,
     5          MIM   , MIC   , MIN   , MPH   , MIRETN,
     6          NDUM  , NBLM  , NCOVAR, NWR   , NIWR  ,
     7          KEXT  , KLNK  , KFOUT , KFOUT1, KPHV  ,
     8          KPHL  , KLNGM , MF1   , MFST  , MSTOIL,
     9          MSTOIS, HV    , HL    , HL1   , HL2   ,
     1          SV    , SL    , SL1   , SL2   , VV    ,
     2          VL    , VL1   , VL2   , XMWV  , XMWL  ,
     3          XMWL1 , XMWL2 , HCS   , HNCS  , SSALT ,
     4          VSALT , MSTOI , MLNKL , MLNKS , MLNKIN,
     5          MZWK  , MST   , MIEXST, MIZWK , HSALT ,
     6          FSALT , RATIO
C
C     THESE TWO OUTPUT FILES ARE USED FOR DEBUGGING PURPOSES.
C
      OPEN (UNIT=52,FILE='KINET.OUT',STATUS='UNKNOWN')
      OPEN (UNIT=53,FILE='BULK.OUT',STATUS='UNKNOWN')
C
C        REASSIGN THE VARIABLE NAMES OF THE FLAGS.  THE SYSTEM
C        FLAG IS CALLED ISYS. THIS FLAG TAKES THE FOLLOWING
C         VALUES: 1 = DEA IS PRESENT, 2 = MEA IS PRESENT,
C        3 = DGA IS PRESENT, 4 = ONLY MDEA IS PRESENT BUT
C        ANOTHER AMINE'S FLOW RATE IS SET TO ZERO.
C        IMOL, ICAT, AND IAN REPRESENT THE NUMBER OF
C        MOLECULES, CATIONS AND ANIONS, RESPECTIVELY.
C        ICHARG REPRESENTS THE CHARGE OF CATIONS AND ANIONS.  THIS
C        CAN BE USED TO CALCULATE THE IONIC STRENGTH IF NEEDED.
C         THESE VALUES ARE PASSED FROM THE REACTIONS PARAGRAPH
C        IN THE INPUT FILE USING THE VARIABLE INT.
C
      WRITE (52,*) 'STAGE # ',N
      WRITE (52,*) 'TEMP = ',T
```

```
      ISYS = INT(1)
      IMOL = INT(2)
      ICAT = INT(3)
      DO 4 I = 1,IMOL
       ICHARG(I) = 0.0
 4    CONTINUE
      DO 5 I = IMOL+1,IMOL+ICAT
       ICHARG(I) = INT(3+I)
 5    CONTINUE
      IAN = INT(4+ICAT)
      DO 10 I = IMOL+ICAT+1,IMOL+ICAT+IAN
       ICHARG(I) = INT(4+ICAT+I)
 10   CONTINUE
C
C          CALCULATE THE MIXTURE MOLAR VOLUME WITH THE CALCULATION
C          CODE (KV) SET TO GIVE ONLY THE PROPERTY AND NOT THE
C          TEMPERTURE DERIVATIVE.
C
      TOTLIQ = (1-VF)*F
      IF (TOTLIQ .LE. 0.0) THEN
       TOTLIQ = 1.5*TLOLD
       TLOLD = TOTLIQ
      ELSE
       TLOLD = TOTLIQ
      ENDIF
      WRITE (52,*) 'TOTLIQ = ',TOTLIQ
      KV = 1
      CALL VOLL (T    , P     , X     , NC    , IDX      ,
     1          NBOPST, KDIAG , KV    , VMX   , DVMX     ,
     2          KER   )
      TOTVOL = VMX*TOTLIQ
C       WRITE (52,*) 'TOTVOL = ',TOTVOL
C        WRITE (52,*) 'GAMMA AFTER VOLL'
C        DO 708 I = 1,IMOL+ICAT+IAN
C          WRITE (52,*) 'GAMMA ',I,'= ',GAMMA(I)
C 708     CONTINUE
C
C          USE ASPEN'S FLASH ROUTINE TO OBTAIN THE ACTIVITY
C          COEFFICIENTS FOR ALL TRUE SPECIES.  THE TRUE SPECIES
C          FLOW RATES WERE NOT OBTAINABLE FOR SOME REASON.  IN
C          CONVERATIONS WITH ASPEN THE PROBLEM WAS NEVER RESOLVED.
C          THE FLASH ROUTINE WAS NOT RETURNING CORRECT VALUES
C          FOR SEVERAL VARIABLES. NBOPST(4) IS SET EQUAL TO 1 TO
C          OBTAIN THE TRUE SPECIES FLASH.  NBOPST(4) = 0 MUST
C          IMMEDIATELY FOLLOW THE FLASH TO RESET TO APPARENT APPROACH.
C
      DO 20 I = 1,IMOL
       SVEC(I) = X(I)*TOTLIQ
       TOTFLO(I) = X(I)*TOTLIQ
        WRITE (52,*) 'X ',I,' = ',X(I)
        WRITE (52,*) 'TOTFLO ',I,'= ',TOTFLO(I)
 20   CONTINUE
```

```
      DO 25 I = IMOL+1,IMOL+ICAT+IAN
        SVEC(I) = 0.0
       TOTFLO(I) = X(I)*TOTLIQ
 25   CONTINUE
      SVEC(IMOL+ICAT+IAN+1) = TOTLIQ
      SVEC(IMOL+ICAT+IAN+2) = T
      SVEC(IMOL+ICAT+IAN+3) = P
      NSUBS = 1
      IDXSUB(1) = 1
      ITYPE(1) = 1
      NBOPST(4) = 1
      KODE = 2
      NPKODE = 1
      KPHASE = 2
      MAXIT = 30
      TOL = 1D-4
      SPEC1 = T
      SPEC2 = P
      LMSG = KDIAG
      LPMSG = KDIAG
      JRES = 0
      KRESLT = 1
C       CALL FLASH (SVEC  , NSUBS , IDXSUB, ITYPE , NBOPST,
C     1             KODE  , NPKODE, KPHASE, MAXIT , TOL   ,
C     2              SPEC1 , SPEC2 , GUESS , LMSG  , LPMSG ,
C     3             JRES  , KRESLT, RESLTS(MRETN), INDEX(MIRETN),
C     4             LCFLAG)
C       WRITE (52,*) 'GAMMA AFTER FLASH'
C       DO 707 I = 1,IMOL+ICAT+IAN
C         WRITE (52,*) 'GAMMA ',I,'= ',GAMMA(I)
C 707   CONTINUE
      NBOPST(4) = 0
C       WRITE (52,*) 'TCALC = ',TCALC
C       WRITE (52,*) 'PCALC = ',PCALC
C       DO 709 I = 1,50
C         WRITE (52,*) 'RESLTS ',I,' = ',RESLTS(I)
C 709   CONTINUE
C
C          CALL THE USER ROUTINES TO SPECIATE THE LIQUID.
C
C       IF (ICONST. EQ. 1) THEN
C         ICONST = 0
        CALL USRCON (T)
C       ENDIF
      GUESS1 = 10**(-4.0)*TOTVOL
      GUESS2 = 10**(-5.0)*TOTVOL
      CALL USRSEC (GUESS1, GUESS2, FLOW)
      DO 301 I = 1,IMOL+ICAT+IAN
        WRITE (52,*) 'FLOW ',I,'= ',FLOW(I)
 301  CONTINUE
C
C          CALCULATE THE ACTIVITY FOR EACH COMPONENT.  THE
```

```
C         THE ACTIVITY COEFFICIENTS ARE CALCULATED IN SUBROUTINE
C         USRCON USING THE COMMON BLOCK GAMMA.
C
    DO 340 I = 1,IMOL+ICAT+IAN
     ACT(I) = FLOW(I)/TOTLIQ*ACTCOF(I)
 340  CONTINUE
C
C      CALCULATE THE KINETIC RATE CONSTANTS (RK) FOR
C      BICARBONATE AND CARBAMATE FORMATION.  VARIABLES
C      BEGINNING WITH 'A' REPRESENT THE PREEXPONENTIAL
C      FACTORS, AND VARIABLES BEGINNING WITH 'EA'
C      REPRESENT THE ACTIVATION ENERGIES.  THESE
C      CONSTANTS WERE FIT BY GLASSCOCK (1990).  THE
C      PREEXPONENTIAL FACTORS REPORTED BY GLASSCOCK HAVE
C      TO BE ADJUSTED BY THE DENSITY OF WATER TO CONVERT
C      TO A MOLE FRACTION BASIS.  THIS IS HANDLED BY
C      ENTERING THE CORRECT PREEXPONENTIAL FACTORS IN
C      THE INPUT READ BY THIS SUBROUTINE.
C
C      REACTION RATE CONSTANTS REPRESENTING THE REACTION
C      OF CO2 TO BICARBONATE:
C
C      RKTAMW  - REACTION FOR CO2, TERTIARY AMINE AND WATER
C      RKAMWB  - REACTION FOR CO2, PRIMARY OR SECONDARY
C              AMINE, AND WATER TO YIELD BICARBONATE. THIS
C              CONSTANT WAS NOT FIT BY GLASSCOCK BUT
C              INCLUDED FOR COMPLETENESS.  CURRENTLY,
C              THIS CONSTANT IS ALWAYS ZERO.
C      RKTAMH  - REACTION FOR CO2, TERTIARY AMINE AND OH-
C      RKOH    - REACTION FOR CO2 AND OH-
C
C      REACTION RATE CONSTANTS REPRESENTING THE REACTION
C      OF CO2 TO CARBAMATE:
C
C      RKPAM   - REACTION FOR CO2 AND PRIMARY AMINE
C      RKAMAM  - REACTION FOR CO2 AND TWO PRIMARY AMINES
C      RKAMTA  - REACTION FOR CO2, SECONDARY AMINE, AND
C              TERTIARY AMINE
C      RKAMWC  - REACTION FOR CO2, SECONDARY AMINE, AND
C              WATER TO YIELD CARBAMATE
C
C      THE CONSTANT CION IS USED TO REMOVE THE IONIC
C      STRENGTH DEPENDENCE OF THE HYDROXIDE RATE CONSTANT.
C      GLASSCOCK (1990) MISTAKENLY USED THE ACTIVITY OF
C      OH- WITH THE EXPRESSION FOR RKOH CONTAINING CION=0.08
C      AS REPORTED BY ASTARITA ET AL. (1983).  HOWEVER,
C      THIS CONSTANT IS A CONCENTRATION BASED RATHER THAN
C      ACTIVITY BASED CONSTANT.  THEREFORE, THE OH- ACTIVITY
C      IS USED BY SETTING CION=0.0 IN ORDER TO NOT ACCOUNT
C      FOR NONIDEALITIES TWICE (THROUGH THE IONIC STRENGTH
C      AND ACTIVITY).  AT A LATER TIME, THIS INCONSISTENCY
C      MIGHT BE CORRECTED. C1RKOH AND C2RKOH ARE USED TO ENTER
```

```
C      THE TEMPERATURE DEPENDENT CONSTANTS FOR THIS EXPRESSION.
C
C      THE VARIABLE FLPAM IS USED AS A FLAG TO REMOVE OR INCLUDE
C      RKPAM DEPENDING ON WHETHER A PRIMARY AMINE IS PRESENT.
C      C1PAM AND C2PAM ARE USED TO ENTER THE TEMPERATURE DEPENDENT
C      CONSTANTS FOR THIS EXPRESSION.
C
C      READ THE RATE CONSTANT PARAMETERS FROM THE KINETIC
C      INPUT FILE 'KINETIC.IN'
C
   ATAMW = REAL(1)
   EATAMW = REAL(2)
   AAMWB = REAL(3)
   EAAMWB = REAL(4)
   ATAMOH = REAL(5)
   EATAMH = REAL(6)
   C1RKOH = REAL(7)
   C2RKOH = REAL(8)
   CION = REAL(9)
   FLPAM = REAL(10)
   C1PAM = REAL(11)
   C2PAM = REAL(12)
   AAMAM = REAL(13)
   EAAMAM = REAL(14)
   AAMAM = REAL(15)
   EAAMAM = REAL(16)
   AAMWC = REAL(17)
   EAAMWC = REAL(18)
C
C    READ (51,*) ATAMW,EATAMW
C    READ (51,*) AAMWB,EAAMWB
C    READ (51,*) ATAMOH,EATAMH
C    READ (51,*) C1RKOH,C2RKOH,CION
C    READ (51,*) FLPAM,C1PAM,C2PAM
C    READ (51,*) AAMAM,EAAMAM
C    READ (51,*) AAMTAM,EAAMTA
C    READ (51,*) AAMWC,EAAMWC
C
   RKTAMW = ATAMW*DEXP(-EATAMW/1.987*(1/T - 1/298))
   RKAMWB = AAMWB*DEXP(-EAAMWB/1.987*(1/T - 1/298))
   RKTAMH  = ATAMOH*DEXP(-EATAMH/1.987*(1/T - 1/298))
   RKOH = 10.0**(C1RKOH + C2RKOH/T + CION*SUMION)
   RKPAM = FLPAM*10.0**(C1PAM + C2PAM/T)
   RKAMAM = AAMAM*DEXP(-EAAMAM/1.987*(1/T - 1/298))
   RKAMTA = AAMTAM*DEXP(-EAAMTA/1.987*(1/T - 1/298))
   RKAMWC = AAMWC*DEXP(-EAAMWC/1.987*(1/T - 1/298))
C
C     CALCULATE THE EQUILIBRIUM CO2 ACTIVITY.  THE CO2
C     ACTIVITY IN EQUILIBRIUM WITH BICARBONATE IS REPRESENTED
C     WITH ABCO2E.  THE CO2 ACTIVITY IN EQUILIBRIUM WITH
C     CARBAMATE IS ACCO2E.  THE OVERALL EQUILIBRIUM CONSTANTS
C     FOR BICARBONATE AND CARBAMATE ARE OBTAINED BY COMBINING
```

```
C       THE APPROPRIATE CONSTANTS CALCULATED IN SUBROUTINE USRCON.
C
      ABCO2E = ACT(3+IMOL+ICAT)*EKW/EKCO2/ACT(1+IMOL+ICAT)
      IF (ISYS.EQ.4) THEN
        ACCO2E = 0.0
      ELSE
       ACCO2E = ACT(1)*ACT(2+IMOL+ICAT)*EKW*EKCARB/EKCO2/
     &          ACT(1+IMOL+ICAT)/ACT(3)
      ENDIF
C
C       CALCULATE THE RATE OF BICARBONATE AND CARBAMATE
C       FORMATION.  THESE VALUES ARE MULTIPLIED BY THE
C       LIQUID HOLDUP TO GIVE APPROPRIATE UNITS (KMOL/S).
C       ALSO CHECK TO BE SURE RATE ISN'T TOO LARGE
C
      RTHCO3 = (ACT(4) - ABCO2E)*(RKTAMW*ACT(2)*ACT(1) + RKAMWB*
     1      ACT(3)*ACT(1) + RKTAMOH*ACT(2)*ACT(1+IMOL+ICAT) +
     2      RKOH*ACT(1+IMOL+ICAT))*TIMLIQ*TOTVOL
      WRITE (52,*) 'RTHCO3 =',RTHCO3
      RTCARB = ACT(3)*(ACT(4) - ACCO2E)*(RKPAM + RKAMAM*ACT(3) +
     1      RKAMTAM*ACT(2) + RKAMWC*ACT(1))*TOTLIQ*TOTVOLZ
      WRITE (52,*) 'RTCARB = ',RTCARB
C
C       CALCULATE THE RATES OF INDIVIDUAL COMPONENTS. AS A
C       REMINDER:  1 = H2O, 2 = MDEA, 3 = DEA(MEA,DGA),
C                4 = CO2, 5 = H2S, 6 = H2CO3, 7 = AMCOOH
C       THE RATES CALCULATED ABOVE HAVE TO BE MULTIPLIED
C       BY THE LIQUID HOLDUP TO OBTAIN THE APPROPRIATE UNITS
C        FOR ASPEN PLUS.
C
      RATES(1) = -RTHCO3
      RATES(2) = 0.0
      RATES(3) = -RTCARB
      RATES(4) = -RTHCO3 - RTCARB
      RATES(5) = 0.0
      RATES(6) = RTHCO3
      RATES(7) = RTCARB
C
      CLOSE UNIT=51
      CLOSE UNIT=52
C
      RETURN
      END
C
C ******************************************************************
C
      SUBROUTINE USRCON ( T )
C
C       THIS SUBROUTINE CALCULATES THE EQUILIBRIUM CONSTANTS
C       NEEDED TO SPECIATE THE LIQUID PHASE USING THE
C       SUBROUTINE USREQ.  THE NATURAL LOG OF THE ACTIVITY
C       COEFFICIENTS IS PASSED THROUGH THE COMMON /GAMMA/.
```

```
C       THESE VALUES ARE CALCULATED FROM THE ASPEN FLASH.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 MDEA, MDEAH, MEA, MEAH
C
      COMMON /GAMMA/  GAMMA(1)
      COMMON /USREK/  EKW   , EKMDEA, EKDEA , EKMEA , EKDGA , EKCO2 ,
     1               EKH2S , EKCARB, EKHCO3
      COMMON /USRFLG/ ISYS  , IMOL  , ICAT  , IAN
      COMMON /USRACT/ ACTCOF(1)
C
      DO 10 I = 1,IMOL+ICAT+IAN
       ACTCOF(I) = DEXP(GAMMA(I))
       WRITE (52,*) 'GAMMA ',I,' = ',GAMMA(I)
       WRITE (52,*) 'ACTCOF',I,'= ',ACTCOF(I)
       IF (ACTCOF(I) .GT. 100 .OR. ACTCOF(I) .LT. 1D-6) THEN
        WRITE (52,*) 'ACTCOF OUT OF RANGE'
        ACTCOF(I) = 1.0
       ENDIF
 10   CONTINUE
C
      EKW = DEXP(132.899 - 13445.9/T - 22.4773*DLOG(T))/
     &      (ACTCOF(1+IMOL)*ACTCOF(1+IMOL+ICAT)/ACTCOF(1)**2)
      EKMDEA = DEXP(-9.4165 - 4234.98/T)/(ACTCOF(1+IMOL)*ACTCOF(2)/
     &        ACTCOF(2+IMOL)/ACTCOF(1))
      IF (ISYS .EQ. 1) THEN
       EKDEA = DEXP(-6.7936 - 5927.65/T)/(ACTCOF(1+IMOL)*ACTCOF(3)/
     &        ACTCOF(3+IMOL)/ACTCOF(1))
       EKCARB = DEXP(4.5146 - 3417.34/T)/(ACTCOF(3+IMOL+ICAT)*
     &       ACTCOF(3)/ACTCOF(2+IMOL+ICAT)/ACT(1))
      ELSE IF (ISYS .EQ. 2) THEN
       EKMEA = DEXP(2.1211 - 8189.38/T - 0.007484*T)/(ACTCOF(1+IMOL)*
     &        ACTCOF(3)/ACTCOF(3+IMOL)/ACTCOF(1))
       EKCARB = DEXP(2.8898 - 3635.09/T)/(ACTCOF(3+IMOL+ICAT)*
     &       ACTCOF(3)/ACTCOF(2+IMOL+ICAT)/ACT(1))
      ELSE IF (ISYS .EQ. 3) THEN
       EKDGA = DEXP(1.6957 - 8431.65/T - 0.005037*T)/(ACTCOF(1+IMOL)*
     &        ACTCOF(3)/ACTCOF(3+IMOL)/ACTCOF(1))
       EKCARB = DEXP(8.8334 - 5274.4/T)/(ACTCOF(3+IMOL+ICAT)*
     &       ACTCOF(3)/ACTCOF(2+IMOL+ICAT)/ACT(1))
      ENDIF
      EKH2S = DEXP(214.582 - 12995.4/T - 33.5471*DLOG(T))/
     &        (ACTCOF(1+IMOL)*ACTCOF(4+IMOL+ICAT)/ACTCOF(5)/
     &         ACTCOF(1))
      EKHCO3 = DEXP(216.049 - 12431.7/T - 35.4819*DLOG(T))/
     &    (ACTCOF(1+IMOL)*ACTCOF(5+IMOL+ICAT)/ACTCOF(3+IMOL+ICAT)/
     &     ACTCOF(1))
      EKCO2 = DEXP(231.465 - 12092.1/T -36.4819*DLOG(T))/
     &    (ACTCOF(1+IMOL)*ACTCOF(3+IMOL+ICAT)/ACTCOF(4)/
     &      ACTCOF(1)**2)
C
      RETURN
```

```
      END
C
C *****************************************************************
C
      SUBROUTINE USRSEC ( GUESS1, GUESS2, FLOW )
C
C        THIS SUBROUTINE USES THE SECANT METHOD TO DIRECT
C        CONVERGENCE OF THE USER FLASH ROUTINE.
C
      IMPLICIT REAL*8 (A-H,O-Z)
C
      DIMENSION  FLOW(1)
C
      ITER = 0
      XOLD = GUESS1
      X = GUESS2
C
      DELTA = X - XOLD
      CALL USREQ (ITER,XOLD,FLOW,BULK)
      FOLD = BULK
C
 10   CALL USREQ (ITER,X,FLOW,BULK)
      F = BULK
      DELTA = -DELTA*F/(F-FOLD)
      X = X + DELTA
      IF (X .LT. 0.0) X = DABS(X)
C
      ITER = ITER + 1
      IF (ITER .GT. 100) THEN
        WRITE (52,*) 'SECANT DID NOT CONVERGE IN 100 ITERATIONS.'
        RETURN
      ENDIF
C
      IF (DABS(DELTA/X) .GT. 0.0005) THEN
        FOLD = F
        GOTO 10
      ENDIF
C
      WRITE (52,*) 'SECANT CONVERGED IN ',ITER,'ITERATIONS.'
      WRITE (52,*) 'SECANT CONVERGED. BULK = ',BULK
C
      RETURN
      END
C
C *****************************************************************
C
      SUBROUTINE USREQ ( ITER, OH, FLOW, BULK )
C
C        THIS SUBROUTINE SPECIATES THE APPARENT COMPONENT
C        COMPOSITION.
C
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      REAL*8 MDEA, MDEAH, MEA, MEAH
C
      COMMON /USRERK/ EKW   , EKMDEA, EKDEA , EKMEA , EKDGA , EKCO2 ,
     1             EKH2S , EKCARB, EKHCO3
      COMMON /USRFLG/   ISYS  , IMOL  , ICAT  , IAN
      COMMON /USRFLO/ TOTFLO(1)
C
      DIMENSION FLOW(1)
C
      H2O = OH*(-1. + DSQRT(1.0 - 4.0*EKW/OH*(OH - TOTFLO(1))))/2.0/EKW
      IF (H2O.EQ.0.0) H2O = 0.999*TOTFLO(1)
      IF (H2O.LT.0.0) THEN
       H2O = DABS(H2O)
       OH = 0.001*OH
      ENDIF
      H3O = EKW*H2O**2/OH
      WRITE (53,*) 'FREE H2O = ', H2O
      WRITE (53,*) 'H3O = ',H3O
      WRITE (53,*) 'OH = ',OH
C
      EFACT = EKW*H2O/EKH2S/OH
      HS = TOTFLO(5)/(1.0 + EFACT)
      H2S = EFACT*HS
      WRITE (53,*) 'FREE H2S = ',H2S
      WRITE (53,*) 'HS = ',HS
C
      EFACT = EKHCO3*OH/EKW/H2O
      HCO3 = TOTFLO(6)/(1.0 + EFACT)
      CO3 = EFACT*HCO3
      WRITE (53,*) 'CO2 = ',TOTFLO(4)
      WRITE (53,*) 'HCO3 = ',HCO3
      WRITE (53,*) 'CO3 = ',CO3
C
      EFACT = EKMDEA*OH/EKW/H2O
      MDEAH = TOTFLO(2)/(1.0 + EFACT)
      MDEA = EFACT*MDEAH
      WRITE (53,*) 'FREE MDEA = ',MDEA
      WRITE (53,*) 'MDEAH = ',MDEAH
C
      IF (ISYS .EQ. 1) THEN
       EFACT = EKDEA*OH/EKW/H2O
       DEAH = TOTFLO(3)/(1.0 + EFACT)
       DEA = EFACT*DEAH
      ELSE
       DEAH = 0.0
      ENDIF
      IF (ISYS .EQ. 2 ) THEN
       EFACT = EKMEA*OH/EKW/H2O
       MEAH = TOTFLO(3)/(1.0 + EFACT)
       MEA = EFACT*MEAH
      ELSE
       MEAH = 0.0
```

```
       ENDIF
       IF (ISYS .EQ. 3) THEN
        EFACT = EKDGA*OH/EKW/H2O
        DGAH = TOTFLO(3)/(1.0 + EFACT)
        DGA = EFACT*DGAH
       ELSE
        DGAH = 0.0
       ENDIF
C
      BULK = H3O + MDEAH + DEAH + MEAH + DGAH - OH - HCO3 - 2*CO3 -
     &       TOTFLO(7) - HS
      WRITE (53,*) 'BULK = ',BULK
C
      FLOW(1) = H2O
      FLOW(2) = MDEA
      IF (ISYS.EQ.1) THEN
       FLOW(3) = DEA
       FLOW(3+IMOL) = DEAH
      ELSE IF (ISYS.EQ.2) THEN
       FLOW(3) = MEA
       FLOW(3+IMOL) = MEAH
      ELSE IF (ISYS.EQ.3) THEN
       FLOW(3) = DGA
       FLOW(3+IMOL) = DGAH
      ELSE
       FLOW(3) = 0.0
       FLOW(3+IMOL) = 0.0
      ENDIF
      FLOW(4) = TOTFLO(4)
      FLOW(5) = H2S
      FLOW(6) = 0.0
      FLOW(7) = 0.0
      FLOW(8) = TOTFLO(8)
      FLOW(1+IMOL) = H3O
      FLOW(2+IMOL) = MDEAH
      FLOW(1+IMOL+ICAT) = OH
      FLOW(2+IMOL+ICAT) = TOTFLO(7)
      FLOW(3+IMOL+ICAT) = HCO3
      FLOW(4+IMOL+ICAT) = HS
      FLOW(5+IMOL+ICAT) = CO3
C
      RETURN
      END
```

Appendix D

SRP Annual Report: Rate-Based Modeling of Acid Gas Absorption and Stripping Using Aqueous Alkanolamine Solutions

Due to the importance of absorption using alkanolamine solutions, the development of computer models to simulate the absorption/stripping process using these solutions is important for design and retrofit purposes. This system is governed by complicated mass transfer with simultaneous chemical reaction. Mass transfer models have been developed based on rigorous, numerical solution of the differential equations describing the simultaneous transfer of H_2S and CO_2 with chemical reaction (Bou-Hamra, 1990; Glasscock, 1990; Versteeg, 1986; Blauwhoff and van Swaaij, 1985; Cornelisse et al., 1980). Unfortunately, these rigorous solutions generally require a large amount of computer time and are not practical for use in a complete process simulator. Therefore, some simplifying approximations must be chosen in order to solve for the mass transfer analytically in a process model.

Many approaches have been used in representing the mass transfer which occurs for simultaneous absorption and desorption of H_2S and CO_2 in alkanolamines. The simplest and crudest assumption is that the system is not mass transfer but equilibrium controlled. This type of model is sometimes useful for nonselective, ethanolamine systems (Vaz et al., 1981); however, this approximation is inadequate for design of a selective treating system because typical design procedures include estimation of stage efficiencies. The effect of chemical reactions in this system makes the prediction of stage efficiencies difficult because efficiencies are different for H_2S and CO_2 and vary at each stage. Stage efficiencies are usually underestimated as a safety factor; however, this overdesign destroys the selectivity of an absorption/stripping system. The more recent approach to modeling H_2S and CO_2 absorption into alkanolamines is the rate or nonequilibrium approach. This approach avoids the standard use of efficiencies by basing the amount of absorption at each stage on actual mass fluxes. The effect of chemical reaction on the mass fluxes is usually calculated with an analytical expression for the mass transfer enhancement factor. The enhancement factor is defined as the actual flux occurring across the gas-liquid interface divided by the flux that would occur without the chemical reaction.

Recent work at the University of Texas has been concerned with the rate-based modeling of alkanolamine absorption/stripping systems, specifically selective absorption using MDEA and absorption using blended amines (Carey, 1990). MDEA modeling was done by extending the absorption/stripping model developed by Hermes (1987). The simulation program ASPEN PLUS™ by Aspen Technology, Inc., was developed to model MEA, DGA, DEA, and amine blends.

The work of Hermes (1987) has been extended in several ways (Carey, 1990). The system physical property calculations were extended by adding expressions to calculate diffusion coefficients, MDEA solution viscosity and density, and water viscosity. A subroutine was also added to calculate the mass transfer coefficients and interfacial area for both sieve and bubble cap trays. The Henry's constant expressions and some of the chemical reaction equilibrium constants were changed. Using these new equilibrium expressions, the CO_2 and H_2S equilibrium constants were fit to an empirical expression with six adjustable parameters. Finally, the CO_2-MDEA rate constant expression was updated. The extended model continues to use an analytical expression for the CO_2 enhancement factor by solving the diffusion equations using the approximation of DeCoursey (1982) for the reaction rate term.

The MDEA model was used to evaluate the performance of an absorber/stripper system using 50 wt% MDEA. System performance was calculated as the amount of H_2S in the absorber off-gas (H_2S leak). Specifically, the effect of adding a strong acid to the amine solution and lowering the stripper pressure was studied. Sensitivity of the model predictions to values of the H_2S equilibrium constant, the H_2S heat of reaction, the mass transfer coefficients, and the CO_2-MDEA rate constant was also investigated.

A base case set of system conditions was established to represent a typical Claus tail gas application. For the base case conditions, a H_2S leak of 98 ppm was obtained using a steam rate of 1.7 lb/gal solvent. Figure D.1 shows that addition of a strong acid to MDEA solutions drastically improves the H_2S leak. Using the same solvent circulation rate while adding acid improves performance to 25 ppm; however, the H_2S leak can be further improved to 6 ppm by increasing the liquid rate by about 35%. Analysis of the model results showed that this improvement was due to linearization of the H_2S equilibrium in the stripper, thus H_2S was more easily removed when acid is present.

Figure D.2 shows that reducing the stripper pressure also improves H_2S leak. As the stripper pressure is reduced, the CO_2 lean loading increases because the CO_2-MDEA reaction rate constant is reduced in the stripper. This extra CO_2 acts as an acid and causes the H_2S equilibrium to be linearized in the stripper. However, examination of Figure D.2 shows that the CO_2 loading does not have to be as high as the acid loading to reach the same performance level. Closer examination of the stripper pressure reduction results shows that in addition to linearizing the H_2S equilibrium, the gas phase mass transfer coefficient and number of gas phase transfer units are increased when the pressure is reduced. Because H_2S absorption is partially gas phase controlled and CO_2 absorption is totally liquid phase controlled, an increase in these gas phase mass transfer parameters also helps to improve H_2S leak.

Finally, the sensitivity of various system performance indicators to changes in model and operating parameters was investigated. Table D.1 shows the sensitivity of H_2S leak, CO_2 lean loading, and percent CO_2 removed to changes in the H_2S equilibrium constant, the H_2S heat of reaction, the liquid phase mass transfer coefficient (k_l°), the gas phase mass transfer coefficient (k_g), and the CO_2-MDEA rate constant. These results show that the estimated H_2S leak is very sensitive to the value of the H_2S equilibirum constant and heat of reaction in the stripper which suggests that determination of these values at high temperatures is warranted. The H_2S leak is sensitive to both the liquid and gas mass transfer coefficient because H_2S absorption is partially liquid and gas phase controlled; however, the selectivity, as indicated by the percent CO_2 removed, is only sensitive to k_l° because CO_2 absorption is totally liquid phase controlled. Finally, the H_2S leak is sensitive to the CO_2-MDEA rate constant because the CO_2 lean loading changes with values of this constant. As found in the case of stripper pressure reduction, increases in CO_2 lean loading can result in dramatic changes in the H_2S leak.

In order to model amines other than MDEA, Aspen Technology's ASPEN PLUS™ was developed to model all of the common alkanolamine systems. ASPEN PLUS™ was chosen because it contains an accurate thermodynamic model for electrolytes, a rate-based column model, and the ability to include complicated reaction rate expressions. Input files containing physical properties and chemical reaction equilibrium constants specific to the alkanolamine systems were developed. In addition, subroutines were developed to calculate the reaction rate for rate limited reactions. These files can be used to perform equilibrium or rate-based modeling.

Using the NRTL parameters regressed by Austgen (1989), equilibrium flash calculations using ASPEN PLUS™ were compared to the experimental data for CO_2 in the mixed amine systems MEA-MDEA and DEA-MDEA. The experimental data is reported as the CO_2 partial pressure versus the CO_2 loading (moles of CO_2 absorbed per mole of MDEA); therefore, for a given CO_2 loading, the ASPEN PLUS™ equilibrium flash calculated the CO_2 partial pressure. Figures D.3 and D.4 compare the model results to the experimental data for CO_2 in MEA-MDEA and DEA-MDEA solutions, respectively. As shown by the figures, the model does a good job of representing the equilibrium for these complex systems.

In order to perform rate-based calculations for MEA, DGA, DEA, MDEA, or mixed amine systems, a kinetic subroutine containing complex rate expressions from Glasscock (1990) has been developed. The ASPEN PLUS™ rate-based column model is currently unavailable; therefore, the kinetic subroutine was tested using an equilibrium-based model containing rate-limited reactions. Unfortunately, convergence problems prevented column results from being produced; however, the kinetic subroutine calculated reasonable reaction rates for CO_2.

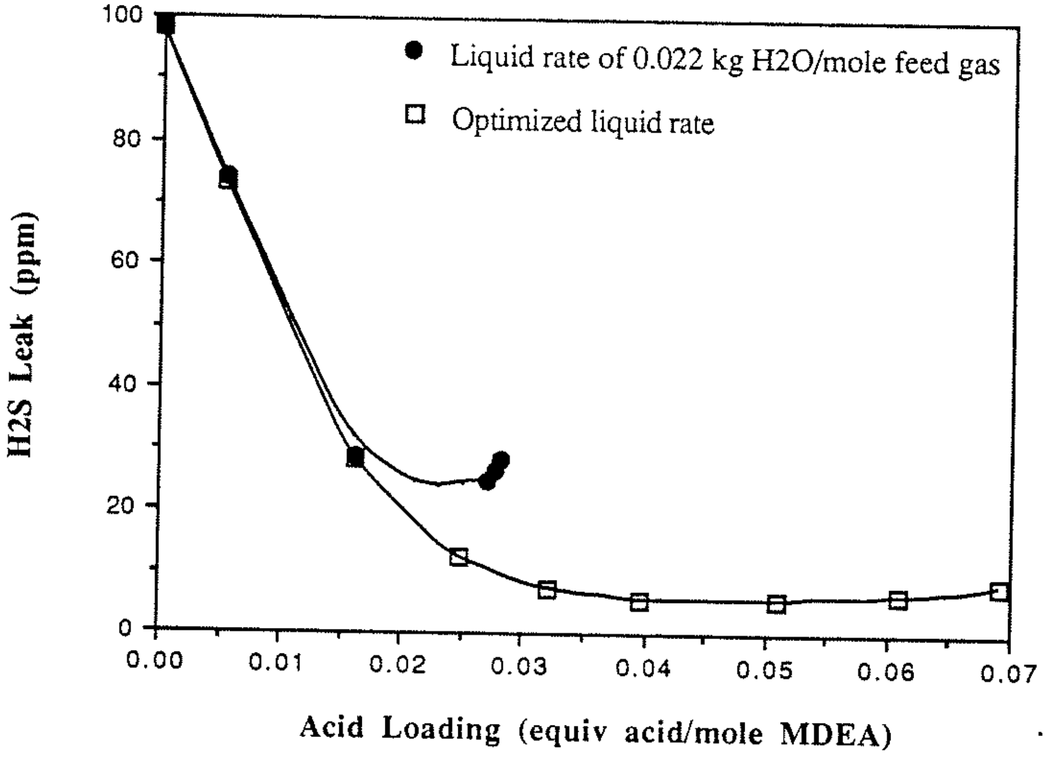

Figure D.1: Effect of Acid Addition on System Performance (1.1 atm absorber with 20 trays, 2.0 atm stripper with 25 trays, feed gas with 1% H_2S, 10% CO_2, 0.028 lb steam/SCF feed gas).

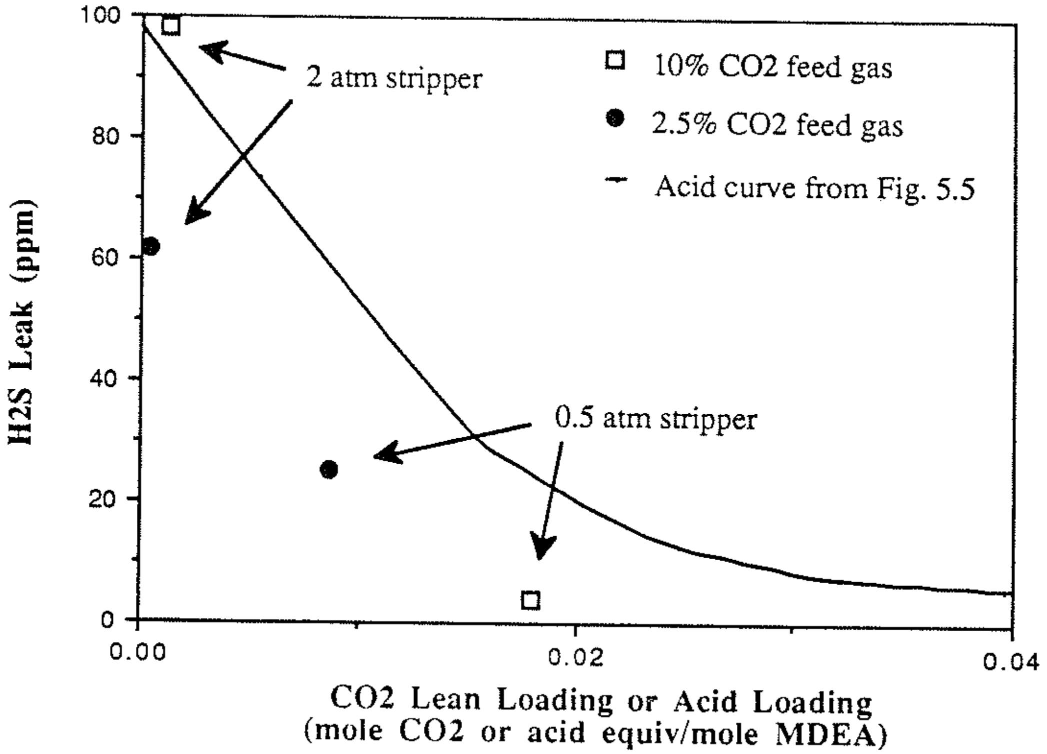

Figure D.2: Comparison of the Effect of Acid Addition and Stripper Pressure Reduction on System Performance (1.1 atm absorber with 20 trays, stripper with 25 trays, feed gas with 1% H_2S, 0.028 lb steam/SCF feed gas).

Table D.1: Base Case Sensitivity of System Responses to Various Parameters.

$$\text{Sensitivity of response} = \frac{d[\ln(\text{response})]}{d[\ln(\text{parameter})]} = \frac{\Delta(\text{response})}{\Delta(\text{parameter})} \; \frac{\text{parameter}}{\text{response}}$$

	Sensitivity to Response		
Adjusted Parameter	H_2S Leak (ppm)	CO_2 Lean Loading	Percent CO_2 Removed
H_2S equilibrium constant in both columns	0.33	-0.96	-0.20
H_2S equilibrium constant in only the stripper	1.72	-1.05	0.0
H_2S heat of reaction	-1.29	0.78	0.0
k_g	-0.27	0.0	0.0
k_l°	-0.48	0.14	0.57
CO_2-MDEA rate constant	0.17	-0.60	0.11

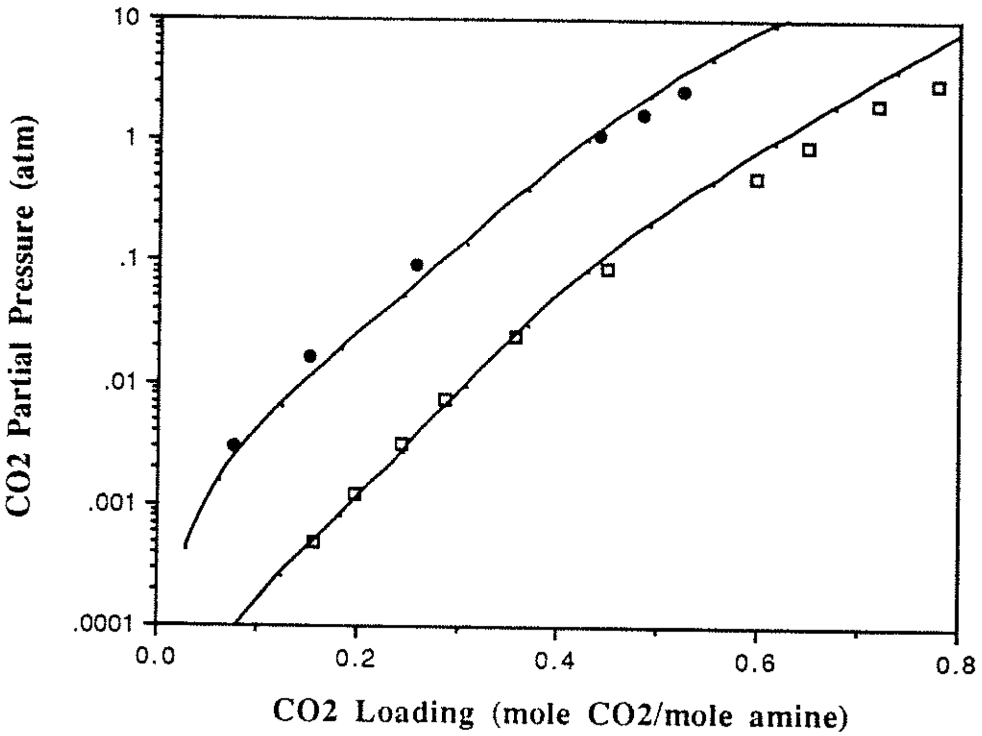

Figure D.3: Comparison of Model Prediction to Experimental Data for CO_2 in 2.0M MEA - 2.0M MDEA. Model prediction: (—). Experimental data from Austgen (1989): (◻) - 40°C, (•) - 80°C

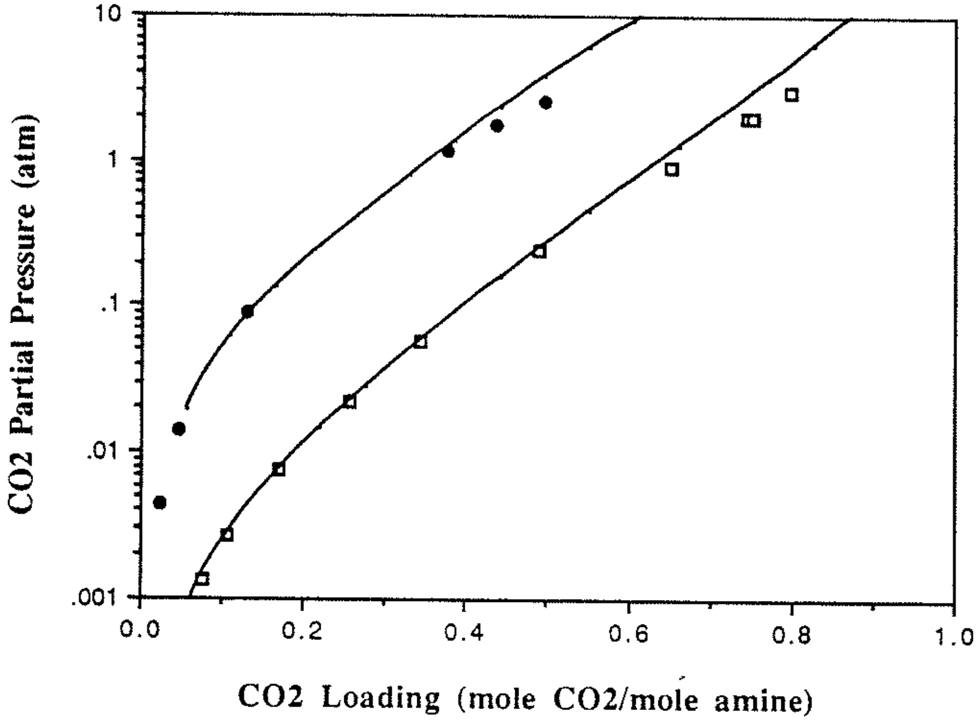

Figure D.4: Comparison of Model Prediction to Experimental Data for CO_2 in 2.0M DEA - 2.0M MDEA. Model prediction: (—). Experimental data from Austgen (1989): (◻) - 40°C, (•) - 80°C

Nomenclature

a	component activity
a'	effective interfacial area per unit floor area of the plate (dm^2/dm^2)
a''	effective interfacial area per liquid froth volume on plate (dm^2/dm^3)
C	concentration of species i (moles/L)
C_3	arbitrary constant from enhancement factor derivation, 1.5
C_M	molarity to molality conversion factor (L/kg H_2O)
C_p	heat capacity (J/mole/°C)
d	dielectric constant
D	diffusion coefficient (m^2/s)
D_G	overall gas phase diffusion coefficient (cm^2/s)
D_L	CO_2 liquid phase diffusion coefficient (cm^2/s)
DF	gas phase mass transfer driving force (atm)
E	enhancement factor
f	fractional approach to vapor flood velocity
F	corrected velocity through active area of tray (cm/s)$(kg/L)^{0.5}$
G	total gas rate flux ($mole/dm^2/s$)
H	Henry's law constant (atm-kg H_2O/mole)
ΔH	stream enthalpy (cal/mole)
ΔH_{rxn}	heat of reaction (cal/mole)
I	ionic strength
k	reaction rate constant
k_1	pseudo-first order rate constant (1/s)
k_g	gas phase mass transfer coefficient ($mole/atm/dm^2/s$)
k_l°	liquid phase mass transfer coefficient (dm/s)
k_{MDEA}	reaction rate constant of mechanism 3.65 (m^3/kmol-s)
k_{OH}	reaction rate constant of mechanism 3.64 (m^3/kmol-s)
K	equilibrium constant
L	liquid flow rate (mole/s)
M	enhancement factor rate parameter
N	absorption flux rate (kmole/m^2-s)

N_g	number of gas phase mass transfer units per stage
N_q	number of gas phase heat transfer units per stage
P	total or partial pressure (atm)
R_i	net production rate of component i (kmol/m^3-s)
R	gas constant, 1.987 (cal/mole/K)
R_3N	tertiary amine (MDEA)
S	submergence of liquid for bubble cap trays or liquid holdup on a tray for sieve trays (cm)
S_{eff}	effective froth height on a tray (cm)
t_g	average vapor residence time (s)
T	temperature (K)
U	superficial gas velocity (cm/s)
V	gas flow rate (mole/s)
y	gas phase mole fraction

Greek Symbols

Θ	enhancement factor dimensionless driving force
ϕ	froth density
κ	thermal conductivity (cal/cm/K/s)
ρ	density (kg/L)
μ	viscosity (cp)

Superscripts

o	unloaded solution
∞	infinite dilution

Subscripts

am	primary or secondary amine
aq	aqueous phase
b	bulk
e	equilibrium
g	gas
i	interface
in	flow into a stage
l	liquid
pam	primary amine
tam	tertiary amine
out	flow out of a stage
w	water

References

Al-Ghawas, H.A., D.P. Hagewiesche, G. Ruiz-Ibanez, and O.C. Sandall, "Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine," *J. Chem. Eng. Data*, **34**(4), 385, 1989.

American Institute of Chemical Engineers, *AIChE Bubble Tray Design Manual*, American Institute of Chemical Engineers, New York, 1958.

American Society of Mechanical Engineers, *ASME Steam Tables in SI (Metric) Units*, New York, 1977.

Aspen Technology, Inc., ASPEN PLUS™ *Electrolytes Manual*, Second Edition, Aspen Technology, Inc., Cambridge, MA, 1988.

Aspen Technology, Inc., ASPEN PLUS™ *Notes on Interfaces and User Models*, Second Edition, Aspen Technology, Inc., Cambridge, MA, 1988.

Aspen Technology, Inc., ASPEN PLUS™ *RATEFRAC User Manual*, Aspen Technology, Inc., Cambridge, MA, 1989.

Aspen Technology, Inc., ASPEN PLUS™ *System Maintenance Guide: VAX/VMS Version*, Aspen Technology, Inc., Cambridge, MA, 1988.

Aspen Technology, Inc., ASPEN PLUS™ *User Guide*, Aspen Technology, Inc., Cambridge, MA, 1988.

Astarita, G., D.W. Savage, and A. Bisio, *Gas Treating with Chemical Solvents*, John Wiley and Sons, New York, 1983.

Austgen, D.M., *A Model of Vapor-Liquid Equilibria for Acid Gas-Alkanolamine-Water Systems*, Ph.D. Dissertation, The University of Texas at Austin, Austin, TX, 1989.

Bates, R.G., and G.D> Pinching, "Acidic Dissociation Constant and Related Thermodynamic Quantities for Monoethanolammonium Ion in Water from 0° to 50°C," *J. Res. Nat. Bur. Stand.*, **46**(5), 349, 1951.

Bisio, A., and R.L. Kabel, Eds., *Scaleup of Chemical Processes: Conversion from Laboratory Scale Tests to Successful Commercial Size Design*, John Wiley and Sons, New York, 1985.

Blauwhoff, P.M.M. , Ph.D. Dissertation, Twente University of Technology, The Netherlands, 1982.

Blauwhoff, P.M.M. , and W.P.M. van Swaaij, *Proceedings of the 2nd International Conference on Phase Equilibria Fluid Properties in the Chemical Industry, Berlin, March 1980*, EFCE Publ. Ser. 11, Part I, 78, Dechema, Frankfurt/Main, 1980.

Blauwhoff, P.M.M. and W.P.M. van Swaaij, "Simultaneous Mass Transfer of H_2S and CO_2 with Complex Chemical Reactions in an Aqueous Diisopropanolamine Solution", *Chem. Eng. Process.*, **19**, 67, 1985a.

Blauwhoff, P.M.M., B. Kamphuis, W.P.M. van Swaaij, and K.R. Westerterp, "Absorber Design in Sour Natural Gas Treatment Plants. Impact of Process Variables on Operation and Economics," *Chem. Eng. Process.*, **19**, 1, 1985b.

Blauwhoff, P.M.M. , G.F. Versteeg, and W.P.M. van Swaaij, "A Study on the Reaction Between CO_2 and Alkanolamines in Aqueous Solutions," *Chem. Eng. Sci.*, **39**(2), 207, 1984.

Bottoms, R.R., U.S. Patent 1,783,901, 1930.

Bou-Hamra, W., "Mathematical Modeling of the Selectivity of a Tertiary Amine for Hydrogen Sulfide in the Presence of Carbon Dioxide," Presented at the AIChE Spring National Meeting, Orlando, FL, 1990.

Bower, V.E., R.A. Robinson, and R.G. Bates, "Acidic Dissociation Constant and Related Thermodynamic Quantities for Diethanolammonium Ion in Water from 0° to 50°C," *J. Res. Nat. Stands. - A. Physics and Chemistry*, **66A**(1), 71, 1962.

Bullin, J.A., J.C. Polasek, and J.W. Holmes, "Optimization of New and Existing Amine Gas Sweetening Plants by Computer Simulation," *Proceedings of the 60th Annual Gas Processors Association Convention*, 142, San Antonio, TX, 1981.

Campbell, S.W., and R.H. Weiland, "Modeling CO_2 Removal by Amine Blends", Presented at the AIChE Spring National Meeting, Paper No. 56d, Houston, TX, 1989.

Chakravarty, T., *Solubility Calculations for Acid Gases in Amine Blends*, Ph.D. Dissertation, Clarkson University, 1985.

Chakravarty, T., U.K. Phukan, and R.H. Weiland, "Reaction of Acid Gases with Mixtures of Amines," *Chem. Eng. Prog.*, **81**(4), 32, 1985.

Chan, H., and J.R. Fair, "Prediction of Point Efficiencies on Sieve Trays. 1. Binary Systems," *Ind. Eng. Chem. Process Des. Dev.*, **23**(4), 814, 1984.

Chen, C.C., H.I. Britt, J.F. Boston, and L.B. Evans, "Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes," *AIChE J.*, **25**(5), 820, 1979.

Cheuh, P.L., and J.M. Prausnitz, "Vapor-Liquid Equilibria at High Pressures. Vapor-Phase Fugacity Coefficients in Nonpolar and Quantum-Gas Mixtures," *Ind. Eng. Chem. Fundam.*, **6**, 492, 1967.

Cornelisse, R., A.A.C.M. Beenackers, F.P.H. van Beckum, and W.P.M. van Swaaij, "Numerical Calculation of Simultaneous Mass Transfer of Two Gases Accompanied by Complex Reversible Reactions", *Chem. Eng. Sci.*, **35**(5), 1245, 1980.

Cornelissen, A.E., "Simulation of Absorption of H_2S and CO_2 into Aqueous Alkanolamines in Tray and Packed Columns," *Trans. Inst. Chem. Eng.*, **58**, 242, 1980.

Critchfield, J.E., *CO_2 Absorption/Desorption in Methyldiethanolamine Solutions Promoted with Monoethanolamine and Diethanolamine: Mass Transfer and Reaction Kinetics*, Ph.D. Dissertation, The University of Texas at Austin, Austin, TX, 1988.

Cross, C., D. Edwards, J. Santos, and E. Stewart, "Gas Treating Through the Accurate Process Modeling of Specialty Amine Plants," Presented at the Laurance Reid Gas Conditioning Conference, Norman, OK, March, 1990.

Danckwerts, P.V., *Gas-Liquid Reactions*, McGraw-Hill, New York, 1970.

Danckwerts, P.V., and M.M. Sharma, *Chem. Eng. (London)*, **10**, 244, 1966.

Daubert, T.E., and R.P. Danner, *Data Compilation Tables of Properties of Pure Compounds*, Design Institute for Physical Property Data - Americal Institute of Chemical Engineers, New York, NY, 1985.

DeCoursey, W.J., "Enhancement Factors for Gas Absorption with Reversible Reaction," *Chem. Eng. Sci.*, **37**(10), 1483, 1982.

Deshmukh, R.D., and A.W. Mather, "A Mathematical Model for Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Alkanolamine Solutions," *Chem. Eng. Sci.*, **36**(2), 362, 1981.

Dingman, J.C., J.L. Jackson, T.F. Moore, and J.A. Branson, "Equilibrium Data for the H_2S - CO_2 - Diglycolamine Agent - Water System," Presented at the 62nd Annual Gas Processors Association Convention, San Francisco, CA, 1983.

Dow Chemical Co. *Gas Treating Handbook*, Gas/Spec Technology Group, Dow Chemical Co., Houston, TX, 1987.

Edwards, T.J., *Thermodynamics of Aqueous Solutions Containing One or More Volatile Weak Electrolytes*, Ph.D. Dissertation, University of California at Berkeley, 1974.

Edwards, T.J., G. Maurer, J. Newman, and J.M. Prausnitz, "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes," *AIChE J.*, **24**(6), 966, 1978.

Felder, R.M., and R.W. Rousseau, *Elementary Principles of Chemical Processes*, John Wiley and Sons, New York, 1978.

Fukushima, S., and K. Kusaka, "Application of Particle Enlargement by Condensation to Industrial Dust Collection," *J. Chem. Eng. Jpn.*, **10**, 468, 1978.

Fuller, E.N., P.D. Schettler, and J.C. Giddings, "A New Method for Prediction of Binary Gas-Phase Diffusion Coefficients," *Ind. Eng. Chem.*, **58**(5), 19, 1966.

Glasscock, D.A., *Modelling and Experimental Study of Carbon Dioxide Absorption into Aqueous Alkanolamines*, Ph.D. Dissertation, The University of Texas at Austin, Austin, TX, 1990.

Glasscock, D.A., and G.T. Rochelle, "Approximate Simulation of CO_2 and H_2S Absorption into Aqueous Alkanolamines," Submitted to *AIChE J.*, September, 1990a.

Glasscock, D.A., and G.T. Rochelle, "Modelling of CO_2 Absorption/Desorption in Mixtures of Methyldiethanolamine with Monoethanolamine or Diethanolamine," Presented at the AIChE Spring National Meeting, Orlando, FL, 1990b.

Haimour, N., A. Bidarian, and O.C. Sandall, "Absorption of CO_2 into Aqueous Solutions of Methyldiethanolamine," Presented at the AIChE National Meeting, Houston, TX, 1985.

Heinzelmann, F.J., N.S. Rothblatt, J.P. Glass, Jr., G.R. Say, G.R. Chludziaski, G. Sartori, and W.S. Winston Ho, "Absorbent Composition Containing a Severely Hindered Amino Compound and an Amine Salt and Process for the Absorption of H_2S Using the Same," U.S. Patent 4,618,481, 1986.

Hermes, J.E., *A Mass Transfer-Based Process Model of Acid Gas Absorption/Stripping Using Methyldiethanolamine*, M.S. Thesis, The University of Texas at Austin, Austin, TX, 1987.

Hermes, J.E., and G.T. Rochelle, "A Mass Transfer-Based Process Model of Acid Gas Absorption/Stripping Using Methyldiethanolamine," Presented at the ACS National Meeting, New Orleans, LA, 1987.

Hikita, H., and S. Asai, "Gas Absorption with (*m*, *n*)-th Order Irreversible Chemical Reactions, *Kagaku Kogaku*, **27**(11), 823, 1963.

Holmes, J.W., M.L. Spears, and J.A. Bullin, "Sweetening LPG's with Amines," *Chem. Eng. Prog.*, **80**(5), 47, 1984.

Ikada, E., Y. Hida, H. Okamoto, and N. Koizumi, "Dielectric Properties of Ethanolamines," *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**(5), 239, 1968.

Incropera, F.P., and D.P. DeWitt, *Fundamentals of Heat Transfer*, John Wiley and Sons, New York, 1981.

Ishii, Y., and F.D. Otto, "A General Algorithm for Multistage Multicomponent Separation Calculations," *Can. J. of Chem. Eng.*, **51**(5), 601, 1973.

Jou, F.Y., A.E. Mather, and F.D. Otto, "Solubility of H_2S and CO_2 in Aqueous Methyldiethanolamine Solutions," Presented at the AIChE Spring National Meeting, New Orleans, LA, 1981.

Jou, F.Y., A.E. Mather, and F.D. Otto, "Solubility of H_2S and CO_2 in Aqueous Methyldiethanolamine Solutions," *Ind. Eng. Chem. Process Des. Dev.*, **21**(4), 539, 1982.

Jou, F.Y., F.D. Otto, and A.E. Mather, "Solubility of Mixtures of H_2S and CO_2 in a Methyldiethanolamine Solution," Presented at the AIChE Annual Meeting, Paper No. 140b, Miami Beach, FL, 1986.

Katti, S.S., and B.D. Langfitt, "Development of a Simulator for Commercial Absorbers Used for Selective Chemical Absorption Based on a Mass Transfer Rate Approach," Presented at the 65th Annual Gas Processors' Association Convention, San Antonio, TX, 1986.

Katti, S.S., and R.A. Wolcott, "Fundamental Aspects of Gas Treating with Formulated Amine Mixtures," Presented at the AIChE Summer National Meeting, Minneapolis, MN, 1987.

Katti, S.S., K.A. Kenny, and R.A. Wolcott, "Gas Treating with Formulated Amine Mixtures: Optimization through Modeling and Simulation," Presented at the AIChE Spring National Meeting, New Orleans, LA, 1988.

Kent, R.L., and B. Eisenberg, "Better Data for Amine Treating," *Hydrocarbon Processing*, **55**(2), 87, 1976.

Kevorkian, A.K., and J. Snoek, in Himmelblau, D.M., ed., *Decomposition of Large-Scale Problems*, North-Holland Publishing Co., Amsterdam, 1973.

Kohl, A.L., and F.C. Riesenfeld, *Gas Purification*, 4th ed., Gulf Publishing Co., Houston, TX, 1985.

Laddha, S.S., and P.V. Danckwerts, "Reactions of CO_2 with Ethanolamines: Kinetics from Gas-Absorption," *Chem. Eng. Res.*, **36**, 479, 1981.

Lindner, J.R., "Simulation of Gas Absorption with Chemical Reaction: The Selective Removal of Hydrogen Sulfide by Aqueous MDEA in Packed Columns", Ph.D. Dissertation, Johns Hopkins University, Baltimore, MD, 1988.

Lindner, J.R., C.N. Schubert, and R.M. Kelly, "Influence of Hydrodynamics on Physical and Chemical Gas Absorption in Packed Columns", *Ind. Eng. Chem. Res.*, **27**(4), 636, 1988.

Lindner, J.R., C.N. Schubert, and R.M. Kelly, "Packed Absorber Model for CO_2 and H_2S Absorption into Aqueous Methyldiethanolamine", submitted to *AIChE J.*, January, 1987.

Littel, R.J., W.P.M. van Swaaij, and G.F. Versteeg, "The Kinetics of Carbon Dioxide with Tertiary Amines in Aqueous Solution," Presented at the AIChE Spring National Meeting, Orlando, FL, 1990.

Nonhebel, G., *Gas Purification Processes for Air Pollution Control*, Newnes-Butterworths, London, 1972.

Olander, D.R., "Simultaneous Mass Transfer and Equilibrium Chemical Reactions," *AIChE J.*, **6**, 233, 1960.

Onda, K., H. Takeuchi, and Y. Okumoto, "Mass Transfer Coefficient Between Gas and Liquid Phases in Packed Columns," *J. Chem. Eng. Japan*, **1**(1), 56, 1968.

Peng, X., SINOPEC Beijing Design Institute, Private communication with Dave Austgen at Aspen Technology, Inc., 1988.

Perry, R.H., and D.W. Green, Eds., *Perry's Chemical Engineers' Handbook*, Sixth Edition, McGraw-Hill, New York, 1984.

Pinsent, B.R.W., L. Pearson, and F.J.W. Roughton, "The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions," *Trans. Faraday Soc.*, **52**, 1512, 1956.

Polasek, J.C., and J.A. Bullin, "Selecting Amines for Sweetening Units," *Energy Progress*, **4**(3), 146, 1984.

Polasek, J.C., J.A. Bullin, and S.T. Donnelly, "How to Reduce Costs in Amine Sweetening Units," *Chem. Eng. Prog.*, **79**(3), 63, 1983.

Polasek, J.C., S.T. Donnelly, and J.A. Bullin, "The Use of MDEA and Mixtures of Amines for Bulk CO_2 Removal," Presented at the AIChE National Spring Meeting, Orlando, FL, 1990.

Sada, E., H. Kumazawa, and M.A. Butt, "Solubility and Diffusivity of Gases in Aqueous Solutions of Amines", *J. Chem. Eng. Data*, **23**(2), 161, 1978.

Sardar, H., M.S. Sivasubramanian, and R.H. Weiland, "Simulation of Commercial Amine Treating Units", Presented at the Laurance Reid Gas Conditioning Conference, Norman, OK, 1985a.

Sardar, H., M.S. Sivasubramanian, and R.H. Weiland, "Simulation of Absorbers and Strippers in Commercial Amine Treating Units", Presented at the AIChE Spring National Meeting, Paper No. 87c, Houston, TX, 1985b.

Scheffe, R.D., *Mass Transfer Characteristics of Valve Trays*, M.S. Thesis, Clarkson University, 1984.

Schwabe, K., W. Graichen, and D. Spiethoff, "Physikalisch-chemische Untersuchungen an Alkanolaminen," *Z. Phys. Chem. Neue Folge*, **20**, 68, 1959.

Secor, R.M., and J.A. Beutler, "Penetration Theory for Diffusion Accompanied by a Reversible Chemical Reaction with Generalized Kinetics," *AIChE J.*, **13**(2), 365, 1967.

Sharma, M.M., and R.K. Gupta, "Mass Transfer Characteristics of Plate Columns without Downcomers," *Trans. Inst. Chem. Eng.*, **45**, 169, 1967.

Sharma, M.M., R.A. Mashelkar, and V.D. Mehta, "Mass Transfer in Plate Columns," *Br. Chem. Eng.*, **14**(1), 70, 1969.

Sheu, Y.E., Texaco Chemical Co., Austin, TX, Private communication with Dave Austgen, 1989.

Sivasubramanian, M.S., "The Heat and Mass Transfer Rate Approach for the Simulation and Design of Acid Gas Treating Units", Ph.D. Dissertation, Clarkson University, 1985.

Sivasubramanian, M.S., H.Sardar, and R.H. Weiland, "Simulation Mirrors Commercial Amine Units," *Oil and Gas J.*, **83**(40), 133, 1985a.

Sivasubramanian, M.S., H. Sardar, and R.H. Weiland, "Simulation of Fully-Integrated Amine Units for Acid Gas Removal," Presented at the AIChE Spring National Meeting, Paper No. 87e, Houston, TX, 1985b.

Texaco Chemical Co., *Diglycolamine Agent*, Technical Publication, Austin, TX, undated.

Toman, J.J., Ph.D. Dissertation, The University of Texas at Austin, Austin, TX, 1990.

Toman, J.J., and G.T. Rochelle, "Carbon Dioxide Absorption Rates and Physical Solubility in 50% Aqueous Methyldiethanolamine Partially Neutralized with Sulfuric Acid," Presented at the AIChE Spring National Meeting, Paper No. 56c, Houston, TX, 1989.

Tomcej, R.A., and F.D. Otto, "Absorption of CO_2 and N_2O into Aqueous Solutions of Methyldiethanolamine," *AIChE J.*, **35**(5), 861, 1989.

Tomcej, R.A., and F.D. Otto, "Improved Design of Amine Treating Units by Simulation Using Personal Computers," Presented at the World Congress III of Chemical Engineering, Tokyo, Japan, 1986.

Tomcej, R.A., F.D. Otto, and F.W. Nolte, "Computer Simulation of Amine Treating Units," Presented at the Laurance Reid Gas Conditioning Conference, Norman, OK, 1983.

Tomcej, R.A., D. Lal, H.A. Rangwala, and F.D. Otto, "Absorption of Carbon Dioxide into Aqueous Solutions of Methyldiethanolamine," Presented at the AIChE Fall National Meeting, Miami Beach, FL, 1986.

Tomcej, R.A., F.D. Otto, H.A. Rangwala, and B.R. Morrell, "Tray Design for Selective Absorption," Presented at the Laurance Reid Gas Conditioning Conference, Norman, OK, 1987.

Union Carbide, European Patent Application, Publication Number 0134948, 1984.

Van Krevelen, D.W., and P.J. Hoftijzer, *Chimie et Industrie*, Numero special du XXIe Congres International de Chimie Industrielle, 168, 1948.

Vaz, R.N., G.J. Mains, and R.N. Maddox, "Ethanolamine Process Simulated by Rigorous Calculation," *Hydrocarbon Processing*, **60**(4), 139, 1981.

Versteeg, G. F., *Mass Transfer and Chemical Reaction Kinetics in Acid Gas Treating Processes*, Ph.D. Dissertation, University of Twente, Netherlands, 1986.

Versteeg, G.F., and W.P.M. van Swaaij, "Solubility and Diffusivity of Acid Gases (CO_2, N_2O) in Aqueous Alkanolamine Solutions," *J. Chem. Eng. Data*, **33**(1), 29, 1988.

Vickery, D.J., and R.H. Weiland, "Solubility of Acid Gases in Blends of Amines," Presented at the AIChE Annual Meeting, Paper No. 140c, Miami Beach, FL, 1986.

Vickery, D.J., S.W. Campbell, and R.H. Weiland, "Gas Treating with Promoted Amines," Presented at the Laurance Reid Gas Conditioning Conference, Norman , OK, 1988.

Weast, R.C., Ed., *CRC Handbook of Chemistry and Physics*, 61st Edition, CRC Press Inc., Boca Raton, 1980.

Welleck, R.M., R.J. Brunson, and F.H. Law, "Enhancement Factors for Gas-Absorption with Second-Order Irreversible Chemical Reactions," *Can. J. Chem. Eng.*, **56**(4), 181, 1978.

Yu, W.C., "Selective Removal of Hydrogen Sulfide from Carbon Dioxide Containing Gases with Methyldiethanolamine Aqueous Solutions," Ph.D. Dissertation, University of Delaware, 1985.

Yu, W.C. and G. Astarita, "Design of Packed Towers for Selective Chemical Absorption," *Chem. Eng. Sci.*, **42**(3), 425, 1987a.

Yu, W.C. and G. Astarita, "Selective Absorption of Hydrogen Sulfide in Tertiary Amine Solutions," *Chem. Eng. Sci.*, **42**(3), 419, 1987b.

Yu, W.C., G. Astarita, and D.W. Savage, "Kinetics of Carbon Dioxide Absorption in Solutions of Methyldiethanolamine," *Chem. Eng. Sci.*, **40**(8), 1585, 1985.

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