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

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by

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Copyright
by
Todd Ronald Carey
1990
To my parents
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Abstract

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SUPERVISING PROFESSOR: GARY ROCHELLE

Two models for the simultaneous absorption and stripping of H$_2$S 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$_2$S 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$_2$S 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$_2$S 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$_2$S 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$_2$S and CO$_2$ with alkanolamines. The feed gas containing undesirable amounts of H$_2$S 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$_2$S and CO$_2$ react exothermically with the amine solution. The gas exiting the absorber contains the desired amount of H$_2$S 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 H₂S and CO₂ 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 H₂S concentration; therefore, in many cases this gas stream is sent to a Claus or other type of sulfur recovery unit which converts the H₂S into useful elemental sulfur. Many times the Claus process includes an acid gas treating system which recovers the unconverted H₂S in the Claus tail gas. In this way the maximum amount of H₂S is converted into elemental sulfur. If the cost of a sulfur recovery system cannot 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 H₂S and CO₂. The most common industrial alkanolamines include monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (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 CO₂ (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$_2$S, 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$_2$S 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 selectively remove H$_2$S 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$_2$S and CO$_2$ Removal

Many acid gas applications require bulk removal of both H$_2$S and CO$_2$. Bulk removal means purifying the feed gas to very low concentrations of H$_2$S and CO$_2$. For example, a typical natural gas purification application might process a
feed gas with 1% H₂S and 30% CO₂ down to an outlet gas composition of less than 4 ppm H₂S and 1% CO₂ (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 H₂S and CO₂ removal. These amines react directly with both acid gases. Primary and secondary amines react with H₂S through an instantaneous proton transfer mechanism. The reaction with CO₂, although not instantaneous, is very fast and forms a carbamate species. These fast reactions result in easy removal of H₂S and CO₂. 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 H₂S

For many applications, a feed gas may contain both H₂S and CO₂ but only the H₂S needs to be removed. These applications require selective removal of the H₂S. For example, the feed gas to a Claus unit needs to be rich in H₂S to obtain a reasonable efficiency. Therefore, a gas stream containing both H₂S and CO₂ can be selectively treated so that the gas leaving the stripper is rich in H₂S and can be fed to a Claus unit. Other selective applications include Claus tail gas cleanup and recovery of CO₂ 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 H₂S but slowly with CO₂. Before reacting with tertiary or hindered amines, CO₂ must first react with water to form carbonic acid which is a slow reaction; however, H₂S 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 H₂S over CO₂ because CO₂ 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 CO₂ 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 CO₂ 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 H₂S and CO₂ 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 H₂S and CO₂ 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 H₂S and CO₂ 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 H₂S and CO₂ 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 CO₂ and H₂S equilibrium constants were fit to an empirical expression with six adjustable parameters. Finally, the CO₂-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$_2$S equilibrium constant, H$_2$S 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-H₂S-CO₂ 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
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<th>Gas</th>
<th>CO2 Kinetic Model</th>
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<td>Cornelissen</td>
<td>Trayed absorber</td>
<td>Exptl data from a 0.11 m diameter absorber</td>
<td>H2S-amine equil. determined by experiment.</td>
<td>not available</td>
<td>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.</td>
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<tr>
<td>Yu and Astarita</td>
<td>packed absorbers</td>
<td>none</td>
<td>Semi-empirical fit to data from Jou et al. (1981).</td>
<td>not available</td>
<td>Reversible, second order kinetics are considered. The rate constant is from Yu et al. (1985).</td>
</tr>
<tr>
<td>Kelly et al.</td>
<td>Packed absorbers</td>
<td>Exptl data from a 0.053 m i.d. absorber</td>
<td>Edwards (1974). Several other methods were compared.</td>
<td>Redlich-Kwong modified by Cheuh and Prausnitz (1967)</td>
<td>Reversible, second order kinetics are considered. CO2 kinetic data is taken from Yu (1985).</td>
</tr>
<tr>
<td>van Swaaij et al.</td>
<td>absorber/stripper, Claus sulfur recovery unit, Shell Claus off-gas treater tail gas unit</td>
<td>none</td>
<td>Blauwboff and van Swaaij (1980)</td>
<td>Soave-Redlich-Kwong</td>
<td>Reversible reactions are considered. Rate constants from Danckwerts and Sharma (1966), Blauwboff et al. (1984), and Blauwboff (1982).</td>
</tr>
<tr>
<td>This work</td>
<td>trayed absorbers and strippers</td>
<td>none</td>
<td>Empirical fit to experimental data of Jou et al. (1982, 1986)</td>
<td>Ideal gas</td>
<td>Reversible, second order kinetics are considered. CO2-MDEA rate constant is from Litel et al. (1990). CO2-OH-value is from Astarita et al (1983).</td>
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<tr>
<td>Cornelissen</td>
<td>Uses analytical expressions from Danckwerts (1970). The concentration profiles are</td>
<td>Single trays are solved using Kevorkian and Snoek (1973)</td>
<td>not available</td>
<td>Cornelissen (1980)</td>
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<td>linearized to yield algebraic equations. Mass transfer parameters are from experiments.</td>
<td>A second method iterates on the absorber tray-by-tray</td>
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<tr>
<td>Yu and Astarita</td>
<td>Algebraic model that uses the pseudo-first order enhancement factor with the amine concentration included. Mass transfer parameters: Onda et al. (1968)</td>
<td>Runge-Kutta</td>
<td></td>
<td>Yu (1985); Yu and Astarita (1987a); Yu and Astarita (1987b)</td>
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</table>
were unavailable; however, the H$_2$S-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$_2$S can cause H$_2$S 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$_2$S 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

<table>
<thead>
<tr>
<th>Model</th>
<th>Type of Amine Simulated</th>
<th>Flow Sheet Options</th>
<th>Thermodynamic Models Liquid</th>
<th>Gas</th>
<th>CO₂ Kinetic Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bullin et al.</td>
<td>MEA, DEA, DGA, MDEA, mixed amines</td>
<td>Trayed or packed absorbers/stripers, flash tanks, heat exchangers, column side streams, pumps, reclaimer, holdup tank</td>
<td>Modified Kent and Eisenberg (1976) model</td>
<td>Soave-Redlich-Kwong</td>
<td>Developed a kinetic model to predict effect of residence time, solution concentration, pressure, temperature, and type of amine on the CO₂ absorption rate.</td>
</tr>
<tr>
<td>Weiland et al.</td>
<td>MEA, DEA, DIPA, MDEA, DGA, mixed amines</td>
<td>Trayed or packed absorbers/stripers, flash tanks, heat exchangers, column side streams</td>
<td>Chakravarty (1985) added to Deshmukh and Mather (1981).</td>
<td>Peng-Robinson</td>
<td>The MEA/DEA reactions are second order, irreversible in the absorber. All reactions are considered instantaneous in the stripper.</td>
</tr>
<tr>
<td>Model</td>
<td>Mass Transfer Model</td>
<td>Numerical Approach</td>
<td>Computer Specifications</td>
<td>References</td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------------------------------------------</td>
<td>---------------------------------------------------------</td>
<td>-------------------------</td>
<td>---------------------------------</td>
<td></td>
</tr>
<tr>
<td>Bullin et al.</td>
<td>not available</td>
<td>Rigorous tray-by-tray calculations using Ishii-Otto (1973)</td>
<td>PC version</td>
<td>Bullin et al. (1981); Holness et al. (1984); Polasek et al. (1983); Polasek et al. (1990).</td>
<td></td>
</tr>
<tr>
<td>Tomcej et al.</td>
<td>Enhancement factor:&lt;br&gt; Uses pseudo-first order expression&lt;br&gt; Mass transfer coefficients:&lt;br&gt; Bubble cap trays - Sharma et al. (1969)</td>
<td>Rigorous tray-by-tray calculations using a revised version of Ishii-Otto (1973)</td>
<td>Amdahl 470V (1 to 3 cpu seconds)&lt;br&gt; PC version</td>
<td>Tomcej et al. (1983); Tomcej et al. (1986); Tomcej and Ott (1986); Tomcej et al. (1987)</td>
<td></td>
</tr>
<tr>
<td>Weiland et al.</td>
<td>Enhancement factor:&lt;br&gt; Abs: MEA/DEA - Welleck et al. (1978)&lt;br&gt; MDEA - 1.0. Str: Olander (1960)&lt;br&gt; Mass transfer coefficients:&lt;br&gt; Packing - Onda et al. (1968)&lt;br&gt; Trays - Scheffe (1984)</td>
<td>Simultaneous solution of equations using Newton-Raphson (Jacobi evaluated using finite differences)</td>
<td>IBM 4341 or VAX 11/780 (2 to 5 cpu minutes)&lt;br&gt; PC version</td>
<td>Chakravarty et al. (1985); Sardar et al. (1985a, 1985b); Sivasubaramaniam et al. (1985a, 1985b); Sivasubaramaniam (1985); Vickery and Weiland (1986); Vickery et al. (1988)</td>
<td></td>
</tr>
<tr>
<td>Dow Chemical Company</td>
<td>CO₂ enhancement factor:&lt;br&gt; Calculated from the free amine profile. The amine profile is determined by the H₂S absorption rate assuming CO₂ has no effect on this rate. Mass transfer coefficients: AIChE correlation (1958), proprietary correlations, and Scheffe (1984).</td>
<td>Restructure the nonlinear equations to reduce the degree of the system and solve using Newton-Raphson or substitution</td>
<td>VAX 11/780 (5 to 10 cpu seconds)</td>
<td>Katti and Langfitt (1986); Katti and Wolcott (1987); Katti et al. (1988)</td>
<td></td>
</tr>
</tbody>
</table>
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 flows 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 CO₂ absorption in mixed amine systems**

For mixed amine systems, correct representation of the CO₂ 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 CO₂ 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$_2$S-MDEA-H$_2$O 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$_2$S 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 H₂S and CO₂ 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 H₂S and CO₂ based on mass transfer. This process consists of solving the following equations:

\[ V_{\text{out},k} = V_{\text{in},k} + y_k \left( V_{\text{out}} - V_{\text{in}} \right) + k_g a' D_{\text{avg},k} \]  \hspace{1cm} (3.1)

where \( k \) is CO₂ or H₂S and

\[ D_{\text{avg},k} = \frac{D_{\text{in},k} - D_{\text{out},k}}{\ln \frac{D_{\text{in},k}}{D_{\text{out},k}}} \]  \hspace{1cm} (3.2)

\[ D_{\text{in},k} = P_{\text{in},k,i} - P_{\text{in},k,b} \]  \hspace{1cm} (3.3)

\[ D_{\text{out},k} = P_{\text{out},k,i} - P_{\text{out},k,b} \]  \hspace{1cm} (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:

\[ T_{\text{out}} = T_{\text{Lout}} + (T_{\text{in}} - T_{\text{Lout}}) \exp (-N_q) \]  \hspace{1cm} (3.5)

\[ V_{\text{out},w} (\Delta H_{\text{out},w} + \Delta H_{\text{rxn},w}) = \sum_{k=1}^{n} V_{\text{in},k} \Delta H_{\text{V}_{\text{in},k}} - \sum_{k=1}^{n} L_{\text{out},k} \Delta H_{\text{L}_{\text{out},k}} - \sum_{k=1}^{n-1} V_{\text{out},k} \Delta H_{\text{V}_{\text{out},k}} + \sum_{k=1}^{n-1} (V_{\text{in},k} - V_{\text{out},k}) \Delta H_{\text{rxn},k} + V_{\text{in},w} \Delta H_{\text{rxn},w} \]  \hspace{1cm} (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:

\[
L_{in,k} = L_{out,k} + V_{out,k} - V_{in,k}
\]  

(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:

\[
P - P_{H_2S,i} - P_{CO_2,i} - P_{w,i} - P_{inert,i} = 0
\]  

(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 H₂S and CO₂. A two variable secant method is used to update the guesses and the towers are repetitively converged until the rich loadings of H₂S and CO₂ 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 H₂S and CO₂ 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 (H₂S, CO₂, H₂O, inert)
  - Steam to the stripper
  - Rich liquid out of the absorber (H₂O, 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): H₂S dissociation
  - H₂CO₃ dissociation
  - Amine protonation
  - Heat of vaporization of H₂O (cal/mole)

Initial Guesses:
- Rich solution loadings (mole/s): Two guesses for both H₂S and CO₂
- 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):

\[ \ln \mu^0 = B_1 + \frac{B_2}{T} + B_3T \]  \hspace{1cm} (3.9)

\[ B_1 = -19.52 - 23.40wam - 31.24wam^2 + 36.17wam^3 \]
\[ B_2 = 3912 + 4894wam + 8477wam^2 - 8358wam^3 \]
\[ B_3 = 0.02112 + 0.03339wam + 0.0278wam^2 - 0.04202wam^3 \]
\[ wam = \text{wmdea} + 0.980\text{wdea} + 0.876\text{wmea} \]

where \( \text{wmdea}, \text{wdea}, \) and \( \text{wmea} \) 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:

\[ \ln \mu^0 = -34.51 + \frac{7443}{T} + 0.03951T \]  \hspace{1cm} (3.10)
Toman and Rochelle (1989) report the effect of CO$_2$ loading at 25°C on the viscosity of 50 wt% MDEA solutions:

\[
\ln \frac{\mu}{\mu^0} = 0.7527 \text{ [CO}_2\text{ loading]} \tag{3.11}
\]

where $\mu^0$ 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):

\[
\ln \frac{\mu}{\mu^0} = 0.7527 \left(\frac{298}{T}\right)^2 \text{ [CO}_2\text{ loading]} \tag{3.12}
\]

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:

\[
\rho^0_{\text{MDEA}} = 1.0589 - 6.2606 \times 10^{-4} (T - 273) \tag{3.13}
\]

Equation (3.13) was then corrected for CO$_2$ loading using data from Toman and Rochelle (1989) to obtain:

\[
\rho_{\text{MDEA}} = \rho^0_{\text{MDEA}} + 0.009998 \text{[wt% CO}_2\text{]} \tag{3.14}
\]

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:

\[ \ln \mu_w = 0.55479 - 0.028401 (T-273) + 0.000104 (T-273)^2 \]  \hspace{1cm} (3.15)

\[ \rho_w = \frac{999.84 + 16.945 (T-273) - 0.007987 (T-273)^2}{1000 [ 1.0 + 0.01688 (T-273) ]} \]  \hspace{1cm} (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 \( \text{H}_2\text{S}, \text{CO}_2, \) 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 \( \text{CO}_2 \) diffusion coefficient in MDEA is obtained using the \( \text{N}_2\text{O} \) analogy (see section 3.3). Tomcej and Otto (1989) plotted \( \ln(D_{\text{N}_2\text{O}}/T) \) 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 \( D_{\text{N}_2\text{O}} \) 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:

\[ \ln \frac{D_{\text{N}_2\text{O}}}{T} = -30.7509 - 0.7785 \ln \mu^o \]  \hspace{1cm} (3.17)

The value of the \( \text{CO}_2 \) diffusivity for unloaded, 50 wt\% MDEA (\( \text{D}^o\text{CO}_2 \)) is then given by multiplying \( D_{\text{N}_2\text{O}} \) from equation (3.17) by 1.1. The value of the \( \text{CO}_2 \) diffusivity for the loaded solution is then (Toman and Rochelle, 1989):
\[ D_{CO_2} = D^{0}_{CO_2} \left( \frac{\mu^0}{\mu} \right)^{0.6} \]  \hspace{1cm} (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 $8.08 \times 10^{-10}$ m²/s. To correct this diffusivity for temperature and viscosity, the modified Stokes-Einstein relationship is used:

\[ D_{MDEA} = 8.08 \times 10^{-10} \left( \frac{T}{298} \right) \left( \frac{\mu_w}{\mu} \right)^{0.6} \]  \hspace{1cm} (3.19)

The diffusion coefficient for H₂S is calculated in an analogous way to MDEA. From the CRC Handbook of Physics and Chemistry the diffusion coefficient for H₂S in water at 16°C is $1.77 \times 10^{-9}$ m²/s. Using the modified Stokes-Einstein equation:

\[ D_{H_2S} = 1.77 \times 10^{-9} \left( \frac{T}{289} \right) \left( \frac{\mu_w}{\mu} \right)^{0.6} \]  \hspace{1cm} (3.20)

### 3.2.4 Conversion of Molality to Molarity

Liquid concentrations throughout the model are represented in units of molality (mole/kg H₂O). 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

\[ C_M = \frac{0.044 \ TCO_2 + 0.034 \ TH_2S + 0.119 \ TAM + 1.0}{\rho_{MDEA}} \]  \hspace{1cm} (3.21)
where TCO₂, TH₂S, and TAM represent the molal concentration of CO₂, H₂S, 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 H₂S and CO₂ are calculated from the interfacial liquid concentrations using Henry's law.

The physical absorption of CO₂ and H₂S into aqueous alkanolamines cannot be measured directly because both gases react with these solutions. In the case of H₂S, 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):

\[
\ln (H_{H₂S}) = 342.595 + 0.0595651(T) - 55.0551 \ln(T) - \frac{13236.8}{T} \quad (3.22)
\]

In the case of CO₂, many researchers have obtained the CO₂ Henry's constant by measuring the N₂O Henry's constant in aqueous amine solutions and assuming the following relationship holds:

\[
\frac{H_{CO₂}}{H_{N₂O}} = \frac{H_{∞CO₂}}{H_{∞N₂O}} \quad (3.23)
\]

where \(H_{∞CO₂}\) and \(H_{∞N₂O}\) are aqueous, infinite dilution values (Haimour et al., 1985). Using data based on this N₂O analogy, an expression for the CO₂ 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):

\[
\ln \left( H_{\infty}^{\text{CO}_2} \right) = 94.4914 - 0.010454(T) - 11.4519 \ln(T) - \frac{6789.04}{T} \quad (3.24)
\]

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:

\[
H^{\text{CO}_2} = H_{\infty}^{\text{CO}_2} + C_M \left[ 0.032361(\text{wt } \% \text{ MDEA}) + 0.0035283(\text{wt } \% \text{ MDEA})^2 \right] \quad (3.25)
\]

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:

\[
\log_{10} \frac{H}{H^0} = 0.09[MDEAH^+] \quad (3.26)
\]

where \(H^0\) 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 \(H^0\) from equation (3.25) at the desired temperature. The final expression for the CO_2 Henry's constant is then:

\[
\log_{10} (H_{\text{CO}_2}) = \log_{10} (H_{\infty}^{\text{CO}_2}) + C_M (0.09[MDEAH^+]) \quad (3.27)
\]
Figure 3.1: Comparison of CO₂ 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 \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) in MDEA consists of the following reactions:

\[
\begin{align*}
\text{H}_2\text{S} \text{(aq)} + \text{R}_3\text{N} & \leftrightarrow \text{HS}^- + \text{R}_3\text{NH}^+ & K_{\text{H}_2\text{S}} & \quad (3.28) \\
\text{CO}_2 \text{(aq)} + \text{R}_3\text{N} + \text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^- + \text{R}_3\text{NH}^+ & K_{\text{CO}_2} & \quad (3.29) \\
\text{HCO}_3^- + \text{OH}^- & \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} & K_{\text{HCO}_3} & \quad (3.30) \\
\text{R}_3\text{N} + \text{H}_2\text{O} & \leftrightarrow \text{R}_3\text{NH}^+ + \text{OH}^- & K_{\text{MDEA}} & \quad (3.31)
\end{align*}
\]

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 \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) 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 \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) 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:

\[
\ln \frac{H}{K} = (\frac{H}{K})_0 + aI + bI^{1/2} + c[R_3N]^d + \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \tag{3.32}
\]

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

where \( (\frac{H}{K})_0, a, b, c, d, \) 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:

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

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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\text{H}_2\text{S}$</th>
<th>$\text{CO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(H/K)_o$</td>
<td>-17.28</td>
<td>2.961</td>
</tr>
<tr>
<td>a</td>
<td>-0.1119</td>
<td>0.3932</td>
</tr>
<tr>
<td>b</td>
<td>-0.5602</td>
<td>-2.178</td>
</tr>
<tr>
<td>c</td>
<td>19.390</td>
<td>0.1082</td>
</tr>
<tr>
<td>d</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>$\Delta H/R$</td>
<td>-4896</td>
<td>-7036</td>
</tr>
</tbody>
</table>

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:

\[
\log_{10} K_w = 285.52 - \frac{11988}{T} + 0.061656 T - 48.737 \ln T
\]  
(3.35)

\[
\log_{10} \left( \frac{K_{MDEA}}{K_w} \right) = 14.309 - 0.019416 T
\]  
(3.36)

\[
\ln (K_{\text{HCO}_3}K_w) = 220.067 - 35.4819 \ln T - \frac{12431.7}{T}
\]  
(3.37)

The above set of equilibrium expressions were used to compare the calculated partial pressure of $\text{CO}_2$ and $\text{H}_2\text{S}$ to the experimental values over which the equilibrium constants were fit. The results of this comparison for $\text{CO}_2$ and $\text{H}_2\text{S}$ are shown in Figures 3.2 and 3.3, respectively. For both $\text{CO}_2$ and $\text{H}_2\text{S}$ the fit is within 20% for loadings greater than about 0.1; however, the predictions show a
Figure 3.2: Comparison of the Calculated CO₂ Partial Pressures to Experimental CO₂ 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$_2$S Partial Pressures to Experimental H$_2$S 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: (○) - 3.04M, (∆) - 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 \( \text{H}_2\text{S}, \text{CO}_2, \) and amine, this subroutine divides the totals into species molalities for the bulk solution. Given that there are eight unknown species concentrations (\( \text{OH}^- \), \( \text{R}_3\text{NH}^+ \), \( \text{R}_3\text{N} \), \( \text{HS}^- \), \( \text{H}_2\text{S} \), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), \( \text{CO}_2 \)) the eight equations to be solved are:

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

5) \[ [\text{R}_3\text{N}]_{\text{total}} = [\text{R}_3\text{N}] + [\text{R}_3\text{NH}^+] \] (3.38)

6) \[ [\text{H}_2\text{S}]_{\text{total}} = [\text{H}_2\text{S}] + [\text{HS}^-] \] (3.39)

7) \[ [\text{CO}_2]_{\text{total}} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \] (3.40)

8) \[ [\text{R}_3\text{NH}^+] = [\text{HS}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \] (3.41)

These equations are solved by converging on the \( \text{OH}^- \) 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 \( \text{H}_2\text{S} \) with aqueous MDEA is a proton transfer and is instantaneous with respect to diffusion; therefore, \( \text{H}_2\text{S} \) is at equilibrium at the interface. The reaction of \( \text{CO}_2 \) with MDEA is slow with respect to diffusion; therefore, \( \text{CO}_2 \) has to diffuse partially into the liquid phase before its reaction reaches equilibrium. To determine the \( \text{CO}_2 \)
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):

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

\[ k_I' (\text{dm/s}) = 1.3 U^{0.25} S^{-0.5} D_L^{0.5} \] (3.43)

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

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

\[ N_g = \frac{k_g a' P}{G} \] (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:

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

\[
k_{i}a'' \ (1/s) = 10.0 \left[ 197 \ D_L^{0.5} \left( 0.12649 \ F + 0.17 \right) \right] \quad (3.47)
\]

where

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

To obtain the values of \( k_g \) and \( k_{i}^* \), the interfacial area is calculated from the following for weir heights of 25-75 mm (Bisio and Kabel, 1985):

\[
a'' \ (\text{dm}^2/\text{dm}^3) = 0.075794 + 9.8521 \ F - 0.94321 \ F^2 + 0.031225 \ F^3 \quad (3.49)
\]

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):

\[
N_g = k_g a'' t_g \quad (3.50)
\]

where

\[
t_g = \frac{(1 - \phi) \ S}{\phi \ U} \quad (3.51)
\]

\[
\phi = \frac{S}{S_{eff}} \quad (3.52)
\]

Regardless of the type of tray used, the value for \( k_{i}^* \) is calculated using the \( \text{CO}_2 \) 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:

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

(3.53)

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

(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$_2$S 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 \( x=\infty \), and is smooth and continuous in between.
After these differential equations are solved, the following expression for the
enhancement factor is obtained:

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

(3.55)

\[
E_i = \sqrt{1 + M} 
\]

(3.56)

\[
M = \frac{D_{CO_2}}{k_1^{o_2}} \left( k_{MDEA} [R_3N]_i + k_{OH} [OH^-]_i \right) 
\]

(3.57)

\[
\Theta = \frac{[CO_2]_{le} - [CO_2]_b}{[CO_2]_i - [CO_2]_b} 
\]

(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$_2$S 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:

$$\sqrt{D_{R3N}} ([R3N] - [R3N]_i) + \sqrt{D_{R3NH}} ([R3NH^+] - [R3NH^+]_i) = 0 \quad (3.60)$$

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:

$$k_g \left( P_{H2S_i} - P_{H2S} \right) = \frac{k_l}{\sqrt{D_{CO2}}} \left[ \sqrt{D_{H2S}} \left( [H2S] - [H2S]_i \right) + \sqrt{D_{HS}} \left( [HS^-] - [HS^-]_i \right) \right] \quad (3.61)$$

$CO_2$ flux based on species concentrations:

$$k_g \left( P_{CO2_i} - P_{CO2} \right) = k_l \left[ [CO2] - [CO2]_i + \sqrt{\frac{D_{HCO3}}{D_{CO2}}} \left( [HCO3^-] - [HCO3^-]_i \right) + \sqrt{\frac{D_{CO2}}{D_{CO2}}} \left( [CO3^=] - [CO3^=}_i \right) \right] \quad (3.62)$$

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:

$$k_g \left( P_{CO2} - P_{CO2} \right) = E_{CO2} k_l^* \left( [CO2] - [CO2]_i \right) \quad (3.63)$$

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.

$$CO_2 + OH^- \leftrightarrow HCO3^- \quad (3.64)$$

$$CO_2 + R3N + H2O \leftrightarrow HCO3^- + R3NH^+ \quad (3.65)$$
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.

\[
\log_{10} k_{OH} = 13.635 - \frac{2895}{T} + 0.081
\]  \hspace{1cm} (3.66)

\[
k_{MDEA} = 1.34 \times 10^9 \exp\left(-\frac{5771}{T}\right)
\]  \hspace{1cm} (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):

\[
N_q = N_g \left[ \frac{\kappa}{\rho \ C_p \ D_G} \right]^{2/3}
\]  \hspace{1cm} (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

\[ C_p \left( \frac{J}{\text{mole} \cdot ^\circ \text{C}} \right) = C_1 + C_2 \times 10^{-2} T + C_3 \times 10^{-5} T^2 + C_4 \times 10^{-9} T^3 \]

<table>
<thead>
<tr>
<th>Component</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>33.51</td>
<td>1.547</td>
<td>0.3012</td>
<td>-3.292</td>
<td>a</td>
</tr>
<tr>
<td>CO₂</td>
<td>36.11</td>
<td>4.233</td>
<td>-2.887</td>
<td>7.464</td>
<td>a</td>
</tr>
<tr>
<td>H₂O</td>
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<td>0.688</td>
<td>-0.7604</td>
<td>-3.593</td>
<td>a</td>
</tr>
<tr>
<td>Inert (N₂)</td>
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<tr>
<td>H₂S</td>
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<td>0.0</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td>CO₂</td>
<td>75.40</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td>H₂O</td>
<td>75.40</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>a</td>
</tr>
<tr>
<td>MDEA</td>
<td>68.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>c</td>
</tr>
</tbody>
</table>

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 H₂S and CO₂ 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: H₂O, MDEA, DEA, MEA, DGA, CO₂, H₂S, H₂CO₃, RR’NCOOH, other molecules
Cations: H₃O⁺, MDEAH⁺, DEA⁺, MEAH⁺, DAGA⁺, other cations
Anions: OH⁻, RR’NCOO⁻, HCO₃⁻, HS⁻, CO₃²⁻, other anions

The apparent components are those listed as molecular above. The components H₂CO₃ (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-CO₂-H₂S 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 H₂S and CO₂, 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 H₂S and CO₂ 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):

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

(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-H₂O-CO₂-H₂S 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$_2$S and CO$_2$.

\[ \ln H_i \text{ (Pa)} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T \]

<table>
<thead>
<tr>
<th>Gas</th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>C$_4$</th>
<th>Temperature Range (°C)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td>358.138</td>
<td>-13236.8</td>
<td>-55.0551</td>
<td>0.059565</td>
<td>0 - 150</td>
<td>a</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>170.7126</td>
<td>-8477.711</td>
<td>-21.9574</td>
<td>0.005781</td>
<td>0 - 100</td>
<td>b</td>
</tr>
</tbody>
</table>

a - Edwards et al. (1978); b - Chen et al., 1979.
Table 4.2: Rackett Binary Interaction Parameters.

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

<table>
<thead>
<tr>
<th>Comp.</th>
<th>H$_2$O</th>
<th>MDEA</th>
<th>DEA</th>
<th>MEA</th>
<th>DGA</th>
<th>CO$_2$</th>
<th>H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.0</td>
<td>0.1442</td>
<td>0.1286</td>
<td>0.07696</td>
<td>0.1203</td>
<td>0.01115</td>
<td>0.01331</td>
</tr>
<tr>
<td>MDEA</td>
<td>0.1442</td>
<td>0.0</td>
<td>5.87E-4</td>
<td>0.01286</td>
<td>1.41E-3</td>
<td>0.08107</td>
<td>0.07593</td>
</tr>
<tr>
<td>DEA</td>
<td>0.1286</td>
<td>5.87E-4</td>
<td>0.0</td>
<td>7.99E-3</td>
<td>1.77E-4</td>
<td>0.06873</td>
<td>0.06395</td>
</tr>
<tr>
<td>MEA</td>
<td>0.07696</td>
<td>0.01286</td>
<td>7.99E-3</td>
<td>0.0</td>
<td>5.80E-3</td>
<td>0.03118</td>
<td>0.02788</td>
</tr>
<tr>
<td>DGA</td>
<td>0.1203</td>
<td>1.41E-3</td>
<td>1.77E-4</td>
<td>5.80E-3</td>
<td>0.0</td>
<td>0.06234</td>
<td>0.05776</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.01115</td>
<td>0.08107</td>
<td>0.06873</td>
<td>0.03118</td>
<td>0.06234</td>
<td>0.0</td>
<td>9.77E-5</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.01331</td>
<td>0.07593</td>
<td>0.06395</td>
<td>0.02788</td>
<td>0.05776</td>
<td>9.77E-5</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 4.3: Pure Component Molecular Weight and Critical Properties for DEA, MDEA, and DGA.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>MW</th>
<th>$T_c$ (°K)</th>
<th>$P_c$ (kPa)</th>
<th>$V_c$ (m³ kmol⁻¹)</th>
<th>$Z_c$</th>
<th>$\omega$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEA</td>
<td>105.14</td>
<td>715.0</td>
<td>3270.0</td>
<td>0.3490</td>
<td>0.192</td>
<td>1.046</td>
<td>a</td>
</tr>
<tr>
<td>MDEA</td>
<td>119.16</td>
<td>677.8</td>
<td>3876.1</td>
<td>0.3932</td>
<td>0.192</td>
<td>1.242</td>
<td>b</td>
</tr>
<tr>
<td>DGA</td>
<td>105.14</td>
<td>674.6</td>
<td>4354.9</td>
<td>0.327</td>
<td>0.254</td>
<td>1.046</td>
<td>c</td>
</tr>
</tbody>
</table>

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.

\[
\ln P^0 (Pa) = D_1 + \frac{D_2}{T + D_3} + D_4 T + D_5 \ln T
\]

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

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.

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

<table>
<thead>
<tr>
<th>Amine</th>
<th>A</th>
<th>B</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>36.76</td>
<td>14836.0</td>
<td>a</td>
</tr>
<tr>
<td>DEA</td>
<td>28.01</td>
<td>9277.0</td>
<td>a</td>
</tr>
<tr>
<td>MDEA</td>
<td>24.74</td>
<td>8989.3</td>
<td>b</td>
</tr>
<tr>
<td>DGA</td>
<td>28.01</td>
<td>9277.0</td>
<td>*</td>
</tr>
</tbody>
</table>

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:

\[
\begin{align*}
2\text{H}_2\text{O} & \Leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+ \\
\text{H}_2\text{S} + \text{H}_2\text{O} & \Leftrightarrow \text{HS}^- + \text{H}_3\text{O}^+ \\
\text{HCO}_3^- + \text{H}_2\text{O} & \Leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \\
\text{RR'}\text{R}''\text{NH}^+ + \text{H}_2\text{O} & \Leftrightarrow \text{RR'}\text{R}''\text{N} + \text{H}_3\text{O}^+ \\
\text{CO}_2 + 2\text{H}_2\text{O} & \Leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \\
\text{RR'}\text{NCOO}^- + \text{H}_2\text{O} & \Leftrightarrow \text{RR'}\text{NH} + \text{HCO}_3^- \\
\end{align*}
\]

\[K_w \quad (4.2) \quad K_{\text{H}_2\text{S}} \quad (4.3) \quad K_{\text{HCO}_3^-} \quad (4.4) \quad K_{\text{amine}} \quad (4.5) \quad K_{\text{CO}_2} \quad (4.6) \quad K_{\text{carb}} \quad (4.7)\]

Equation (4.7) applies only when a primary or secondary amine is present. The dissociation of bisulfide (HS^-) to sulfide (S^2-) 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

\[ \tau = a + b/T \]

<table>
<thead>
<tr>
<th>Molecule Pair</th>
<th>a</th>
<th>b</th>
<th>Accentric Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O - MEA</td>
<td>1.674</td>
<td>0.00</td>
<td>0.2</td>
</tr>
<tr>
<td>MEA - H_2O</td>
<td>0.000</td>
<td>-649.75</td>
<td>0.2</td>
</tr>
<tr>
<td>H_2O - DEA</td>
<td>-0.965</td>
<td>1317.63</td>
<td>0.2</td>
</tr>
<tr>
<td>DEA - H_2O</td>
<td>-0.661</td>
<td>-718.08</td>
<td>0.2</td>
</tr>
<tr>
<td>H_2O - MDEA</td>
<td>0.000</td>
<td>0.00</td>
<td>0.2</td>
</tr>
<tr>
<td>MDEA - H_2O</td>
<td>0.000</td>
<td>0.00</td>
<td>0.2</td>
</tr>
<tr>
<td>H_2O - DGA</td>
<td>1.992</td>
<td>0.00</td>
<td>0.2</td>
</tr>
<tr>
<td>DGA - H_2O</td>
<td>0.000</td>
<td>-770.41</td>
<td>0.2</td>
</tr>
<tr>
<td>H_2O - H_2S</td>
<td>-3.674</td>
<td>1155.9</td>
<td>0.2</td>
</tr>
<tr>
<td>H_2S - H_2O</td>
<td>-3.674</td>
<td>1155.9</td>
<td>0.2</td>
</tr>
<tr>
<td>H_2O - CO_2</td>
<td>10.064</td>
<td>-3268.14</td>
<td>0.2</td>
</tr>
<tr>
<td>CO_2 - H_2O</td>
<td>10.064</td>
<td>-3268.14</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* 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

\[ \tau = a + b/T \]

<table>
<thead>
<tr>
<th>Molecule - Ion Pair</th>
<th>( a )</th>
<th>( b )</th>
<th>Accentric Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MEA = RNH₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MEA}^+\text{, HS}^-) )</td>
<td>6.844</td>
<td>501.83</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MEA}^+\text{, HS}^-) - \text{H}_2\text{O} )</td>
<td>-3.560</td>
<td>-197.12</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MEA}^+\text{, HCO}_3^-) )</td>
<td>4.550</td>
<td>1218.19</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MEA}^+\text{, HCO}_3^-) - \text{H}_2\text{O} )</td>
<td>-4.088</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MEA}^+\text{, MEACOO}^-) )</td>
<td>10.268</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MEA}^+\text{, MEACOO}^-) - \text{H}_2\text{O} )</td>
<td>-5.098</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>DGA = RNH₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{DGA}^+\text{, HS}^-) )</td>
<td>7.744</td>
<td>375.72</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{DGA}^+\text{, HS}^-) - \text{H}_2\text{O} )</td>
<td>-4.337</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{DGA}^+\text{, HCO}_3^-) )</td>
<td>0.0</td>
<td>2960.94</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{DGA}^+\text{, HCO}_3^-) - \text{H}_2\text{O} )</td>
<td>-4.251</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{DGA}^+\text{, DGACOO}^-) )</td>
<td>11.424</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{DGA}^+\text{, DGACOO}^-) - \text{H}_2\text{O} )</td>
<td>-5.328</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>DEA = R₂NH</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{DEA}^+\text{, HS}^-) )</td>
<td>5.199</td>
<td>1519.60</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{DEA}^+\text{, HS}^-) - \text{H}_2\text{O} )</td>
<td>-2.836</td>
<td>-636.95</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{DEA}^+\text{, HCO}_3^-) )</td>
<td>4.204</td>
<td>1588.19</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{DEA}^+\text{, HCO}_3^-) - \text{H}_2\text{O} )</td>
<td>-4.434</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{DEA}^+\text{, DEACOO}^-) )</td>
<td>11.549</td>
<td>102.66</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{DEA}^+\text{, DEACOO}^-) - \text{H}_2\text{O} )</td>
<td>-5.580</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>MDEA = R₃N</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MDEA}^+\text{, HS}^-) )</td>
<td>3.735</td>
<td>1036.04</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MDEA}^+\text{, HS}^-) - \text{H}_2\text{O} )</td>
<td>-3.225</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MDEA}^+\text{, HCO}_3^-) )</td>
<td>5.864</td>
<td>1147.90</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MDEA}^+\text{, HCO}_3^-) - \text{H}_2\text{O} )</td>
<td>-4.511</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MDEA}^+\text{, RHNCOO}^-) )</td>
<td>9.903</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MDEA}^+\text{, RHNCOO}^-) - \text{H}_2\text{O} )</td>
<td>-4.776</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} - (\text{MDEA}^+\text{, DEACOO}^-) )</td>
<td>10.387</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( (\text{MDEA}^+\text{, DEACOO}^-) - \text{H}_2\text{O} )</td>
<td>-4.965</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 4.8: Mole Fraction- Based Equilibrium Constants Used in the Model

\[
\ln K_i = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T
\]

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>Comp</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(C_4)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>H2O</td>
<td>132.899</td>
<td>-13445.9</td>
<td>-22.4773</td>
<td>0.0</td>
<td>a</td>
</tr>
<tr>
<td>4.3</td>
<td>H2S</td>
<td>214.582</td>
<td>-12995.4</td>
<td>-33.5471</td>
<td>0.0</td>
<td>a</td>
</tr>
<tr>
<td>4.4</td>
<td>CO2</td>
<td>231.465</td>
<td>-12092.1</td>
<td>-367816</td>
<td>0.0</td>
<td>a</td>
</tr>
<tr>
<td>4.5</td>
<td>HCO3^-</td>
<td>216.049</td>
<td>-12431.7</td>
<td>-354819</td>
<td>0.0</td>
<td>a</td>
</tr>
<tr>
<td>4.6</td>
<td>MEA</td>
<td>2.1211</td>
<td>-8189.38</td>
<td>0.0</td>
<td>-0.007484</td>
<td>b</td>
</tr>
<tr>
<td>4.6</td>
<td>DEA</td>
<td>-6.7936</td>
<td>-5927.65</td>
<td>0.0</td>
<td>0.0</td>
<td>c</td>
</tr>
<tr>
<td>4.6</td>
<td>MDEA</td>
<td>-9.4165</td>
<td>-4234.98</td>
<td>0.0</td>
<td>0.0</td>
<td>d</td>
</tr>
<tr>
<td>4.6</td>
<td>DGA</td>
<td>1.6957</td>
<td>-8431.65</td>
<td>0.0</td>
<td>-0.005037</td>
<td>e</td>
</tr>
<tr>
<td>4.7</td>
<td>MEA</td>
<td>2.8898</td>
<td>-3635.09</td>
<td>0.0</td>
<td>0.0</td>
<td>f</td>
</tr>
<tr>
<td>4.7</td>
<td>DEA</td>
<td>4.5146</td>
<td>-3417.34</td>
<td>0.0</td>
<td>0.0</td>
<td>f</td>
</tr>
<tr>
<td>4.7</td>
<td>DGA</td>
<td>8.8334</td>
<td>-5274.4</td>
<td>0.0</td>
<td>0.0</td>
<td>f</td>
</tr>
</tbody>
</table>

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:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]  
\[ \text{CO}_2 + \text{RR'}\text{NH} \rightleftharpoons \text{RR'}\text{NCOOH} \]  

The molecular species carbonic acid (H₂CO₃) 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:

\[
\begin{align*}
H_2CO_3 + H_2O & \rightleftharpoons HCO_3^- + H_3O^+ \quad K_{H_2CO_3} \quad (4.10) \\
RR'NCOOH + H_2O & \rightleftharpoons RR'NCOO^- + H_3O^+ \quad K_{carbH} \quad (4.11)
\end{align*}
\]

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):

\[
\begin{align*}
CO_2 + H_2O + MDEA & \rightleftharpoons HCO_3^- + MDEAH^+ \quad (4.12) \\
CO_2 + OH^- + MDEA & \rightleftharpoons HCO_3^- + MDEA \quad (4.13) \\
CO_2 + OH^- & \rightleftharpoons HCO_3^- \quad (4.14)
\end{align*}
\]

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:
\[ R_{\text{HCO}_3} = [a_{\text{CO}_2} - a_{\text{CO}_2\text{,HCO}_3,e}] [k_{\text{tam, w}} a_{\text{tam}} a_{\text{w}} + k_{\text{am, w}} a_{\text{am}} a_{\text{w}} + k_{\text{tam, OH}} a_{\text{tam}} a_{\text{OH}} + k_{\text{OH}} a_{\text{OH}}] \quad (4.15) \]

where \( k_{\text{tam, w}} \) represents the rate constant for reaction (4.12), \( k_{\text{am, w}} \) represents (4.12) with a primary or secondary amine, \( k_{\text{tam, OH}} \) represents (4.13), and \( k_{\text{OH}} \) represents (4.14). The constants \( k_{\text{tam, w}} \) and \( k_{\text{tam, OH}} \) are activity based constants regressed by Glasscock (1990) and are discussed in section 4.3.4. The value for \( k_{\text{am, w}} \) was not fit by Glasscock so it is set to zero. The reaction rate constant \( k_{\text{OH}} \) 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 \( a_{\text{CO}_2\text{,HCO}_3,e} \) represents the activity of \( \text{CO}_2 \) 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 \( a_{\text{CO}_2\text{,HCO}_3,e} \) must be calculated. Reaction (4.14) conveniently represents the equilibrium between \( \text{CO}_2 \) and \( \text{HCO}_3^- \). The equilibrium constant for (4.14) is represented by combining the constants for reactions (4.2) and (4.6):

\[ K_{\text{CO}_2\text{,HCO}_3} = \frac{K_{\text{CO}_2}}{K_{\text{w}}} \quad (4.16) \]

The equilibrium \( \text{CO}_2 \) activity is then given by:

\[ a_{\text{CO}_2\text{,HCO}_3,e} = \frac{a_{\text{HCO}_3}}{K_{\text{CO}_2\text{,HCO}_3} a_{\text{OH}}} \quad (4.17) \]

Equation (4.17) is used for all amine systems to calculate the equilibrium \( \text{CO}_2 \)
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 CO₂ and amine. For the case of MEA, the rate expression is:

\[
R_{\text{MEACOO}} = k_{\text{pam}} [\text{CO}_2] [\text{MEA}] \tag{4.18}
\]

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:

\[
\begin{align*}
\text{CO}_2 + \text{DEA} + \text{H}_2\text{O} & \rightleftharpoons \text{DEACOO}^- + \text{H}_3\text{O}^+ \tag{4.19} \\
\text{CO}_2 + \text{DEA} + \text{DEA} & \rightleftharpoons \text{DEACOO}^- + \text{DEAH}^+ \tag{4.20} \\
\text{CO}_2 + \text{DEA} + \text{MDEA} & \rightleftharpoons \text{DEACOO}^- + \text{MDEAH}^+ \tag{4.21}
\end{align*}
\]

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:

\[
R_{\text{carb}} = a_{\text{am}} [a_{\text{CO}_2} - a_{\text{CO}_2,\text{carb},e}] \left[ k_{\text{pam}} + k_{\text{am}} a_{\text{am}} + k_{\text{lam}} a_{\text{lam}} + k_w a_w \right] \tag{4.22}
\]
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:

\[
\begin{align*}
\text{CO}_2 + 2\text{H}_2\text{O} & \Leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ & K_{CO2} \\
\text{DEACOO}^- + \text{H}_2\text{O} & \Leftrightarrow \text{DEA} + \text{HCO}_3^- & K_{DEACOO} \\
2\text{H}_2\text{O} & \Leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+ & K_w
\end{align*}
\]

(4.23) (4.24) (4.25)

The overall equilibrium constant is:

\[
K_{CO2, carb} = \frac{K_{CO2}}{K_{DEACOO} K_w}
\]

(4.26)

The equilibrium CO\(_2\) activity is then:

\[
a_{CO2, carb,e} = \frac{a_w a_{DEACOO}}{K_{CO2, carb} a_{OH} a_{DEA}}
\]

(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:

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

<table>
<thead>
<tr>
<th>Rate constant</th>
<th>$k_{298}^*$ (m$^2$/kmol$^2$-s)</th>
<th>Corrected $k_{298}$ (kmol/m$^3$-s)</th>
<th>$E_a$ (kcal/kmol-K)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA constants:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{t_{am,w}}$</td>
<td>0.0157</td>
<td>2668.2</td>
<td>3710</td>
<td>a</td>
</tr>
<tr>
<td>$k_{t_{am,OH}}$</td>
<td>$1.54 \times 10^5$</td>
<td>$2.617 \times 10^{10}$</td>
<td>8107</td>
<td>a</td>
</tr>
<tr>
<td>DEA constants:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{am}$</td>
<td>18500</td>
<td>$3.144 \times 10^9$</td>
<td>9314</td>
<td>a</td>
</tr>
<tr>
<td>$k_{w}$</td>
<td>30.0</td>
<td>$5.098 \times 10^6$</td>
<td>11000</td>
<td>a</td>
</tr>
<tr>
<td>DEA/MDEA constant:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{t_{am}}$</td>
<td>3310</td>
<td>$5.625 \times 10^8$</td>
<td>-105</td>
<td>a</td>
</tr>
<tr>
<td>MEA (DGA) constant:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p_{am}}$</td>
<td>---</td>
<td>5868.45</td>
<td>9846</td>
<td>b</td>
</tr>
<tr>
<td>Hydroxide constant:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{OH}$</td>
<td>---</td>
<td>8322.14</td>
<td>13245</td>
<td>c</td>
</tr>
</tbody>
</table>

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 CO₂ and H₂S using the CO₂ 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 (H₂CO₃), and H₂S allows calculation of the other apparent component concentrations. Using these interface concentrations, the remaining concentrations can be calculated from the following:

\[ C_{\text{MDEA},i} = C_{\text{MDEA},b} \]  \hspace{1cm} (4.29)

\[ C_{\text{CO₂},i} = \frac{P_{\text{CO₂}}}{H_{\text{CO₂}}} \]  \hspace{1cm} (4.30)

\[ C_{\text{DEA},i} = C_{\text{DEA},b} - \frac{k_l^*_{\text{carb}}}{k_l^*_{\text{DEA}}} \Delta C_{\text{carb}} \]  \hspace{1cm} (4.31)

where

\[ \Delta C_k = C_{k,\text{interface}} - C_{k,\text{bulk}} \]  \hspace{1cm} (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 CO₂. 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 CO₂ which is then used to calculate the enhancement factor of DeCoursey (1982) described in Chapter 3. The enhancement factor expression is:

\[ E_{CO₂} = 1 + (E_i - 1) \left[ 1 - \Theta \cdot \frac{\Theta}{E_i + C_3} \right] \]  \hspace{1cm} (4.33)

\[ E_i = \sqrt{1 + M} \]  \hspace{1cm} (4.34)

\[ M = \frac{k_1 D_{CO₂}}{k_{102}} \]  \hspace{1cm} (4.35)

\[ \Theta = \frac{a_{CO₂,i,e} - a_{CO₂,b}}{a_{CO₂,i} - a_{CO₂,b}} \]  \hspace{1cm} (4.36)

where \( k_1 \) is a pseudo-first order rate constant and the dimensionless driving force \( \Theta \) is now in terms of activities. This transformation of \( \Theta \) is done out of convenience because the term \( a_{CO₂,i,e} \) is readily available from the reaction rate subroutine. The constant \( k_1 \) can be approximated using the net reaction rate of CO₂ calculated in the reaction rate subroutine by combining (4.15) and (4.22):

\[ k_1 = \frac{R_{CO₂,i}}{C_{CO₂,i}} \]  \hspace{1cm} (4.37)

where

\[ R_{CO₂,i} = R_{HCO₃,i} + R_{carb,i} \]  \hspace{1cm} (4.38)

For equation (4.36), the CO₂ activity at the interface in equilibrium with the other species must be calculated. For the MDEA system, \( a_{CO₂,i,e} \) can be obtained from the equilibrium activity calculated in equation (4.17). For primary, secondary or mixed amine systems, the value for \( a_{CO₂,i,e} \) depends on the distribution of CO₂ between carbamate and bicarbonate. This distribution is estimated using the MCFLUX approximation (Glasscock and Rochelle, 1990a). This approximation assumes the CO₂ is distributed amongst the bicarbonate and carbamate according to
the rates of reactions, therefore, the fraction of CO\textsubscript{2} considered to be in equilibrium with the carbamate is given by:

\[
f_{\text{carb}} = \frac{R_{\text{carb}}}{R_{\text{carb}} + R_{\text{HCO}_3}}
\]  

(4.39)

The net rates of \( R_{\text{HCO}_3} \) and \( R_{\text{carb}} \) are calculated using (4.15) and (4.22), respectively. The equilibrium value for the CO\textsubscript{2} activity is then approximated by:

\[
\mathbf{a}_{\text{CO}_2,i,e} = f_{\text{carb}} \mathbf{a}_{\text{CO}_2,\text{carb},e} + (1-f_{\text{carb}}) \mathbf{a}_{\text{CO}_2,\text{HCO}_3,e}
\]  

(4.40)

The values for \( \mathbf{a}_{\text{CO}_2,\text{HCO}_3,e} \) and \( \mathbf{a}_{\text{CO}_2,\text{carb},e} \) are calculated using (4.17) and (4.27), respectively.

Using equations (4.33) through (4.40), the CO\textsubscript{2} enhancement factor can be calculated. The guessed interface values are now checked using the following equations:

\[
N_{\text{CO}_2} = k_{l^*,\text{CO}_2} E_{\text{CO}_2} [ C_{\text{CO}_2,i} - C_{\text{CO}_2,b} ]
\]  

(4.40)

\[
N_{\text{CO}_2} = k_{l^*,\text{CO}_2} \Delta C_{\text{CO}_2} + k_{l^*,\text{carb}} \Delta C_{\text{carb}} + k_{l^*,\text{HCO}_3} \Delta C_{\text{HCO}_3}
\]  

(4.41)

\[
\frac{k_{l^*,\text{carb}} \Delta C_{\text{carb}}}{k_{l^*,\text{HCO}_3} \Delta C_{\text{HCO}_3}} = \frac{R_{\text{carb}}}{R_{\text{HCO}_3}}
\]  

(4.42)

\[
k_g [ P_{\text{H}_2\text{S}} - C_{\text{H}_2\text{S}_{i,e}} ] = k_{l^*,\text{H}_2\text{S}} \Delta C_{\text{H}_2\text{S}}
\]  

(4.43)

Equation (4.42) is an approximation developed by Glasscock and Rochelle (1990a). The value for \( C_{\text{H}_2\text{S}_{i,e}} \) 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\textsuperscript{2}RNCOOH, \( \text{H}_2\text{CO}_3 \), and \( \text{H}_2\text{S} \) 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$_2$S in the absorber off-gas (H$_2$S 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$_2$S 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>
<thead>
<tr>
<th>Parameter</th>
<th>Absorber</th>
<th>Stripper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of trays</td>
<td>20 bubble cap</td>
<td>25 bubble cap</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>Pressure drop (atm/tray)</td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>Feed gas</td>
<td>1% H₂S, 10% CO₂, 40°C</td>
<td>Live steam at 127°C</td>
</tr>
<tr>
<td>Inlet liquid temperature (°C)</td>
<td>40</td>
<td>112</td>
</tr>
<tr>
<td>Heats of reaction (cal/mole)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S dissociation</td>
<td>2089</td>
<td>2089</td>
</tr>
<tr>
<td>CO₂ dissociation</td>
<td>6364</td>
<td>6364</td>
</tr>
<tr>
<td>MDEA protonation</td>
<td>7889</td>
<td>7889</td>
</tr>
<tr>
<td>H₂O vaporization</td>
<td>10325</td>
<td>9461</td>
</tr>
<tr>
<td>Tray Specifications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fractional approach to flood</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>liquid depth (cm)</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>effective froth height (cm)</td>
<td>15.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Mass Transfer Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas phase coefficient (mole/atm/dm²/s)</td>
<td>0.02219</td>
<td>0.01958</td>
</tr>
<tr>
<td>liquid phase coefficient (dm/s)</td>
<td>0.001546</td>
<td>0.006441</td>
</tr>
<tr>
<td>interfacial area (dm²/dm²)</td>
<td>892.3</td>
<td>305.3</td>
</tr>
<tr>
<td>gas phase transfer units/tray</td>
<td>2.178</td>
<td>2.174</td>
</tr>
</tbody>
</table>
\[ \frac{\Delta H}{R} = \frac{\partial \ln K_{\text{MDEA}}}{\partial (1/T)} = -0.019416 \ln(10) \ T^2 \]  \quad (5.1)

The heat of reaction data for H₂S and CO₂ 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 (H₂S 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 H₂S 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 H₂S 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 H₂S 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% H₂S, 10% CO₂).
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% H₂S, 10% CO₂, 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 H₂S occur in the absorber (from 225 at the bottom to 1050 at the top), the mass transfer of H₂S is somewhat liquid phase controlled because the gas phase coefficient is much larger than the liquid phase coefficient. Dow Chemical Company has observed similar H₂S resistances (Katti and Langfitt, 1986). In the stripper, the H₂S 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, CO₂ mass transfer is always liquid phase controlled in an MDEA system. With an enhancement factor of about 1.2 in the absorber, CO₂ is practically under physical absorption. In the stripper, the CO₂ 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 CO₂ concentration at the interface is 0.349 x 10⁻⁵ mole/kg H₂O, and the bulk concentration is 0.108 x 10⁻³ mole/kg H₂O. If the CO₂ 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$_2$S, 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% H₂S, 10% CO₂, 1.7 lb steam/gal solvent).
Table 5.2: Base Case Tray Efficiencies and Liquid Phase Mass Transfer Resistances

<table>
<thead>
<tr>
<th></th>
<th>Tray Efficiency (%)</th>
<th>Liquid Phase Resistance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂S</td>
<td>CO₂</td>
</tr>
<tr>
<td>Absorber: Bottom</td>
<td>61</td>
<td>1.0</td>
</tr>
<tr>
<td>Top</td>
<td>89</td>
<td>0.3</td>
</tr>
<tr>
<td>Stripper: Bottom</td>
<td>66</td>
<td>2.2</td>
</tr>
<tr>
<td>Top</td>
<td>24</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The CO₂ concentration at the interface would be at equilibrium and have a value of 0.895 x 10⁻⁴ mole/kg H₂O. These interface and bulk concentrations were used to estimate the CO₂ flux. Assuming the CO₂ reaction to be instantaneous would have resulted in an overestimation of the CO₂ 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 H₂S and leaving CO₂ in the gas is an important characteristic of the MDEA system. This case showed that 6.5% of the CO₂ and 99% of the H₂S in the feed gas is removed in the absorber, giving the off gas from the stripper a composition of 60% H₂S. This high percentage of H₂S 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 H₂S selectivity. Union Carbide Corporation (1984) has also shown that adding acid to alkanolamine solvents improves H₂S removal. According to Union Carbide, typical Claus tail gas units have trouble obtaining an H₂S leak of 100 ppm with just amine solvent; however, H₂S 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 H₂S 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 H₂S equilibrium after adding acid. The following equation represents the H₂S equilibrium:

\[
\frac{P_{H_2S}}{K_{H_2S}} = \frac{[\text{HS}^-][\text{MDEAH}^+]}{[\text{MDEA}]} \quad (5.2)
\]

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% H₂S, 10% CO₂, 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% H₂S, 10% CO₂, 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:

$$\text{Acid} + \text{MDEA} \rightleftharpoons \text{Acid anion} + \text{MDEAH}^+$$  \hspace{1cm} (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 $\text{H}_2\text{S}$, which is approximately the bisulfide concentration, the ratio $[\text{R}_3\text{NH}^+]/[\text{R}_3\text{N}]$ can be considered constant at the lean end and $P_{\text{H}_2\text{S}}$ is proportional to $[\text{H}_2\text{S}]_{\text{total}}$. Thus, the $\text{H}_2\text{S}$ equilibrium is then given by:

$$P_{\text{H}_2\text{S}} = C_{\text{H}_2\text{S}}[\text{HS}^-]$$  \hspace{1cm} (5.4)

where

$$C_{\text{H}_2\text{S}} = \frac{H_{\text{H}_2\text{S}}[\text{MDEAH}^+]}{K_{\text{H}_2\text{S}}[\text{MDEA}]}$$  \hspace{1cm} (5.5)

Equation (5.4) shows that system performance improves because the $\text{H}_2\text{S}$ equilibrium is now essentially linear and the $\text{H}_2\text{S}$ 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 CO₂. By lowering the stripper pressure, and therefore the
temperature, reaction rates are slower. The lower temperature affects the CO₂
reaction rate more than that of H₂S because CO₂ has a higher heat of reaction with
MDEA. The slower reaction rate lowers the CO₂ enhancement factor; therefore, the
mass transfer of CO₂ in the stripper is adversely affected and more CO₂ is left in the
lean solution. The extra CO₂ in solution helps to linearize the H₂S equilibrium by
protonating more amine, especially in the lean end, which leads to lower H₂S lean
loadings. As a test to see if this is true, the amount of CO₂ 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% CO₂ feed gas, the
performance is drastically improved from 98 ppm H₂S 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 CO₂ lean loading from 0.0012 to 0.018 mole/mole
MDEA. This is evidence that the effect of the CO₂ lean loading on H₂S stripping
described above is the cause for the improved performance. Figure 5.8 shows the
operating and equilibrium lines for H₂S 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 H₂S equilibrium.

Figure 5.7 also shows the system performance at various pressures with
only 2.5% CO₂ feed gas. Clearly, the increase in performance by reducing the
pressure is reduced with only 2.5% CO₂ in the feed gas. With 2.5% CO₂ in the
feed gas, the H₂S 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% CO₂ feed gas. Comparison of Figure 5.9 with Figure 5.8
shows that a greater stripper pinch occurs with a smaller amount of CO₂ in the feed
gas.

Although the presence of CO₂ is helpful in H₂S removal at lower pressures
because it linearizes the equilibrium, CO₂ hinders H₂S removal at higher pressures
as seen by the higher leak at 2 atm stripper pressure with 10% CO₂. 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% H2S, 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% H2S, 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% H2S, 1.9 lb steam/gal solvent).
of the absorber, CO₂ at the gas/liquid interface creates protonated amine which decreases the ability to absorb H₂S. 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 H₂S leak. However, in the case of pressure reduction a CO₂ lean loading of only about 0.018 is required to produce the same leak. This large difference in acid loading and CO₂ loading suggests that linearization of the H₂S 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 H₂S is partially gas phase controlled as shown in Table 5.2, the increase in these mass transfer parameters improves H₂S 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 CO₂ lean loading improves system performance. Conceivably, if reducing the number of stripper stages affected the stripping of CO₂ more than that of H₂S, the CO₂ 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 CO₂ 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 H₂S 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% H₂S, 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% H₂S, 10% CO₂, 0.028 lb steam/SCF feed gas).
increased; therefore, H₂S 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 H₂S equilibrium constant, the H₂S heat of reaction, the mass transfer coefficients, and the CO₂-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 CO₂ per moles of MDEA entering the absorber in the liquid phase. Percent CO₂ slip is the percent of CO₂ 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 H₂S equilibrium constant defined by equation (3.28) and fit to experimental data. This parameter was varied in two ways. First, the H₂S 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 H₂S heat of reaction. As shown in Table 5.3, the H₂S leak is very sensitive to changes in the H₂S equilibrium constant in the stripper and the H₂S heat of reaction. The percent CO₂ slip is slightly sensitive to changing the H₂S equilibrium constant in the absorber because changing this constant varies the solution capacity. Figure 5.12 shows the effect of changing the H₂S 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.

The sensitivity of response is given by:

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

<table>
<thead>
<tr>
<th>Adjusted Parameter</th>
<th>H\textsubscript{2}S Leak (ppm)</th>
<th>CO\textsubscript{2} Lean Loading</th>
<th>Percent CO\textsubscript{2} Slip</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}S equilibrium constant in both columns</td>
<td>0.33</td>
<td>-0.96</td>
<td>0.01</td>
</tr>
<tr>
<td>H\textsubscript{2}S equilibrium constant in only the stripper</td>
<td>1.72</td>
<td>-1.05</td>
<td>0.0</td>
</tr>
<tr>
<td>H\textsubscript{2}S heat of reaction</td>
<td>-1.29</td>
<td>0.78</td>
<td>0.0</td>
</tr>
<tr>
<td>kg</td>
<td>-0.27</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(k_1^*)</td>
<td>-0.48</td>
<td>0.14</td>
<td>-0.032</td>
</tr>
<tr>
<td>CO\textsubscript{2}-MDEA rate constant</td>
<td>0.17</td>
<td>-0.60</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
Figure 5.12: Effect of Varying the H$_2$S 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$_2$S, 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$_2$S 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$_2$S 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$_2$S can more easily approach total equilibrium and the H$_2$S 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 kg because CO$_2$ absorption is liquid phase controlled. Figure 5.13 illustrates that when adjusting the liquid transfer coefficient, either the H$_2$S 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$_2$S 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$_2$S 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$_2$S leak is sensitive to values of this rate constant. The change in H$_2$S 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% H₂S, 10% CO₂, 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% H₂S, 10% CO₂, 1.7 lb steam/gal solvent).
Figure 5.15: Effect of Changing the CO₂-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% H₂S, 10% CO₂, 1.7 lb steam/gal solvent).
decrease in CO₂ lean loading results in an improved H₂S leak. Table 5.4 compares the variation of CO₂ lean loading for the cases of reducing the stripper pressure and changing the CO₂-MDEA rate constant. Clearly, reducing the stripper pressure has the same effect on H₂S leak as varying the kinetic rate constant. Percent CO₂ slip decreases slightly as the CO₂-MDEA rate constant is increased because CO₂ 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 H₂S and CO₂ 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 H₂S and CO₂ equilibrium data for MEA, DEA, MDEA, DGA, and mixed amines. For purposes of this work, a set of experimental data for each amine with H₂S and CO₂ 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 H₂S and CO₂.
Table 5.4: Variation of CO₂ Lean Loading for Different Operating Conditions

<table>
<thead>
<tr>
<th>Case</th>
<th>H₂S Leak (ppm)</th>
<th>CO₂ Lean Loading (mole CO₂/mole MDEA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 atm stripper with 25 trays, 10% CO₂ feed gas</td>
<td>98.2</td>
<td>0.00130</td>
</tr>
<tr>
<td>2 atm stripper with 25 trays, 2.5% CO₂ feed gas</td>
<td>61.8</td>
<td>0.000325</td>
</tr>
<tr>
<td>0.5 atm stripper with 25 trays, 10% CO₂ feed gas</td>
<td>4.0</td>
<td>0.0180</td>
</tr>
<tr>
<td>0.5 atm stripper with 25 trays, 2.5% CO₂ feed gas</td>
<td>25.3</td>
<td>0.00871</td>
</tr>
<tr>
<td>2 atm stripper with 18 trays, 10% CO₂ feed gas</td>
<td>131</td>
<td>0.00205</td>
</tr>
<tr>
<td>Increase the CO₂-MDEA rate constant by 100% using 18 stripper trays</td>
<td>150</td>
<td>0.00130</td>
</tr>
<tr>
<td>Decrease the CO₂-MDEA rate constant by 50% using 18 stripper trays</td>
<td>117</td>
<td>0.00291</td>
</tr>
</tbody>
</table>
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$_2$S 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 H₂S 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 CO₂ 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$_2$S in 5.0M DEA. Model prediction: (—). Experimental data from Lee et al. (1973): (a) - 25°C, (•) - 75°C, (+) - 120°C
Figure 5.22: Comparison of Model Prediction to Experimental Data for CO₂ 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$_2$S 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 CO₂ 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\textsubscript{2}O, amine, CO\textsubscript{2}, H\textsubscript{2}S, H\textsubscript{3}O\textsuperscript{+}, protonated amine, OH\textsuperscript{-}, carbamate, HS\textsuperscript{-}, HCO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}). 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:

\[
K_i = \frac{K_i^\infty}{\prod_{k=1}^{n} \gamma_k v_k} \tag{5.6}
\]

where \(K_i^\infty\) is the mole fraction based, infinite dilution equilibrium constant from Table 4.8, \(n\) is the number of components for reaction \(i\), \(\gamma_k\) is the activity coefficient for component \(k\), and \(v_k\) is the stoichiometric coefficient for component \(k\). The equilibrium constants for the dissociation of H\textsubscript{2}CO\textsubscript{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:

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

\[
[H_2S]_{tot} = H_2S + HS^- \tag{5.8}
\]
\[ [RR'R''N]_{\text{tot}} = RR'R''N + RR'R''NH^+ \]  
(5.9)

\[ [CO_2]_{\text{tot}} = CO_2 \]  
(5.10)

\[ [H_2CO_3]_{\text{tot}} = HCO_3^- + CO_3^{2-} \]  
(5.11)

\[ [RR'NCOOH]_{\text{tot}} = RR'NCOO^- \]  
(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:

\[
\sum_{i=1}^{n_{\text{ion}}} z_i [\text{flow}]_i = 0 \]  
(5.13)

where $n_{\text{ion}}$ is the number of ions in solution, $z_i$ is the charge of ion $i$, and $[\text{flow}]_i$ 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 \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) 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 \( \text{H}_2\text{S} \) 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 \( \text{CO}_2 \) enhancement factor in the stripper can result in a large overestimation of the \( \text{CO}_2 \) flux.
3. System performance in an MDEA system can be improved by increasing the protonated amine concentration which linearizes the H₂S 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 CO₂ lean loading is increased by lowering the stripper pressure which partially linearizes the H₂S equilibrium. In addition, lowering the stripper pressure increases the gas phase mass transfer coefficient and number of transfer units. Because H₂S is partially gas phase controlled, the increase in these parameters decreases the H₂S 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 H₂S 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 in 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 PLOT.C.OUT. These files contain the necessary data to make McCabe-Thiele plots for H2S and CO2, respectively. Generation of these files can be avoided with the use of a flag in the file INPUT.IN.

C

PROGRAM ABSTR

C


C

SUBROUTINES AND FUNCTIONS:

1) TCONV - DETERMINES TEMPERATURE CONVERGENCE FOR BOTH COLUMNS. THIS ROUTINE CALLS ONLY TOWER.

2) TOWER - COMBINES ALL OF THE INDIVIDUAL STAGES INTO A COMPLETE TOWER. THIS ROUTINE INITIALLY CALLS DIFFUSE AND COEFF TO ESTABLISH THE DIFFUSIVITIES AND MASS TRANSFER PARAMETERS. SECANT2 IS THEN
3) DIFFUSE - CALLS THE FUNCTION STAGE AND DIRECTS THE CONVERGENCE OF EACH STAGE.

4) COEFF - PERFORMS THE MASS AND ENERGY BALANCES ON EACH STAGE. CALLS THE SUBROUTINE SECANT WITH THE FUNCTION BULK OR FACE.

7) SECANT - PERFORMS THE BULK LIQUID SPECIATION CALCULATIONS.

8) BULK - PERFORMS THE CALCULATION OF THE LIQUID INTERFACE.

9) FACE - CALLED BY EITHER BULK OR FACE TO CALCULATE THE KINETIC RATE CONSTANTS AT THE CURRENT CONDITIONS.

10) RATE - CALLED BY EITHER BULK OR FACE TO CALCULATE THE EQUILIBRIUM CONSTANTS AND HENRY'S CONSTANTS AT THE CURRENT CONDITIONS.

12) DENS - A FUNCTION USED TO CALCULATE THE DENSITY OF WATER.

13) DENSAM - A FUNCTION USED TO CALCULATE THE DENSITY OF MDEA.

14) PRINT - A SUBROUTINE CALLED BY STAGE AT THE APPROPRIATE TIME TO PRINT THE RESULTS OF A RUN.

15) ERROR - A SUBROUTINE CALLED BY STAGE IF CERTAIN PROBLEM CONDITIONS OCCUR.

OTHERS - SEVERAL FUNCTIONS EXIST TO CALCULATE THE HEAT CAPACITY OF THE COMPONENTS.

COMMON BLOCKS ARE USED TO TRANSFER MOST OF THE VARIABLE VALUES BETWEEN SUBROUTINES. THE COMMON BLOCKS ARE AS FOLLOWS:

1) FLAG - CONTAINS FLAG VARIABLES AND OTHER INTEGER VARIABLES.

2) DIFF - CONTAINS THE DIFFUSIVITIES OF EACH SPECIES IN THE LIQUID PHASE, AN OVERALL LIQUID DIFFUSIVITY, AND AN OVERALL GAS DIFFUSIVITY.

3) FLUX - CONTAINS MASS TRANSFER PARAMETERS.

4) DH - CONTAINS THE HEATS OF REACTION AND VAPORIZATION.

5) EK - CONTAINS THE EQUILIBRIUM CONSTANTS AND HENRY'S CONSTANTS.

6) LIN - CONTAINS THE TOTAL MOLES OF EACH CHEMICAL IN THE LIQUID INTO A STAGE.

7) LOUT - CONTAINS THE TOTAL MOLES OF EACH CHEMICAL IN THE LIQUID OUT OF A STAGE.

8) GIN - CONTAINS THE MOLES OF EACH CHEMICAL IN THE GAS INTO A STAGE.

9) GOUT - CONTAINS THE MOLES OF EACH CHEMICAL IN THE GAS OUT OF A STAGE.
10) CONB - CONTAINS THE BULK LIQUID CONCENTRATIONS OF EACH SPECIES
11) CONT - CONTAINS THE TOTAL BULK LIQUID CONCENTRATION OF EACH CHEMICAL
12) CONI - CONTAINS THE LIQUID CONCENTRATIONS OF EACH SPECIES AT THE INTERFACE
13) PI - CONTAINS THE PARTIAL PRESSURES AT THE INTERFACE
14) PRESS - CONTAINS THE OTHER PRESSURE VARIABLES NEEDED
15) TEMP - CONTAINS THE TEMPERATURES OF THE STREAMS ASSOCIATED WITH A STAGE
16) ENHANC - CONTAINS THE ENHANCEMENT FACTORS
17) TRAY - CONTAINS PHYSICAL PARAMETERS TO DESCRIBE THE SPECIFIC TRAY CHARACTERISTICS

INPUT FILES:

INPUT.IN - THIS FILE CONTAINS THE MINIMUM INFORMATION REQUIRED TO BEGIN A RUN.
INITIAL.IN - THIS FILE IS USED TO READ IN AN INITIAL TEMPERATURE PROFILE FOR BOTH COLUMNS (OFTEN FROM A PREVIOUS RUN). IF THIS FILE IS NOT USED, INITIAL PROFILES ARE GENERATED INTERNALLY.

OUTPUT FILES:

OUT.OUT - CONTAINS THE DETAILED, STAGE-BY-STAGE RESULTS
TEMP.OUT - CONTAINS THE TEMPERATURE PROFILES FOR BOTH COLUMNS
PLOTS.OUT - CONTAINS THE MCCABE-THEILE INFORMATION FOR H2S
PLOT2.OUT - CONTAINS THE MCCABE-THEILE INFORMATION FOR CO2

IMPLICIT REAL*8 (A,H,O,Y)
REAL*4 Z1, Z2
REAL*8 G1A(4,50), G1S(4,50), LOA(5,50), LOS(5,50), TEMPA(50),
& TEMPS(50)
REAL*8 NG,NGREB,LINH2S,LINCO2,LINH2O,LINAM,LINION,
& LINTOT,MKUPH2O

CHARACTER RUNSUM*100

COMMON /DIFE/ DOH,DRNH,DRN,DHS,DH2S,DHCO3,DCO3,DCO2,DL,DG
COMMON /DH/ DH2S,DHCO2,DH2O,DHAM
COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
COMMON /LIN/ LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
COMMON /GOUT/ GOUTH2S,GOUTCO2,GOUTH2O,GOUNRT,GOUTTOT
COMMON /TRAY/ TRAY,F,HL,HFROTH

CALL A VAX FUNCTION THAT WILL REPORT THE EXECUTION TIME

Z1 = SECNDS(0.0)
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='PLOT.C.OUT', STATUS='UNKNOWN')
OPEN (UNIT=9, FILE='INITIAL.IN', STATUS='UNKNOWN')
OPEN (UNIT=10, FILE='TEMP.OUT', STATUS='UNKNOWN')

A run number and description is asked for. This is used to keep
track of the various runs that are made by writing this
information to the output file 'OUT.OUT'.

WRITE (*,*) 'INPUT THE RUN NUMBER'
READ (*,*) IRUN
WRITE (*,*) 'INPUT A BRIEF DESCRIPTION OF THIS RUN'
READ (*,*) RUNSUM
WRITE (3,1) 'RUN # ',IRUN,RUNSUM
FORMAT (/A1X,A6,I3,/A100/)

The following data is the standard information that needs to be
input for each run. Each READ statement is followed by a WRITE
statement in order to write the input information to the output
file 'OUT.OUT' for future reference.

WRITE (3,*) 'THE FOLLOWING INPUT FILE WAS USED FOR THIS RUN:'
WRITE (3,*) '

READ THE INPUT FOR THE ABSORBER FROM FILE 'INPUT.IN'.

READ: 1) number of actual stages 2) max no. of temp convergence
iterations 3) print option 4) reboiler flag.
If imaxa is exceeded for a system model, temperature
convergence is ignored and execution continues. If it is exceeded
for a single tower model execution is stopped.
The print option takes the following values:
0 print every stage convergence
1 print every temperature profile convergence
2 print only after system convergence
3 same as 2 but also print plots.out and plotc.out
The reboiler flag takes the following values:
0 no reboiler
1 bottom stage is reboiler

READ (I,*) NLAST,IMA,XA,IPRINTA,IREBA
WRITE (3,1001) NLAST,IMA,XA,IPRINTA,IREBA

READ: 1) Tray type (1=bubble cap, 2=sieve)
2) fraction approach to flood
3) liquid holdup on each tray (cm)
4) effective froth height on each tray (cm) for sieve trays
or liquid submergence measured as half of the slot height
to the top of the dispersion for bubble cap trays
READ (1,*) ITRAYA, FA, HLA, HFROTHA
WRITE (3,1002) ITRAYA, FA, HLA, HFROTHA

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
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
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
READ: 1) PRESSURE AT THE BOTTOM OF THE ABSORBER (ATM)
   2) PRESSURE DROP PER STAGE (ATM)
C
READ (1,*) PBOTA, DPA
WRITE (3,1000) PBOTA, DPA

C
READ: TEMPERATURES (K): 1) GAS IN  2) LIQUID IN
   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
READ: HEATS OF RXN (CAL/MOLE): 1) H2S DISSOCIATION  2) H2CO3
   DISSOCIATION  3) H2O VAPORIZATION  4) AMINE PROTONATION
C
READ (1,*) DHHS2A, DHOCO2A, DHH2OA, DHAMA
WRITE (3,1000) DHHS2A, DHOCO2A, DHH2OA, DHAMA

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
READ: 5) NUMBER OF GAS PHASE TRANSFER UNITS FOR THE REBOILER
C
READ (1,*) ITRAYA, 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,*) DHHS2S, DHOCO2S, DHH2OS, DHAMS

C
WRITE (3,1002) ITRAYA, 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

READ 1) MAXIMUM NUMBER OF SYSTEM ITERATIONS 2) H2S DAMPING FACTOR 3) CO2 DAMPING FACTOR 4) SYSTEM FLAG
IF JMAX IS EXCEEDED, THE USER CAN EITHER SUPPLY NEW GUESSES AND CONTINUE WITH A NEW JMAX OR HAVE THE UNCONVERGED SYSTEM WRITTEN AS OUTPUT AND STOP.
The damping factors are used to help convergence of the loading values and can be changed interactively.
The system flag takes the following values:
=0 MODEL ONLY THE ABSORBER
=1 MODEL ONLY THE STRIPPER
=2 MODEL THE SYSTEM

READ (1,*) JMAX, H2SDAMP, CO2DAMP, ISYS
WRITE (1,1003) JMAX, H2SDAMP, CO2DAMP, ISYS

IF ONLY ONE TOWER IS TO BE MODELLED, INPUT THE LIQUID OUT OF THE TOWER AND IGNORE THE VALUES GIVEN IN THE ABSORBER INPUT.

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

NOW ALL OF THE STANDARD INPUT HAS BEEN READ. THE USER CAN NOW USE THE PREVIOUSLY SAVED FILE 'INITIAL.IN' TO GET THE INITIAL TEMPERATURE PROFILE. IF THE USER DECIDES NOT TO USE THE PREVIOUSLY SAVED FILE, THEN INITIALIZE THE TEMPERATURE PROFILE WITH ZERO VALUES.

WRITE ('*,*) 'DO YOU WANT TO USE A PREVIOUSLY SAVED INITIAL & TEMPERATURE PROFILE?'
WRITE ('*,*) '1=YES, 2=NO'
READ ('*,*) IINPUT

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.
  CONTINUE
  DO 310 M=1,NLASTS-1
    TEMPS(M)=0.
  CONTINUE
ENDIF

C INITIALIZE THE ERROR FLAG, THE PRINT FLAG, THE SYSTEM ITERATION
C COUNTER
C
IERR=0
IPR=0
J=0

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.

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 SET THE INITIAL ERROR BETWEEN THE CALCULATED AND GUESSED LOADING
C VALUES FOR H2S AND CO2.
C
ERR = 1D10

C BEGINNING OF THE SYSTEM ITERATION LOOP.

30 J=J+1
C THIS IS THE CODE WHICH DIRECTS SYSTEM CONVERGENCE. FIRST, IF ONLY
C ONE TOWER IS TO BE MODELED 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
C IF (ISYS .NE. 2) GOTO 100
C IF (J .GT. JMAX) THEN
C WRITE (*,*) 'SYSTEM DID NOT CONVERGE IN 'JMAX;' ITERATIONS.'
C WRITE (*,*) 'WOULD YOU LIKE TO CONTINUE? (1=YES)'
C READ (*,*) ICONT
C IF (ICONT.EQ.1) THEN
C WRITE(*,*) 'PLEASE INPUT THE NUMBER OF CONVERGENCE ITERATIONS'
C READ (*,*) JMAX
C IERR = 1
C GOTO 50
C ELSE
C WRITE (*,*) 'THE FINAL ITERATION WILL BE WRITTEN AS OUTPUT:'
C LOA(1,1) = XS2
C LOA(2,1) = XC2
C IFLAG = 4
C GOTO 100
C ENDIF
C ENDF
C
C INITIALIZE THE CO2 AND H2S LOADINGS FOR THIS ITERATION
C
C LOA(1,1)=XS2
C LOA(2,1)=XC2
C 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
C 100 CONTINUE
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
C IF (TEMPA(NLASTA/2) .EQ. 0.) THEN
C XH2O=LOA(3,1)/(LOA(1,1)+LOA(2,1)+LOA(3,1)+LOA(4,1)+LOA(5,1))
C PH2O=PBO+GIA(3,1)-(GIA(1,1)+GIA(2,1)+GIA(3,1)+GIA(4,1))
C IF (TBO+GIA(1,1)+GIA(2,1)+GIA(3,1)+GIA(4,1)
C ENDIF
C &
C +273.228.)
DT = TEMPAM(NLASTA) - TBOTA
DO 10 M = 1, NLASTA - 1
   TEMPAM(M) = TBOTA + DT * DFLOAT(M) / DFLOAT(NLASTA)
10    CONTINUE
ENDIF
C
IF THE FLAGS INDICATE THAT THE SYSTEM HAS CONVERGED AND THAT
PRINTING IS DESIRED, SET THE PRINT FLAG.
C
IF ( (IPRINT .GE. 2) .AND. ( FLAG .EQ. 4 ) ) THEN
   IPR = 1
ENDIF
C
SET THE VALUES NEEDED FOR THE ABSORBER CALCULATIONS TO THE
VARIABLE NAMES IN THE COMMON BLOCKS (TAKE THE "A" OF THE END OF
THE NAMES). THE COLUMN FLAG IS SET TO 1 TO INDICATE THE ABSORBER
CALCULATION IS BEING DONE.
C
ICOLUMN = 1
IREB = IREBA
IPRINT = IPRINTA
ITRAY = ITRAYA
F = FA
HL = HLA
HFROTH = HFROTHA
DHH2S = DHH2SA
DHO2 = DHO2A
DH2O = DH2OA
DHAM = DHAMA
MKUPH2O = 0.
C
CONVERGE THE TEMPERATURE PROFILE FOR THE ABSORBER. CHECK FOR
AN ERROR. PRINT TO THE TERMINAL THAT THE ABSORBER HAS BEEN
CONVERGED. REINITIALIZE THE PRINT FLAG. IF ONLY THE ABSORBER IS TO
BE MODELED, STOP.
C
ICOEFF = 0
CALL TCONV (GIA, LOA, TGIA, TEMPAM, TBOTA, PBOTA, DPA, NLASTA, IMAXA,
&
   MKUPH2O)
IF (IERR .GT. 0) GOTO 50
WRITE (*, *) 'ABSORBER'
WRITE (*, *)
IPR = 0
IF ( ISYS .EQ. 0 ) STOP
C
THE LIQUID INTO THE ABSORBER IS THE LIQUID OUT OF THE STRIPPER.
C
LOS(1,1) = LINH2S
LOS(2,1) = LINH2O
LOS(3,1) = LINCO2
LOS(4,1) = LINAM
LOS(5,1) = LINION
MAKEUP THE WATER LOST TO THE ABSORBER OFF GAS. THIS IS ADDED TO
THE LIQUID INTO THE STRIPPER IN TOWER.

MKUPH2O=GOUTH2O-GIA(3,1)

CALCULATE AN INITIAL TEMPERATURE PROFILE FOR THE STRIPPER.

IF (TEMPS(NLASTS/2).EQ.0.) THEN
    XH2O=LOS(3,1)/(LOS(1,1)+LOS(2,1)+LOS(3,1)+LOS(4,1))
    PH2O=PBO*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-DLOG(10(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

IF THE FLAGS INDICATES THAT THE SYSTEM HAS CONVERGED AND THAT
PRINTING IS DESIRED, SET THE PRINT FLAG.

IF ((IPRINT.GE.2) .AND. (IFLAG.EQ.4)) THEN
    IPR=1
ENDIF

SET THE VALUES NEEDED FOR THE STRIPPER CALCULATIONS TO THE
VARIABLE NAMES IN THE COMMON BLOCKS (TAKE THE "S" OF THE END OF
THE NAMES).

ICOLUMN = 2
IREB=IREBS
IPRINT=IPRINTS
ITRAY=ITRAYS
F = FSS
HL = HLS
HFROTH = HFROTHS
DHH2S=DHH2SS
DHCO2=DHCO2S
DHH2O=DHH2OS
DHAM=DHAM

IF ONLY THE STRIPPER IS MODELED THERE IS NO MAKEUP WATER.

IF (ISYS.EQ.1) THEN
    MKUPH2O=0.
ENDIF

CONVERGE THE TEMPERATURE PROFILE FOR THE STRIPPER. CHECK FOR AN
ERROR. PRINT TO THE TERMINAL THAT THE STRIPPER HAS BEEN
CONVERGED. REINITIALIZE THE PRINT FLAG. IF ONLY THE STRIPPER IS TO
BE MODELED, STOP.

ICOEFF = 0
CALL TCONV (GIS,LOS,TGIS,TEMS,TBOTS,PBOTS,DPS,NLASTS,IMAXS,
& MKUPH2O)
IF (IERR .GT. 0) GOTO 50
WRITE (*,*) 'STRIPPER'
WRITE (*,*)
IPR=0
IF (ISYS .EQ. 1) STOP

CALCULATE THE ERRORS IN THE LOADING GUESSES FOR THIS SYSTEM
CALCULATION. IF THE ERRORS MEET THE CONVERGENCE CRITERION AND
THE SYSTEM HAS NOT ALREADY CONVERGED, THEN SET IFLAG AND RETURN
TO 100 SO THAT THE FINAL RESULTS CAN BE PRINTED.

FS=LINH2S-LOA(1,1)
FC=LINCO2-LOA(2,1)
ERRS = DABS(FS/LOA(1,1))
ERRC = DABS(FC/LOA(2,1))

WRITE THE GUESSES AND ERRORS ASSOCIATED WITH EACH SYSTEM
ITERATION TO THE SCREEN TO ASSIST IN FUTURE GUESSES.

WRITE (*,101) LOA(1,1),FS,LOA(2,1),FC
101 FORMAT (/4(F13.9/)

IF (ERRS.LT.0.005.AND.ERRC.LT.0.005.AND.IFLAG.NE.4) THEN
IFLAG = 4
GOTO 100
ENDIF

KEEP THE BEST VALUES FOR CO2 AND H2S LOADING FOR THE NEXT SYSTEM
ITERATION.

IF ((ERRS + ERRC).LT.ERR) THEN
XS1NEW = LOA(1,1)
XC1NEW = LOA(2,1)
ERR = ERRS + ERRC
ENDIF

IF THE SYSTEM HAS NOT CONVERGED, NEW LOADING VALUES ARE
CALCULATED. A QUASI-NEWTON METHOD IS USED TO CONVERGE THE
SYSTEM AND UPDATE THE GUESSES. THE DAMPING FACTORS FOR H2S AND
CO2 ARE USED TO CONTROL THE CHANGE IN THE NEW GUESS. AFTER THE
THIRD SYSTEM CALCULATION, THE GUESSES ARE UPDATED AND THE
PROCESS REPEATED UNTIL CONVERGENCE IS REACHED.

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. 0.0) .AND. (XC2 .EQ. 0.0)) THEN
    XS3 = XS2-(XS2-XS1)*FS1/(FS1-FS3)
    XC3 = 0.
  ELSE IF ((XS1 .EQ. 0.0) .AND. (XS2 .EQ. 0.0)) 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-DFSX*DFCX
    DXS = (DFXS*FC1-DFCX*FS1)/DUM
    DXC = (DFCX*FS1-DFXS*FC1)/DUM
    IF (DABS(DXS)/XS2.GT.2.0DAMP) DXS = DABS(DXS)*1.0DAMP*XS2/DXS
    IF (DABS(DXC)/XC2.GT.2.0DAMP) D XC = DABS(DXC)*1.0DAMP*XC2/DXC
    XS3 = XS2+DXS
    XC3 = XC2+DXC
  EN DIF
  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
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,12))
1002 FORMAT (1X,I2,4(F12.5))
1003 FORMAT (1X,I3,1X,F12.5,1X,F12.5,12)
C
STOP
END
C
SUBROUTINE TCONV (GI,LO,TGI,TEMP,TBOT,PBOT,DP,NLAST,ITERMAX,
& MKUPH2O)
C
TCONV IS THE TEMPERATURE CONVERGENCE ROUTINE FOR A TOWER. GIVEN
AN INITIAL GUESS FOR THE TEMPERATURE PROFILE, WHICH CONSISTS OF
THE TEMPERATURE INTO EACH STAGE, TOWER IS SUCCESSIVELY CALLED
UNTIL THAT PROFILE HAS CONVERGED TO SOME LIMIT. THE CONVERGENCE
IS ACHIEVED 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),MKUPH20
C
COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF
C
SET THE CONVERGENCE FLAG. THIS HELPS DETERMINE WHETHER PRINTING
IS DESIRED OR NOT. IF BOTH IPR AND ICOEFF = 1 THEN PRINT.
C
ICONV = 0
C
CONVERGENCE IS ATTEMPTED UNTIL A MAXIMUM NUMBER OF ITERATIONS,
ITERMAX, HAS BEEN REACHED.
C
DO 20 ITER=1,ITERMAX
C
IF EACH STAGE CONVERGENCE SHOULD BE PRINTED (IPRINT=0), SET THE
PRINT FLAG
C
IF (IPRINT.EQ.0) THEN
  IPR = 1
  ICOEFF = 1
ENDIF
C
SUBSTITUTE THE CURRENT TEMPERATURES INTO STORAGE FOR
COMPARISON AFTER THE NEXT CONVERSION TO GET AN UPDATED VERSION.
C
DO 50 L=1,NLAST-1
T(L)=TEMP(L)
50 CONTINUE
CALL TOWER (GI, LO, TGI, TEMP, T, TBOT, PBOT, DP, NLAST, MKUPH2O, ICONV)
IF (IERR .GT. 0) RETURN

IF THERE IS ONLY ONE STAGE, NO TEMPERATURE CONVERGENCE IS NEEDED.
IF (NLAST .EQ. 1) GOTO 60

COMPARSE THE CALCULATED TEMPERATURES FROM TOWER TO THE
CURRENT TEMPERATURE PROFILE TO SEE IF EACH ONE HAS MET THE
CONVERGENCE CRITERION.

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

WRITE (*,*) 'NO TEMPERATURE CONVERGENCE'

CONTINUE

IF THE ENTIRE SYSTEM AS WELL AS THE TEMPERATURE PROFILE HAS
CONVERGED, THEN CALL TOWER ONE LAST TIME TO PRINT THE RESULTS.

IF ((IPR .EQ. 1) .AND. (IPRINT .GE. 2)) THEN
  CALL TOWER (GI, LO, TGI, TEMP, T, TBOT, PBOT, DP, NLAST, MKUPH2O, ICONV)
  RETURN
ENDIF

IF PRINTING IS DESIRED AFTER EACH TEMPERATURE CONVERGENCE, CHECK
TO SEE IF CONVERGENCE HAS BEEN MET AND THEN PRINT THE RESULTS.

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

RETURN
END

SUBROUTINE TOWER (GI, LO, TGI, TEMP, T, TBOT, PBOT, DP, NLAST,
MKUPH2O, ICONV)

TOWER IS THE ROUTINE WHICH PUTS TOGETHER ALL OF THE CONVERGED
STAGES AS A COMPLETE TOWER SIMULATION. ITS FUNCTION IS TO START AT
THE BOTTOM OF THE TOWER AND CONVERGE THE STAGES MOVING UP. IT
ALSO CALLS THE PRINT ROUTINE WHEN DESIRED.

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,LOUTC02,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
REAL*8 NG, NGREB

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,LOUTC02,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

EXTERNAL STAGE

TGIN=TGI

CONVERGE EACH STAGE OF THE TOWER BY CALLING SECANT2 WITHIN THIS
DO LOOP.

DO 10 N=1,NLAST

FIND THE PRESSURE OF THIS STAGE ACCOUNTING FOR THE PRESSURE DROP.

P=PBOT-DFLOAT(N-1)*DP

IF THIS IS THE FIRST TEMPERATURE CONVERGENCE ITERATION, USE THE GAS
INTO THE FIRST STAGE AS THE GUESS FOR THE GAS OUT. A GUESS FOR THE
COMPOSITION OF THE GAS OUT IS NEEDED FOR STAGE. AFTER THE FIRST
TEMPERATURE CONVERGENCE ITERATION, THE PROFILE OF THE GAS
COMPOSITION FROM THE PREVIOUS ITERATION IS USED FOR THE GUESSES.

IF (ITER.EQ.1) THEN
   DO 30 II=1,4
      GI(II,N+1)=GI(II,N)
   CONTINUE
ENDIF

GET THE GAS IN, GAS OUT, AND LIQUID OUT FROM THE SAVED ARRAYS. THE
LIQUID OUT AND GAS IN ARE KNOWN AND THE GAS OUT MUST BE GUESSED
BEFORE A STAGE CONVERGENCE IS STARTED. THE TEMPERATURE OF THE
LIQUID IN IS ALSO KNOWN FROM ITS PROFILE. THE PROFILE IS ACTUALLY
NOT KNOWN, BUT IS ASSumed TO BE KNOWN FOR THE PURPOSE OF THE
TOWER CALCULATIONS BECAUSE THE TEMPERATURE PROFILE IS
CONVERGED EXTERNAL TO THESE CALCULATIONS.

GINH2S=G(1,N)
GINCO2=G(2,N)
GINH2O=G(3,N)
GINNRT=G(4,N)
GININTOT=GINH2S+GINCO2+GINH2O+GINNRT
GOUTH2S=G(1,N+1)
GOUTCO2=G(2,N+1)
GOUTH2O=G(3,N+1)
GOUTNRT=G(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)

THE TOTAL LIQUID CONCENTRATION OF EACH SPECIES IS CALCULATED. THE
CONCENTRATIONS ARE IN UNITS OF MOLALITY (MOLES/KG WATER).

WTH2O = LOUTH2O*0.018
TH2S = LOUTH2S/WTH2O
TCO2 = LOUTCO2/WTH2O
TAM = LOUTAM/WTH2O
TION = LOUTION/WTH2O

CALCULATE THE LIQUID DIFFUSIVITIES FOR THIS STAGE AND THEN THE MASS
TRANSFER PARAMETERS

CALL DIFFUSE (TLIN)
IF (ICOEFF.EQ.0) THEN
   ICOEFF = 1
   CALL COEFF ( TLIN, TGIN, P )
ENDIF

THE SEACANT2 CONVERGENCE ROUTINE FOR STAGE NEEDS TWO INITIAL
GUESSES FOR THE TEMPERATURE OF THE LIQUID OUT OF THE STAGE. ONE
GUESS IS FROM THE PROFILE, AND THE OTHER IS THAT VALUE PLUS AN
ARBITRARY SMALL AMOUNT.

IF (N.EQ.1) THEN
   XL=TBOT
ELSE
   XL=TEMP(N-1)
ENDIF
XR=XL+.03

CONVERGE THE CURRENT STAGE. CHECK FOR ERRORS. IF THE TOWER HAS
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
        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)=TOUT
    ELSE
        TBOT=TOUT
        ENDIF
C
C END OF DO LOOP.
C
C 10 CONTINUE
C
C RETURN
C END
SUBROUTINE PRINT

THE PRINT ROUTINE IS CALLED BY TOWER FOR EACH STAGE WHEN PRINTING
IS DESIRED. DATA IS TRANSFERRED TO FILE OUT.OUT.

IMPLICIT REAL*8 (A-H-O-Z)
REAL*8 LINH2S, LINCO2, LINH2O, LINAM, LINION, LINTOT, LOUTH2S,
       LOUTCO2, LOUTH2O, LOUTAM, LOUTION, LOUTTOT, NG, NGREB, M

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/, TOUT, TLIN, TGOUT, TGIN
COMMON /CONB/, OH, RNH, RN, HS, H2S, HCO3, CO3, CO2
COMMON /CONT/, TAM, TH2S, TCO2, TION
COMMON /CONI/, OHI, RNIH, RNI, HSI, H2SI, HCO3I, CO3I, CO2I, CO2IE
COMMON /PI/, PH2SI, PCO2I, PH2OI, PNRIT
COMMON /PRESS/, PH2S, PCO2, P
COMMON /FLAG/, N, ITER, IPRINT, IPR, IREB, IERR, ICOLUMN, ICOEFF
COMMON /ENHANC/, EH2S, ECO2, M
COMMON /FLUX/, FK, FKG, NG, NGREB, AREA

WRITE THE TEMPERATURE PROFILES TO FILE 'TEMP.OUT' TO BE USED
FOR LATER RUNS IF DESIRED.

WRITE (10,*) TOUT

WRITE (3,*) ''

WRITE THE MASS TRANSFER PARAMETERS

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

STAGE NUMBER AND HEADINGS

WRITE (3,100) N, H2S, 'CO2', 'H2O', 'AMINE', 'OTHER',
          'TOTAL', 'TEMP(K)'

GAS OUT OF THE STAGE (MOLE/S) AND TEMP
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 LIQUID INTO THE STAGE (MOLE/S) AND TEMP
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 H2S AND CO2 BULK AND INTERFACE LIQUID CONCENTRATION (MOLE/KG H2O)
WRITE (3,103) 'BCONC',H2S,CO2,'---','RN','---','---'
WRITE (3,103) 'ICONC',H2SI,CO2I,'---','RNI','---','---'
C AVERAGE (GAS IN AND GAS OUT) INTERFACIAL PARTIAL PressURES (ATM):
WRITE (3,104) 'PRESS',PH2SI,PCO2I,PH2OI,'---',PNRTI,P
C ENHANCEMENT FACTORS
WRITE (3,105) 'EFACT',EH2S,ECO2
C WHEN THE Print FLAG, IPRINT, EQUALS 3 OUTPUT THE NUMBERS FOR
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,'PH2S = ',GINH2S/GINTOT*P,
  & 'EQ PH2S = ',H2S*HH2S
  WRITE (3,110) 'TCO2 = ',TCO2,'PCO2 = ',GINCO2/GINTOT*P,
  & 'EQ PCO2 = ',CO2*HCO2
  WRITE (3,*) 'THE CO2 HATTA NUMBER = ',DSQRT(M)
C WRITE (5,110) 'TH2S = ',TH2S,'PH2S = ',GINH2S/GINTOT*P,
  & 'EQ PH2S = ',H2S*HH2S
  WRITE (6,110) 'TCO2 = ',TCO2,'PCO2 = ',GINCO2/GINTOT*P,
  & 'EQ PCO2 = ',CO2*HCO2
ENDIF
C 100 FORMAT ('//3X,12,7X,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)
FUNCTION STAGE(T)

STAGE IS A FUNCTION USED TO DO MASS AND HEAT TRANSFER AND
BALANCE CALCULATIONS. THERE IS A CONVERGENCE LOOP WITHIN STAGE
WHICH CONVERGES THE COMPOSITION OF THE GAS OUT OF THE STAGE FOR
A GIVEN TEMPERATURE OF THE LIQUID OUT. THIS TEMPERATURE OF THE
LIQUID OUT IS NOT KNOWN BUT IS CONVERGED BY SECANT2 WHICH IS THE
CONVERGENCE ROUTINE FOR STAGE. THE ERROR IN THE SUM OF THE
PARTIAL PRESSURES AT THE INTERFACE IS MINIMIZED BY MANIPULATING
THE TEMPERATURE OF THE LIQUID OUT OF THE STAGE.

THE MASS TRANSFER EQUATIONS ARE USED TO FIND THE COMPOSITION OF
THE GAS OUT (H2S AND CO2) OF THE STAGE, AND THE MATERIAL BALANCE
SPECIFIES THE COMPOSITION OF THE LIQUID IN. THE COMPOSITIONS OF THE
GAS IN AND LIQUID OUT ARE KNOWN COMING INTO THIS STAGE
CALCULATION BECAUSE THE STAGE BELOW THIS HAS BEEN CONVERGED OR
THIS IS THE BOTTOM STAGE. THE ENTHALPY TRANSFER EQUATION IS USED
TO FIND THE TEMPERATURE OF THE GAS OUT OF THE STAGE, AND THE
ENTHALPY BALANCE SPECIFIES THE AMOUNT OF WATER TRANSFERRED FOR
THE STAGE. AS ALREADY STATED A PRESSURE BALANCE FOR THE
INTERFACE SPECIFIES THE TEMPERATURE OF THE LIQUID OUT OF THE STAGE.
THE TEMPERATURE OF THE GAS INTO THIS STAGE IS KNOWN, AND THE
TEMPERATURE OF THE LIQUID IN IS ASSUMED TO BE KNOWN FROM THE
CURRENT TEMPERATURE PROFILE FOR THE TOWER.

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 LINH2S,LINCO2,LINH2O,LINAM,LINION,LINTOT
REAL*8 LOUTH2S,LOUTC02,LOUTH2O,LOUTAM,LOUTION,LOUTTOT
REAL*8 NG,NGREB,NTU,K

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,LOUTC02,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,RNHl,RNI,HSI,H2SI,HCO3I,CO3I,CO2I,CO2IE
COMMON /EK/ HH2S,HCO2,EKAM,EKHCO3,EKH2S,EEKCO2
COMMON /DH/ DHH2S,DHCO2,DHH2O,DHAM
EXTERNAL BULK,FACE

TLOUT=T

GUESS THE CONCENTRATIONS OF THE IONIC SPECIES SO THAT AN INITIAL
GUESS FOR THE IONIC STRENGTH OF THE BULK SOLUTION CAN BE
CALCULATED IN BULK.

HS=TH2S
HCO3=TCO2
CO3=0.
RNH=TH2S+TCO2

THE SECANT METHOD NEEDS TWO INITIAL GUESSES FOR THE PHO OF THE
BULK SOLUTION. SECANT CONVERGES BULK TO GIVE THE BULK LIQUID
CONCENTRATIONS. IF ANY CONCENTRATION IS LESS THAN ZERO, THERE IS
AN ERROR, AND EXECUTION IS RETURNED.

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

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

IERR=1
CALL ERROR
RETURN
ENDIF

PARTIAL PRESSURES OF THE GAS INTO THE STAGE ARE CALCULATED AND
THE VALUES ARE GIVEN TO THE VARIABLES IN THE COMMON BLOCK USED BY
FACE.

PINH2S=GINH2S/GINTOT*P
PINCO2=GINCO2/GINTOT*P
PINNRT=GINNRT/GINTOT*P
PH2S=PINH2S
PCO2=PINCO2

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.

HSI=HS
HCO3I=HCO3
CO3I=CO3
RNHI=RNH
RN=RN
OH=OH

C THE SECANT METHOD NEEDS TWO INITIAL GUESSES FOR THE POH AT THE
C INTERFACE. 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.

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

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

IERR=2
CALL ERROR
RETURN
ENDIF

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
CALCULATE THE ENTHALPY OF THE KNOWN STREAMS (GAS IN AND LIQUID
C OUT)
C
CPGIN=GINH2S*CH25(TGIN,TLIN)+GINCO2*CPCO2(TGIN,TLIN)+
& GINH2O*CH20(TGIN,TLIN)+GINNRT*CPNRT(TGIN,TLIN)
CPLOUT=(LOUTH2S*CH25(TLOUT)+LOUTC02*CPCO2(TLOUT)+LOUTH20*
& CH20(TLOUT)+LOUTAM*CAM(TLOUT))*TLOUT-TLIN
C
CALCULATE THE THERMAL CONDUCTIVITY, DIFFUSIVITY, HEAT CAPACITY,
C AND DENSITY IN THE GAS PHASE FOR USE IN THE MASS AND HEAT TRANSFER
C 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
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
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
INITIALIZE THE VARIABLES THAT MUST BE CONVERGED WITHIN STAGE.
C
XH2S=GOUTH2S
XCO2=GOUTCO2
XH2O=GOUTH2O
XNRT=PINNRT

INITIALIZE THE STAGE ITERATION COUNTER AND BEGIN THE ITERATION LOOP. WITHIN THE LOOP, IT IS AN ERROR IF THE ITERATIONS EXCEED THE MAXIMUM AMOUNT ALLOWED.

ISTAGE=0
IF (ISTAGE .GT. 1000) THEN
  WRITE (*,*) ''
  WRITE (*,*) 'ERRH2S = ',ERRH2S
  WRITE (*,*) 'ERRCO2 = ',ERRCO2
  WRITE (*,*) 'ERRH2O = ',ERRH2O
  WRITE (*,*) 'ERRNRT = ',ERRNRT
  IERR=3
  CALL ERROR
  RETURN
ENDIF
ISTAGE=ISTAGE+1


GOUTH2S=XH2S
GOUTCO2=XCO2
GOUTH2O=XH2O
GOUTTOT=GOUTH2S+GOUTCO2+GOUTH2O+GOUTNRT
PNRT=XR

PARTIAL PRESSURES OF THE GAS OUT OF THE STAGE ARE CALCULATED AND THE VALUES ARE GIVEN TO THE VARIABLES IN THE COMMON BLOCK USED BY FACE.

POUTH2S=GOUTH2S/GOUTTOT*P
POUTCO2=GOUTCO2/GOUTTOT*P
POUTNRT=GOUTNRT/GOUTTOT*P
PH2S=POUTH2S
PCO2=POUTCO2

SECANT CONVERGES FACE TO GIVE THE INTERFACE CONCENTRATIONS. IF ANY CONCENTRATION IS LESS THAN ZERO, THERE IS AN ERROR, AND EXECUTION IS RETURNED. THESE INTERFACE CONCENTRATIONS ARE ASSOCIATED WITH THE GAS OUT.

CALL SECANT (FACE, XL, XR)
IF ( (OHI .LT. 0.) .OR. (RNHI .LT. 0.) .OR. (RN .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
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 

IERR=2 
CALL ERROR 
RETURN 
ENDIF 

CALCULATE THE PARTIAL PRESSURE AT THE INTERFACE AND THE PARTIAL PRESSURE DRIVING FORCE FOR MASS TRANSFER OF H2S AND CO2 ASSOCIATED WITH THE GAS OUT. CHECK TO MAKE SURE THAT THE MASS TRANSFER HAS NOT EXCEEDED EQUILIBRIUM. IF IT HAS, THE PARTIAL PRESSURE OF H2S OR CO2 IN THE GAS OUT IS EQUAL TO THE PARTIAL PRESSURE AT THE INTERFACE ASSOCIATED WITH THE GAS OUT. 

POUTSI=H2S*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 
DOUTS=POUTSI-POUTH2S 
DOUTC=POUTCI-POUTCO2 

CALCULATE THE DRIVING FORCE FOR MASS TRANSFER OF H2S AND CO2 AS A LOG MEAN AVERAGE OF THE DRIVING FORCES ASSOCIATED WITH THE GAS IN AND GAS OUT. IF THE NUMBERS ARE SUCH THAT THE LOG MEAN CALCULATION WOULD CAUSE AN ARITHMETIC ERROR (SUCH AS DIVIDING BY ZERO), USE AN ARITHMETIC AVERAGE DRIVING FORCE. 

IF (POUTH2S .EQ. PINH2S) THEN 
DAVG=(DFINS+DOUTS)/2. 
ELSE 
IF ( (DFINS .EQ. DOUTS).OR.(DFINS .EQ. 0.).OR. 
& (DOUTS .EQ. 0.).OR.(DFINS .GT. 0.).AND.(DOUTS .LT. 0.)) 
& .OR.(DFINS .LT. 0.).AND.(DOUTS .GT. 0.)) THEN 
DAVG=(DFINS+DOUTS)/2. 
ELSE 
DAVG=(DFINS-DOUTS)/DLOG(DFINS/DOUTS)
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+PINS1+POUTH2S+POUTSI)/4.
PAVGCO2=(PINCO2+PINC1+POUTCO2+POUTC1)/4.
PAVGNRT=(PINNRT+2.*PNRT1+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 TRANSFER.
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
C BALANCE.
DUM=(CPGIN-CPLOUT-GOUTH2S*CPH2S(TGOUT,TLIN)-GOUTCO2*
  & CPCO2(TGOUT,TLIN)-GOUTNRT*CPNRT(TGOUT,TLIN)+(DH2S+DHAM)*
  & (GINH2S-GOUTH2S)+(DHCO2=DHAM)*(GINCO2-GOUTCO2))
GOUTH2O=(DUM+DH2O*GINH2O)/(DH2O+CPH2O(TGOUT,TLIN))

C GOUTTOT=GOUTH2S+GOUTCO2+GOUTH2O+GOUTNRT

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 MATERIAL BALANCE EQUATIONS ARE USED TO CALCULATE THE
C COMPOSITION OF THE LIQUID INTO THE STAGE.

C LINH2S=LOUTH2S+GOUTH2S-GINH2S
LINCO2=LOUTC02+GOUTCO2-GINCO2
LINH2O=LOUTH2O+GOUTH2O-GINH2O
LINAM=LOUTAM
LINION=LOUTION

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 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.
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

LINTOT = LINH2S + LINCO2 + LINH2O + LINION + LINAM

IF THIS IS THE FIRST ITERATION WITHIN THE STAGE CONVERGENCE LOOP,
INITIALIZE THE VARIABLES USED IN THE CONVERGENCE AND DO ANOTHER
ITERATION BY RETURNING TO THE BEGINNING OF THE LOOP. THIS MUST BE
DONE BECAUSE THE SECANT METHOD USED TO CONVERGE THE VARIABLES
IN THIS LOOP REQUIRES TWO INITIAL GUESSES. WHAT THIS AMOUNTS TO IS
USING DIRECT SUBSTITUTION FOR THE FIRST ITERATION AND A SECANT
METHOD FOR THE REST.

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

CALCULATE THE FUNCTIONS WHICH ARE TO BE MINIMIZED BY THE SECANT
METHOD. THESE FUNCTIONS ARE SIMPLY DIFFERENCES BETWEEN THE
CALCULATED VALUES AND THE GUESS FROM THE LAST ITERATION.

FH2S=GOUTH2S-XH2S
FCO2=GOUTCO2-XCO2
FH2O=GOUTH2O-XH2O
FNRT=PNRTI-XNRT

USE THE SECANT METHOD TO CALCULATE THE NEW GUESSES OF THE
VARIABLES TO BE CONVERGED FOR THE NEXT ITERATION, UNLESS IT WOULD
CAUSE A DIVISION BY ZERO, THEN USE DIRECT SUBSTITUTION.
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=PNRT1-XNRT
ELSE
  DELNRT=-DELNRT*FNRT/(FNRT-FOLDNRT)
ENDIF
XH2S=XH2S+DELH2S
XCO2=XCO2+DELCO2
XH2O=IXH2O+DELH2O
XNRT=XNRT+DELNRT

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
THE ERROR IN THE VARIABLES TO BE CONVERGED MUST BE CALCULATED TO
CHECK FOR CONVERGENCE. THE ERROR IS A PERCENT CHANGE, UNLESS
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

IF ANY OF THE ERRORS IS NOT WITHIN THE CONVERGENCE LIMIT, DO
ANOTHER ITERATION.

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

NOW THAT THE CONVERGENCE LOOP WITHIN STAGE IS FINISHED, THE ERROR
IN THE SUM OF THE PARTIAL PRESSURES AT THE INTERFACE IS CALCULATED
FOR USE BY SECAT2 TO CONVERGE THE TEMPERATURE OF THE LIQUID OUT
WHICH OCCURS EXTERNAL TO THIS FUNCTION. THE PARTIAL PRESSURES OF
H2S AND CO2 AT THE INTERFACE IS AN ARITHMETIC AVERAGE VALUE OF THE
GAS IN AND GAS OUT INTERFACIAL VALUES WHICH WERE CALCULATED IN
THE LOOP ABOVE. THE VALUE FOR THE INERT WAS ALSO CALCULATED IN
THE LOOP ABOVE. THE PARTIAL PRESSURE OF WATER AT THE INTERFACE IS
CALCULATED BY ASSUMING THAT IT IS IN EQUILIBRIUM WITH THE LIQUID
INTERFACE AND USING RAOUlt'S LAW. THE ANTOINE EQUATION FOR THE
VAPOR PRESSURE OF WATER IS FROM FELDER AND ROUSSEAU (P.214).

PH2SI=(PINSI+POUTSI)/2.
PCO2I=(PINC1+POUTC1)/2.
P0H2O=(10.**(7.96681-1668.21/(TOUT+228.273)))/760.
XH2O1=1.0/0.018/(1/0.018+OH1+RNHI+RN1+HS1+H2SI+HCO3I+CO3I+CO2I)
PH2OI=P0H2O*XH2O1
STAGE=P-PH2SI-PCO2I-PH2OI-PNRTI

RETURN
END

FUNCTION CPH2S (TEMP,TEMPR)
C CALCULATES THE ENTHALPY CHANGE FOR H2S GOING FROM TEMP TO 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)+3.012D-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 TEMPR. DATA FROM FELDER AND ROUSSEAU.
C
C IMPLICIT REAL*8 (A-H,O-Z)
T=TEMP-273.
TR=TEMPR-273.
& (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 TEMP TO TEMPR. DATA FROM FELDER AND ROUSSEAU.
C
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 TEMP TO TEMPR. DATA FROM FELDER AND ROUSSEAU.
C
C IMPLICIT REAL*8 (A-H,O-Z)
T=TEMP-273.
TR=TEMP-273.
CPNR=(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
FUNCTION CH2S(T)
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
FUNCTION CCO2(T)
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
FUNCTION CH2O(T)
C
THE HEAT CAPACITY OF LIQUID WATER.
C
IMPLICIT REAL*8 (A-H,O-Z)
CH2O=18.
C
RETURN
END
C
FUNCTION CAM(T)
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

RETURN
END

SUBROUTINE ERROR

THIS ERROR ROUTINE IS CALLED IF A SPECIFIED ERROR OCCURS. A
MESSAGE IS PRINTED TO THE TERMINAL AND EXECUTION IS RETURNED.
AFTER THE ERROR IS DETECTED EXECUTION IS RETURNED THROUGH EVERY
SUBROUTINE BACK TO THE MAIN PROGRAM. AN INTEGER SPECIFIES WHICH
ERROR HAS OCCURRED.

IMPLICIT REAL*8 (A-H,O-Z)
COMMON /FLAG/N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF

IF (IERR.EQ.1) THEN
WRITE (*) 'PROBLEM IN BULK SOLUTION'
ENDIF

IF (IERR.EQ.2) THEN
WRITE (*) 'PROBLEM IN INTERFACE SOLUTION'
ENDIF

IF (IERR.EQ.3) THEN
WRITE (*) 'STAGE DOES NOT CONVERGE'
ENDIF

IF (IERR.EQ.5) THEN
WRITE (*) 'H2S LOADING TOO HIGH'
ENDIF

IF (IERR.EQ.6) THEN
WRITE (*) 'LINH2S < 0 AT STAGE
ENDIF

IF (IERR.EQ.7) THEN
WRITE (*) 'LINCO2 < 0 AT STAGE
ENDIF

IF (IERR.EQ.8) THEN
WRITE (*) 'LINH2O < 0 AT STAGE
ENDIF

RETURN
END

SUBROUTINE SECANT (FUNCT,XL,XR)
SECANT IS THE CONVERGENCE ROUTINE FOR BULK AND FACE. OBVIOUSLY, IT IS BASED ON THE SECANT METHOD; THEREFORE, TWO INITIAL GUESSES (XL AND XR) ARE NEEDED TO START THE METHOD. THE VALUE F IS MINIMIZED BY MANIPULATING X. THE CONVERGENCE CRITERION IS BASED ON THE CHANGE IN X.

IMPLICIT REAL*8 (A-H,O-Z)
XOLD=XL
X=XR

DELTAX=X-XOLD
FOLD=FUNCT(XOLD)

BEGINNING OF THE LOOP

10 F=FUNCT(X)
DELTAXX=DELTAX/F/(F-FOLD)
X=X+DELTAX

IF THE CONVERGENCE CRITERION IS NOT MET GO BACK TO THE BEGINNING OF THE LOOP.

IF (DABS(DELTAXX) .GT. .0005) THEN
   FOLD=F
   GOTO 10
ENDIF

RETURN END

******************************************************************************

SUBROUTINE SECANT2 (FUNCT,XL,XR)

SECANT2 IS EXACTLY THE SAME ROUTINE AS SECANT, BUT IS USED FOR CONVERGENCE OF STAGE. SECANT COULD NOT BE USED TO CONVERGE STAGE ALSO BECAUSE STAGE CALLS SECANT. THIS ROUTINE ALSO CHECKS ERROR CONDITIONS COMING OUT OF STAGE. IF THERE IS AN ERROR, EXECUTION RETURNS.

IMPLICIT REAL*8 (A-H,O-Z)
COMMON /FLAG/ N,ITER,IPRINT,IPR,IREB,IERR,ICOLUMN,ICOEFF

XOLD=XL
X=XR

DELTAX=X-XOLD
FOLD=FUNCT(XOLD)

IF (IERR .GT. 0) RETURN
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
FUNCTION BULK (POH)
C
   BULK IS A FUNCTION USED TO CALCULATE THE BULK LIQUID
   CONCENTRATIONS. THE EQUILIBRIUM EQUATIONS DESCRIBING THE BULK
   LIQUID ARE SOLVED SEQUENTIALLY GIVEN A GUESS FOR THE HYDROXIDE
   CONCENTRATION AND VARIABLE BULK IS THE ERROR IN THE BULK CHARGE
   BALANCE WHICH IS MINIMIZED BY THE SUBROUTINE SECANT BY
   MANIPULATING THE POH IN THE BULK SOLUTION. THERE IS A CONVERGENCE
   LOOP WITHIN BULK BECAUSE THE EQUILIBRIUM CONSTANTS ARE A
   FUNCTION OF IONIC STRENGTH WHICH IS NOT KNOWN UNTIL THE BULK
   CONCENTRATIONS ARE KNOWN.
C
   IMPLICIT REAL*8 (A,H,O-Z)
   COMMON /EK/ HH2S,HCO2,EKAM,EKHC03,EKH2S,EKCO2
   COMMON /CONB/ OH,RNH,HN,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
   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
   CALCULATE THE EQUILIBRIUM CONSTANTS AT THE BULK LIQUID
   CONDITIONS.
C
   CALL EQ (T,SUMION,TAM)
C
   CALCULATE THE BULK LIQUID CONCENTRATIONS SEQUENTIALLY GIVEN THE
   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/(EKHCO2*RN+RNH))))
CO2=RNH*(TCO2-CO3)/(EKHCO2*RN+RNH)
HCO3=TCO2-CO3-CO2
BULK=OH+HS+HCO3+2.*CO3-RNH+TION

C IF THE CONVERGENCE CRITERION IS NOT MET GO BACK TO THE BEGINNING
C OF THE LOOP.
C
C IF (DABS((BULK-BULKOLD)/BULK) .GT. .0005) THEN
BULKOLD=BULK
GO TO 10
ENDIF
C
RETURN
END
C
CFUNCTION FACE (POH)
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 EQUILIBRIUM AT THE INTERFACE. THE NINE EQUATIONS INCLUDE FOUR
C EQUILIBRIUM 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
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/ OH1,RNH,RN1,HS1,H2S1,HCO31,CO31,CO21,CO2IE
COMMON /CONB/ OH1,RNH,RRN,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

T=TLOUT
FACEOLD=0.
OHI=10.**(-POH)

THE FOLLOWING IS A CONVERSION FACTOR TO CHANGE THE
CONCENTRATIONS FROM UNITS OF MOLE/KG H2O TO MOLARITY TO ENSURE
UNIT CONSISTENCY WITH THE OTHER PARAMETERS FKL AND FKG.

CONVERT = DENSAM(T)/(0.044*TCO2 + 0.034*TH2S + 0.119*TAM + 1.0)

THIS IS THE BEGINNING OF THE CONVERGENCE LOOP WITHIN FACE.

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

CALCULATE THE EQUILIBRIUM AND RATE CONSTANTS AT THE CONDITIONS
OF THE INTERFACE.

CALL EQ(T,SUMION,TAMI)
CALL RATE(T,SUMION,CONVERT,RKAM,RKOH)

CALCULATE THE INTERFACE CONCENTRATIONS SEQUENTIALLY GIVEN THE
GUESS FOR THE HYDOXIDE CONCENTRATION.

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/EKHH2S/RNI/CONVERT+FKL*
& (DSQRT(DH2S/DCO2)*RNI/EKHH2S/RNI+DSQRT(DHS/DCO2)))
H2SI=HSI*RNHI/EKHH2S/RNI

THIS "IF" STATEMENT DIRECTS DIFFERENT EQUATIONS TO BE USED IF THERE
IS OR IS NOT CO2 IN THE SOLUTION. IF THERE IS NO CO2 IN THE
SOLUTION, THE ERROR EQUATION IS THE CHARGE FLUX BALANCE. IF THERE
IS CO2 IN THE SOLUTION, THE ERROR EQUATION IS THE DIFFERENCE
BETWEEN THE CO2 ENHANCEMENT FACTOR FLUX AND THE CO2 GAS PHASE
FLUX.

IF (TCO2 .EQ. 0.) THEN
HCO3I=0.
CO3I=0.
CO2I=0.
CO2IE=0.
ECO2=0.
FACE=DHS*(HS-HSI)+DOH*(OH-OHI)+DHC03*(HCO3-HCO3I)+
& 2.*DCO3*(CO3-CO3I)-DRNH*(RNH-RNHI)
ELSE
HCO3I=(DHS*(HS-HSI)+DOH*(OH-OHI)+DHC03*HCO3+2.*DCO3*CO3+
& DRNH*(RNH-RNHI))/(DHC03+2.*DCO3*OHI*EKHC03)
C03I=HCO3I*OHI*EKHC03
C02IE=HCO3I*RNHI/EKCO2/RNI
C02I=(FKL*(C02+DSQRT(DHC03/DCO2)*(HCO3-HCO3I)+
& DSQRT(DC03/DCO2)*(C03-C03I))+FKG*PCO2/CONVERT)/
& (FKG*HCO2/CONVERT+FKL)
THETA=(C02IE-C02)/(C021-C02)
M=DCO2/FKL**2*(RKAM*RNHI+RKOH*OHI)*CONVERT
ECO2=DSQRT((1.1+M)*(-1.1+THETA)/(1.1-C3-M/(1.1-M)))*
& C3**2*(M/(1.1-C3**2+M)-1.)
FACE=ECO2*FKL*(C02-C02I)*CONVERT-FKG*(HCO2*CO2I-PCO2)
ENDIF

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 IF THE CONVERGENCE CRITERION IS NOT MET GO BACK TO THE BEGINNING
C OF THE LOOP.

C IF (DABS((FACE-FACEOLD)/FACE) .G.T. .0005) THEN
FACEOLD=FACE
GOTO 10
ENDIF

C RETURN
END

C******************************************************************************

C SUBROUTINE RATE (T,SUMION,CONVERT,RKAM,RKOH)
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 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)

RETURN
END

SUBROUTINE EQ (T, SUMION, AMMOL)

EQ CALCULATES VALUES OF THE EQUILIBRIUM CONSTANTS AND HENRY'S
LAW CONSTANTS AT THE TEMPERATURE (K), IONIC STRENGTH (MOLALITY),
AND AMINE CONCENTRATION (MOLALITY) DESIRED. THE VALUES ARE
TRANSFERRED IN THE COMMON BLOCK /EKG/

EKH2S  H2S(AQ) + R3N = HS + R3NH
EKCO2  CO2(AQ) + R3N = HCO3 + R3NH
EKHCO3 HCO3 + OH = CO3
EKAM   R3N = R3NH + OH
E KW   H2O = H + OH
HH2S   H2S(AQ) = H2S(G)
HCO2   CO2(AQ) = CO2(G)

VARIABLES:
EKW - WATER DISSOCIATION CONSTANT. FIT FROM DATA IN THE CRC
       HANDBOOK OF CHEMISTRY AND PHYSICS (MOLES/L)^2
EKHCO3 - INFINITE DILUTION BICARBONATE DISSOCIATION CONSTANT
         FROM EDWARDS (1978) WITH SOME CONVERSION FACTORS
         BECAUSE THE REACTIONS WERE DEFINED DIFFERENTLY (KG
         H2O/MOLE)
EKAM - INFINITE DILUTION AMINE PROTONATION CONSTANT FIT TO
       DATA FROM SCHWABE (1959) WITH SOME CONVERSION
       FACTORS BECAUSE THE REACTIONS WERE DEFINED
       DIFFERENTLY AND THE HEAT OF RXN EXTRACTED SO IT CAN
       BE CHANGED (MOLE/KG H2O)
EKCO2 - CO2 EQUILIBRIUM CONSTANT FIT TO AN EMPIRICAL EQUATION
       WITH SIX ADJUSTABLE PARAMETERS USING EQUILIBRIUM
       DATA FROM JOU
EH2S - SAME AS EKCO2 BUT FOR H2S
HH2S - H2S HENRY'S CONSTANT FOR INFINITE DILUTION IN H2O FROM
       EDWARDS (1978) (ATM-KG H2O/MOLE)
HC021 - CO2 HENRY'S CONSTANT FOR INFINITE DILUTION IN H2O FROM
HC02M - SAME AS HC021 BUT WITH UNITS (ATM-L/MOLE)
HC02M - CO2 HENRY'S CONSTANT AS A FUNCTION OF TEMP, WT%
       MDEA, AND ION CONCENTRATION WITH UNITS OF MOLARITY
       (ATM-L/MOLE). ION CONCENTRATION IS INDICATED BY THE
       AMOUNT OF PROTONATED AMINE. DATA WAS TAKEN BY
       TOMAN TO GET THIS CORRELATION.
HC02 - SAME AS HC02M BUT WITH UNITS (ATM-KG H2O/MOLE). THIS
       VALUE IS USED ELSEWHERE IN THE PROGRAM.
RNHM - TOTAL PROTONATED AMINE CONCENTRATION IN MOLARITY (MOLE/L).

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,H5,H2S,HCO3,CO3,CO2

THE FOLLOWING DATA STATEMENTS CONTAIN THE PARAMETERS THAT WERE ADJUSTED TO FIT THE EQUILIBRIUM CONSTANTS FOR H2S AND CO2. THE FIRST DATA STATEMENT IS FOR H2S AND THE SECOND FOR CO2.

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/

EKW=10.**(285.521-11987.6/T+.0616564*T-48.737*DLOG(T))

EKHCO3 =DEXP(-12431.7/T - 35.4819*DLOG(T) + 220.067)*(DENSW(T)**2)
& /EKW

PKA=8.523
DHTERM=DHAM/1.987/298.**2
EKAM=EKW*DEXP(-PKA*DLOG(10.D0)+DHTERM*(T-298.))/DENSW(T)

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.))

CALCULATE THE INFINITE DILUTION VALUE TO GET THE TEMPERATURE DEPENDENCE

HCO2i = DEXP(-6789.04/T - 11.4519*DLOG(T) - 0.010454*T + 94.4914)
HCO2iM = HCO2i/DENSW(T)

HCO2M IS CURRENTLY SET FOR 50 WT% MDEA. FOR OTHER COMPOSITIONS, SIMPLY SUBSTITUTE THE 50.0 WITH THE NEW WT%.

RNHM = RNH*DENSAM(T)/(0.044*TCO2 + 0.034*TH2S + 0.119*TAM + 1.0)
HCO2M = 10.0**(DLOG10(HCO2IM + 0.032361*(50.0) +
& 0.0033283*(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.))

RETURN
END

***********************************************************************

SUBROUTINE DIFFUSE (T)
THIS SUBROUTINE CALCULATES THE DIFFUSIVITIES FOR THE VARIOUS
SPECIES AS A FUNCTION OF VISCOSITY. VISCOSITY IN TURN IS A FUNCTION
OF TEMPERATURE AND CO2 LOADING.

VISCOSITIES:

THE EQUATION FOR WATER VISCOSITY WAS FIT TO DATA IN THE CRC
HANDBOOK OF CHEMISTRY AND PHYSICS. THE EQUATION FOR UNLOADED
SOLUTION VISCOSITY COMES FROM GLASSCOCK (1990) WHICH WAS DERIVED
FROM AL-GHAWAS (1988) DATA.
THE EQUATION FOR LOADED SOLUTION VISCOSITY WAS FIT TO DATA FROM
TOMAN (1990) TO OBTAIN THE SLOPE 0.7527. THE FACTOR (298/T)**2 WAS
ARBITRARILY USED TO REDUCE THE DEPENDENCE OF VISCOSITY ON
LOADING AT HIGHER TEMPERATURES. THIS EFFECT IS NOT A PROVEN ONE
BUT TOMAN FELT THAT IT WOULD PROBABLY OCCUR.

DIFFUSIVITIES:

THE UNLOADED SOLUTION DIFFUSIVITY FOR CO2 CAME FROM ANALOGY TO
THE LOADED SOLUTION DIFFUSIVITIES ARE FOUND USING THE MODIFIED
STOKES-EINSTEIN RELATIONSHIP. THE VALUE 8.08D-8 IS THE DIFFUSIVITY
(DM^2/S) OF MDEA AT 25 C IN H2O ASSUMING THAT THE MDEA VALUE IS
EQUAL TO THE DEA VALUE (I.E. THE VALUE IS FOR DEA FOUND FROM
VERSTEEG (1988)). THE VALUE 1.77D-7 IS THE DIFFUSIVITY (DM^2/S) OF H2S
AT 16 C IN H2O FOUND IN THE CRC HANDBOOK OF CHEMISTRY AND
PHYSICS.

THE DIFFUSIVITIES OF THE IONS ARE ARBITRARILY SET EQUAL TO THAT OF
MDEA.

VARIABLES:

D(COMPONENT) - RESPECTIVE COMPONENT DIFFUSIVITY FOR LOADED
SOLUTION (DM^2/S)
DCO2ULD - UNLOADED SOLUTION CO2 DIFFUSIVITY (M^2/S)
VIS H2O - WATER VISCOSITY (CP)
VIS LD - LOADED SOLUTION VISCOSITY (CP)
VISLULD - UNLOADED SOLUTION VISCOSITY (CP)
CO2LDG - CO2 LOADING (MOLE/MOLE)

IMPLICIT REAL*8 (A-H,M-Z)
COMMON /CONT/ TAM,T/2S,TCO2,TION
COMMON /DIFF/ DOH,DRNH,DRN,DHS,DH2S,DHC03,DCO3,DCO2,DL,DCO2ULD

VISLULD = DEXP(-34.51 + 7434.0/T + 0.03951*T)
CO2LDG = TCO2/TAM
VISLULD = DEXP(VISLULD + 0.7527*(298.0/T)**2)*CO2LDG
DCO2ULD = 1.1*T*DEXP(-30.7509 - 0.7785*DLOG(VISLULD/1000.0))

DCO2 = 100.0*DCO2ULD*(VISLULD/VISLULD)**0.6
TEMP = T - 273.0
VISH2O = DEXP(0.55479 - 0.028401*TEMP + 1.04D-4*TEMP**2)

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
DHC03 = DRN
DCO3 = DRN
DOH = DRN

RETURN
END

END OF SUBROUTINE DIFFUSE

SUBROUTINE COEFF ( TLIN, TGIN, P )

THIS SUBROUTINE CALCULATES THE MASS TRANSFER COEFFICIENTS AND
THE NUMBER OF MASS TRANSFER UNITS. CURRENTLY, THE EXPRESSIONS
ARE FOR SIEVE TRAYS OR BUBBLE CAP TRAYS THAT ARE SPACED BY 24
INCHES. THE TRAY SPACING PLAYS A PART IN THE CALCULATION OF
THE GAS VELOCITY BECAUSE THE FLOOD VELOCITY IS CALCULATED USING A
CORRELATION IN PERRY'S HANDBOOK BASED ON 24 INCH TRAYS.


INPUTS (FOUND IN COMMON BLOCK):

F - FRACTION FLOOD, THAT IS RATIO OF GAS TO FLOOD VELOCITY
HL - LIQUID HOLDUP ON EACH TRAY (CM)
HFROTH - EFFECTIVE FROTH HEIGHT ON EACH TRAY (CM)

VARIABLES:

DG - ESTIMATE OF OVERALL GAS DIFFUSION COEFFICIENT, FOR
THE ABSORBER, ASSUMED TO BE H2O DIFFUSING IN N2. FOR
THE STRIPPER, ASSUMED TO BE CO2 DIFFUSING IN H2O. THE
ESTIMATES WERE FOUND USING A METHOD BY FULLER
(1966),(CM^2/S)
FKGA - GAS PHASE MASS TRANSFER COEFFICIENT WITH UNITS (M/S)
MULTIPLIED BY THE AREA AVAILABLE FOR MASS TRANSFER
WITH UNITS (M^2/M^3), (1/S)
GMW - GAS MOLECULAR WEIGHT (KG/KMOLE)
GDENS - GAS DENSITY (KG/M^3)
GVEL - GAS VELOCITY THRU ACTIVE AREA OF TRAY, UNITS (M/S)
FOR SIEVE TRAYS AND (CM/S) FOR BUBBLE CAP TRAYS
FVA - FACTOR DEFINED BY CHAN AND FAIR
ESTIMATE OF OVERALL LIQUID DIFFUSION COEFFICIENT (CM^2/S)

SAME AS FKG BUT FOR THE LIQUID (M/S)

INTERFACIAL AREA AVAILABLE FOR MASS TRANSFER IN M^2/M^3 FROTH. THE CORRELATION SHOULD NOT BE USED FOR FVA GREATER THAN 4.0. THE CORRELATION CAME FROM A GRAPH IN BISIO (1985).

INTERFACIAL AREA AVAILABLE FOR MASS TRANSFER IN DM^2/CM^2 FLOOR AREA.

EFFECTIVE FROTH DENSITY

AVERAGE VAPOR RESIDENCE TIME (S)

NUMBER OF GAS PHASE MASS TRANSFER UNITS

GAS PHASE MASS TRANSFER COEFFICIENT (MOLE/DM^2/S/ATM)

LIQUID PHASE MASS TRANSFER COEFFICIENT (DM/S). THIS COEFFICIENT IS BASED ON THE CO2 DIFFUSIVITY; THEREFORE, IT IS THE CO2 LIQUID PHASE MASS TRANSFER COEFFICIENT. OTHER COMPONENT COEFFICIENTS ARE FOUND BY RATIOING THE SQUARE ROOT OF DIFFUSIVITIES.

ACTUAL AREA FOR MASS TRANSFER IN DM^2

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 NG, NGREB

COMMON /TRAY/I TRAY,F,HL,HFROTH
COMMON /FLUX/FKL,FKG,NG,NGREB,AREA
COMMON /DIFF/DOH,DRNH,DRN,DH,DH2S,DHCO3,DCO3,DCO2,DL,DG
COMMON /GIN/GINH2S,GINCO2,GINH2O,GINNRT,GINTOT
COMMON /FLAG/N,ITER,IPRINT,IFR,IREB,IERR,ICOLUMN,ICOEFF

IF (ICOLUMN.EQ.1) THEN
   DG = 1.233D-5*TGIN**1.75/P
ELSE
   DG = 9.851D-6*TGIN**1.75/P
ENDIF

DL = DCO2*100.0

GMW = (34.0*GINH2S + 44.0*GINCO2 + 18.0*GINH2O + 28.0*GINNRT)/GINTOT
GDENS = P*GMW/TGIN/0.08205

CHECK TRAY TYPE AND CALCULATE THE APPROPRIATE COEFFICIENTS

IF (ITRAY.EQ.1) THEN
   GVEL = 10.7*P/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*DENSA(M(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 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 CALCULATE 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.

AREA = AREAVOL*HFROTH*GINTOT*0.08205*TGIN/P/1000.0/GVEL
PHI = HL/HFROTH
TV = (1 - PHI)*HL/100.0/PHI/GVEL
NG = FKG*TV
ENDIF

C RETURN
END

C END OF SUBROUTINE COEFF

**************************************************************************

FUNCTION DENSW (TEMP)

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.

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 END OF FUNCTION DENSW

**********************************************************************

FUNCTION DENSA (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
C VARIABLES:
C    DENSAM - 50 WT% MDEA SOLUTION DENSITY (KG/L)
C    CO2WTP - WT% CO2 IN SOLUTION
C    T - TEMPERATURE IN CELCIUS
C
C IMPLICIT REAL*8 (A-H,O-Z)
COMMON /CONT/ TAM,TH2S,TCO2,TION
C
C    T = TEMP - 273.0
C    CO2WTP = 100.0*44.0*TCO2/
C    &    (44.0*TCO2 + 34.0*TH2S + 119.0*TAM + 1000.0)
C
C    DENSAM = 1.0580 - 6.2606D-4*T + 0.009998*CO2WTP
C
C RETURN
C 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 McCabe-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): H₂S, CO₂, H₂O, N₂

0.1, 1.0, 0.6, 8.3

Line 4 - amine solution flow rates (mole/s): H₂O, MDEA, acid anion

13.8889, 2.1008, 0.0

Line 5 - guesses for rich solution loadings out of the absorber (mole/s): (H₂S)₁, (H₂S)₂, (CO₂)₁, (CO₂)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): H₂S dissociation, CO₂ dissociation, MDEA protonation, and H₂O vaporization
2089, 6364, 10325, 7889

Stripper:

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): H₂S, CO₂, H₂O, N₂
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$_2$S dissociation, CO$_2$ dissociation, MDEA protonation, and H$_2$O vaporization
2089, 6364, 9461, 7889

General:

Line 15 - max number of system iterations, H$_2$S 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$_2$S, CO$_2$, H$_2$O, 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$_2$S 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)*

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<th>Steam Rate (mole/s)</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
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### Effect of Acid Addition on System Performance

(Run #109-118)

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<th>Acid Rate (mole/s)</th>
<th>Acid Rate (equiv/L)</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
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Effect of Stripper Pressure Reduction on System Performance with 10% CO₂ Feed Gas
(Run #109,121-123)

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<th>Pressure (atm)</th>
<th>H₂O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H₂S Leak (ppm)</th>
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<td>98.8 98.5 98.9 98.2 98.7 99.3 100.1 103.7 124.7 156.1</td>
</tr>
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Effect of Stripper Pressure Reduction on System Performance with 2.5% CO₂ Feed Gas  
(Run #124-126)

<table>
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<tr>
<th>Pressure (atm)</th>
<th>H₂O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H₂S Leak (ppm)</th>
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<tbody>
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Change the Number of Stages to 14 Absorber and 18 Stripper Stages
(Run #128)

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<th>H2O Rate (kg/mole feed gas)</th>
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<th>H2S Leak (ppm)</th>
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<tr>
<td>5.5</td>
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<td>0.014829972</td>
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<td>131.4</td>
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Effect of Stripper Stages on System Performance for a 2 atm Stripper and 14 Stage Absorber
(Run #128-137)

<table>
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<th>Stripper Stages</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
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<td>Stripper Stages</td>
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<td>Liquid Rate (gal/SCF)</td>
<td>H2S Leak (ppm)</td>
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Change the MDEA Equilibrium Constant Using 14 Absorber and 18 Stripper Stages (Run #138-141)

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

<table>
<thead>
<tr>
<th>Ratio of EKAM</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
<th>H2S Selectivity</th>
<th>CO2 % Slip</th>
</tr>
</thead>
<tbody>
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<td>0.0161195</td>
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</tr>
<tr>
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<tr>
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<td>1.9</td>
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<td>0.0154747</td>
<td>123</td>
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</table>
Change the Liquid Phase Mass Transfer Coefficient
Using 14 Absorber and 18 Stripper Stages
(Run #145-152)

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

<table>
<thead>
<tr>
<th>Ratio of (k_l)</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
<th>H2S Selectivity</th>
<th>CO2 % Slip</th>
</tr>
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<tbody>
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</tr>
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Change the Gas Phase Mass Transfer Coefficient
Using 14 Absorber and 18 Stripper Stages
(Run #153-160)

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

<table>
<thead>
<tr>
<th>Ratio of kg</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
<th>H2S Selectivity</th>
<th>CO2 % Slip</th>
</tr>
</thead>
<tbody>
<tr>
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Change the CO₂-MDEA Rate Constant Using 14 Absorber and 18 Stripper Stages
(Run #161-166)

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

<table>
<thead>
<tr>
<th>Ratio of (k_{\text{MDEA}})</th>
<th>H₂O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H₂S Leak (ppm)</th>
<th>H₂S Selectivity</th>
<th>CO₂ % Slip</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.0161195</td>
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<td>1.91</td>
<td>94.8</td>
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<td>0.0161195</td>
<td>145.9</td>
<td>1.77</td>
<td>94.4</td>
</tr>
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<td>0.0167643</td>
<td>149.7</td>
<td>1.7</td>
<td>94.2</td>
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<td>1.68</td>
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<td>0.0161195</td>
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<td>1.97</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>0.026</td>
<td>0.0167643</td>
<td>127.1</td>
<td>1.95</td>
<td>94.9</td>
</tr>
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<td>0.0154748</td>
<td>125.7</td>
<td>2.02</td>
<td>95.1</td>
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<td>0.5</td>
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<td>0.0154748</td>
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<td>95.3</td>
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<td>117.8</td>
<td>2.25</td>
<td>95.6</td>
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<td>0.0141852</td>
<td>106.1</td>
<td>2.32</td>
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</tbody>
</table>
Effect of Stripper Stages on System Performance with a 1 atm Stripper and 20 Absorber Stages
(Run #168-174)

<table>
<thead>
<tr>
<th>Number of Stripper Stages</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.021</td>
<td>0.013540409</td>
<td>22.3</td>
</tr>
<tr>
<td>24</td>
<td>0.02</td>
<td>0.012895628</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>0.021</td>
<td>0.013540409</td>
<td>22.9</td>
</tr>
<tr>
<td>23</td>
<td>0.022</td>
<td>0.014185191</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.012895628</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>0.021</td>
<td>0.013540409</td>
<td>23.7</td>
</tr>
<tr>
<td>22</td>
<td>0.02</td>
<td>0.012895628</td>
<td>24.7</td>
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<tr>
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<td>0.013540409</td>
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</tr>
<tr>
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<td>0.022</td>
<td>0.014185191</td>
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</tr>
<tr>
<td>19</td>
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<td>0.013540409</td>
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**Effect of Stripper Stages on System Performance with a 1 atm Stripper and 14 Absorber Stages**
*(Run #175-178)*

<table>
<thead>
<tr>
<th>Number of Stripper Stages</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>Liquid Rate (gal/SCF)</th>
<th>H2S Leak (ppm)</th>
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</thead>
<tbody>
<tr>
<td>18</td>
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<td>0.016119535</td>
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<td></td>
<td>0.023</td>
<td>0.014829972</td>
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<tr>
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<td>0.022</td>
<td>0.014185191</td>
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Effect of Varying the H$_2$S Equilibrium Constant in Both Columns

(Run #179-182)

<table>
<thead>
<tr>
<th>Ratio of EKH2S</th>
<th>H2O Rate (kg/mole feed gas)</th>
<th>H2S Leak (ppm)</th>
<th>H2S Selectivity</th>
<th>CO2 % Slip</th>
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<tbody>
<tr>
<td>1</td>
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<td>246.3</td>
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<tr>
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**Effect of Changing the H₂S Heat of Reaction**

(Run #183-187)

<table>
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<th>EKH₂S ratio in the stripper</th>
<th>H₂S heat of reaction (kg/mole feed gas)</th>
<th>H₂O Rate</th>
<th>H₂S Leak (ppm)</th>
<th>H₂S Selectivity</th>
<th>CO₂ % Slip</th>
</tr>
</thead>
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<td>116.3</td>
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<td>116.8</td>
<td>1.89</td>
<td>94.8</td>
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</tr>
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<td>94.8</td>
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<td>94.9</td>
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<tr>
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<td>167</td>
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</table>
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 CO₂-H₂S-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 CO₂-H₂S-DEA-MDEA system. This file is constantly edited to perform different ASPEN PLUS runs for this system. This file is the input 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 CO2-H2S-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 CO2 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 H2S.

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

MEA.INP - This file is the working file for the CO2-H2S-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 CO2-H2S-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


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=MDEA MDEA & 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
  PV AL CARB 149.15 / 0.0
PROP-LIST CPIG
  PV AL H2CO3 2.08E4 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2000 3.3256E4 21.29 1.5
PROP-LIST PLXANT
  PV AL H2CO3 -1E35 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2000

SPECIFY THE REACTIONS OCCURRING FOR THE DEA-MDEA SYSTEM

CHEMISTRY MDEA DEA
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 DEA+ -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 DEA+ -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 VARIABLES 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 5 -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 AMINE
RES-TIME 1 3 LTIME=1 VTIME=1.5
T-EST 132 / 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
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
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 , IHBAS , HLDVAP , TIMVAP , NINT ,
4 INT , NREAL , REAL , RATES )
C
C IMPLICIT REAL*8 ( A-H,O-Z)
C 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
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
C DIMENSION SVEC(30), IDXSUB(1), ITYPE(1), RETN(1), IRETN(1),
1 INDEX(1), SUBSTR(1), XX(100)
C 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
C DIMENSION CONC(20), ICHARG(20), ACT(20), FLOW(20)
THE COMMON BLOCK GAMMA IS ASPEN'S AND RETURNS THE NATURAL
LOG OF THE ACTIVITY COEFFICIENTS. THE OTHER COMMON BLOCKS
ARE USER BLOCKS OR ARE FOR ASPEN'S FLASH.

COMMON /GAMMA/ GAMMA(1)
COMMON /USREK/ EKW, EKMDA, EKDEA, EKMEA, EKDGA, EKCO2,
1 EKH2S, EKCARB, EKHC03
COMMON /USRFLG/ ISYS, IMOL, ICAT, IAN
COMMON /USRFLO/ TOTFLO(20)
COMMON /USRACT/ ACTCOF(20)

COMMON /STWKWK/ NCPM, NCPCS, NCPNC, NTrial, IDUM(2),
1 TCALC, PCALC, VCALC, QCALC, BETCAL,
2 RDUM(21), RESLTS(1)

COMMON /STWORK/ NRETN, NIRETN, NHXF, NHYF, NWYF,
1 NSTW, KK1, KK2, KZ1, KZ2,
2 KA1, KA2, KRST, 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, KOFT, KOFT1, KPHY,
8 KPHL, KLNMG, 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, SALT,
4 VSALT, MSTOIL, MLNKL, MLNKS, MLNKIN,
5 MZWK, MST, MIEST, MIZWK, HSALT,
6 FSALT, RATIO

THESE TWO OUTPUT FILES ARE USED FOR DEBUGGING PURPOSES.

OPEN (UNIT=52, FILE=’KINET.OUT’, STATUS=’UNKNOWN’)
OPEN (UNIT=53, FILE=’BULK.OUT’, STATUS=’UNKNOWN’)

REASSIGN THE VARIABLE NAMES OF THE FLAGS. THE SYSTEM
FLAG IS CALLED ISYS. THIS FLAG TAKES THE FOLLOWING
VALUES: 1 = DEA IS PRESENT, 2 = MEA IS PRESENT,
3 = DGA IS PRESENT, 4 = ONLY MDEA IS PRESENT BUT
ANOTHER AMINE'S FLOW RATE IS SET TO ZERO.
IMOL, ICAT, AND IAN REPRESENT THE NUMBER OF
MOLECULES, CATIONS AND ANIONS, RESPECTIVELY.
ICHARG REPRESENTS THE CHARGE OF CATIONS AND ANIONS. THIS
CAN BE USED TO CALCULATE THE IONIC STRENGTH IF NEEDED.
THESE VALUES ARE PASSED FROM THE REACTIONS PARAGRAPH
IN THE INPUT FILE USING THE VARIABLE INT.

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

CALCULATE THE MIXTURE MOLAR VOLUME WITH THE CALCULATION
CODE (KV) SET TO GIVE ONLY THE PROPERTY AND NOT THE
TEMPERATURE DERIVATIVE.

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
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

USE ASPEN'S FLASH ROUTINE TO OBTAIN THE ACTIVITY
COEFFICIENTS FOR ALL TRUE SPECIES. THE TRUE SPECIES
FLOW RATES WERE NOT OBTAINABLE FOR SOME REASON. IN
CONVERGATIONS WITH ASPEN THE PROBLEM WAS NEVER RESOLVED.
THE FLASH ROUTINE WAS NOT RETURNING CORRECT VALUES
FOR SEVERAL VARIABLES. NBOPST(4) IS SET EQUAL TO 1 TO
OBTAIN THE TRUE SPECIES FLASH. NBOPST(4) = 0 MUST
IMMEDIATELY FOLLOW THE FLASH TO RESET TO APPARENT APPROACH.

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(I) = 1
  ITYPE(I) = 1
  NBOPST(4) = 1
  KODE = 2
  NPKODE = 1
  KPHASE = 2
  MAXIT = 30
  TOL = 1D-4
  SPEC1 = T
  SPEC2 = P
  LMSG = KDIAG
  LPMST = KDIAG
  JRES = 0
  KRESLT = 1
C   CALL FLASH (SVEC , NSUBS , IDXSUB , ITYPE , NBOPST ,
C             KODE , NPKODE , KPHASE , MAXIT , TOL ,
C             SPEC1 , SPEC2 , GUESS , LMSG , LPMST ,
C             JRES , KRESLT, RESLTS(MIRETN), INDEX(MIRETN),
C             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
C   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
C     CALL USRCON (T)
C   ENDIF
C   GUESS1 = 10**(4.0)*TOTVOL
C   GUESS2 = 10**(5.0)*TOTVOL
C   CALL USRSEC (GUESS1, GUESS2, FLOW)
C   DO 301 I = 1,IMOL+ICAT+IAN
C     WRITE (52,*) FLOW ',I, ',',FLOW(I)
C 301   CONTINUE
C
C   CALCULATE THE ACTIVITY FOR EACH COMPONENT. THE
THE ACTIVITY COEFFICIENTS ARE CALCULATED IN SUBROUTINE
USRCON USING THE COMMON BLOCK GAMMA.

DO 340 I = 1,IMOL+ICAT+IAN
      ACT(I) = FLOW(I)/TOTLIQ*ACTCOF(I)
340  CONTINUE

CALCULATE THE KINETIC RATE CONSTANTS (RK) FOR
BICARBONATE AND CARBAMATE FORMATION. VARIABLES
BEGINNING WITH 'A' REPRESENT THE PREEXPONENTIAL
FACTORS, AND VARIABLES BEGINNING WITH 'EA'
REPRESENT THE ACTIVATION ENERGIES. THESE
CONSTANTS WERE FIT BY GLASSCOCK (1990). THE
PREEXPONENTIAL FACTORS REPORTED BY GLASSCOCK HAVE
TO BE ADJUSTED BY THE DENSITY OF WATER TO CONVERT
TO A MOLE FRACTION BASIS. THIS IS HANDLED BY
ENTERING THE CORRECT PREEXPONENTIAL FACTORS IN
THE INPUT READ BY THIS SUBROUTINE.

REACTION RATE CONSTANTS REPRESENTING THE REACTION
OF CO2 TO BICARBONATE:

RK TAMW - REACTION FOR CO2, TERTIARY AMINE AND WATER
RKAMWB - REACTION FOR CO2, PRIMARY OR SECONDARY
         AMINE, AND WATER TO YIELD BICARBONATE. THIS
         CONSTANT WAS NOT FIT BY GLASSCOCK BUT
         INCLUDED FOR COMPLETENESS. CURRENTLY,
         THIS CONSTANT IS ALWAYS ZERO.
RK TAMH - REACTION FOR CO2, TERTIARY AMINE AND OH-
RKOH  - REACTION FOR CO2 AND OH-

REACTION RATE CONSTANTS REPRESENTING THE REACTION
OF CO2 TO CARBAMATE:

RK PAM - REACTION FOR CO2 AND PRIMARY AMINE
RKAMAM - REACTION FOR CO2 AND TWO PRIMARY AMINES
RKAMTA - REACTION FOR CO2, SECONDARY AMINE, AND
         TERTIARY AMINE
RKAMWC - REACTION FOR CO2, SECONDARY AMINE, AND
         WATER TO YIELD CARBAMATE

THE CONSTANT CION IS USED TO REMOVE THE IONIC
STRENGTH DEPENDENCE OF THE HYDROXIDE RATE CONSTANT.
GLASSCOCK (1990) MISTAKENLY USED THE ACTIVITY OF
OH- WITH THE EXPRESSION FOR RKOH CONTAINING CION=0.08
AS REPORTED BY ASTARITA ET AL. (1983). HOWEVER,
THIS CONSTANT IS A CONCENTRATION BASED RATHER THAN
ACTIVITY BASED CONSTANT. THEREFORE, THE OH- ACTIVITY
IS USED BY SETTING CION=0.0 IN ORDER TO NOT ACCOUNT
FOR NONIDEALITIES TWICE (THROUGH THE IONIC STRENGTH
AND ACTIVITY). AT A LATER TIME, THIS INCONSISTENCY
MIGHT BE CORRECTED. C1RKOH AND C2RKOH ARE USED TO ENTER
THE TEMPERATURE DEPENDENT CONSTANTS FOR THIS EXPRESSION.

THE VARIABLE FLPAM IS USED AS A FLAG TO REMOVE OR INCLUDE RKPM DEPENDING ON WHETHER A PRIMARY AMINE IS PRESENT.
CIPAM AND C2PAM ARE USED TO ENTER THE TEMPERATURE DEPENDENT CONSTANTS FOR THIS EXPRESSION.

READ THE RATE CONSTANT PARAMETERS FROM THE KINETIC INPUT FILE 'KINETIC.IN'

```c
ATAMW = REAL(1)
EATAMW = REAL(2)
AAMWB = REAL(3)
EAAMWB = REAL(4)
ATAMOH = REAL(5)
EATAMH = REAL(6)
CIRKOH = REAL(7)
C2RKOH = REAL(8)
CION = REAL(9)
FLPAM = REAL(10)
CIPAM = REAL(11)
C2PAM = REAL(12)
AAMAM = REAL(13)
EAAMAM = REAL(14)
AAMAM = REAL(15)
EAAMAM = REAL(16)
AAMWC = REAL(17)
EAAMWC = REAL(18)
```

```c
READ (51,*) ATAMW,EATAMW
READ (51,*) AAMWB,EAAMWB
READ (51,*) ATAMOH,EATAMH
READ (51,*) CIRKOH,C2RKOH,CION
READ (51,*) FLPAM,CIPAM,C2PAM
READ (51,*) AAMAM,EAAMAM
READ (51,*) AAMTA,EAAMTA
READ (51,*) AAMWC,EAAMWC
```

```c
RKATAMW = ATAMW*DEXP(-EATAMW/1.987*(1/T - 1/298))
RKAMWB = AAMWB*DEXP(-EAAMWB/1.987*(1/T - 1/298))
RKATAMH = ATAMOH*DEXP(-EATAMH/1.987*(1/T - 1/298))
RKOH = 10.0**(CIRKOH + C2RKOH/T + CION*SUMION)
RKPM = FLPAM*10.0**(CIPAM + C2PAM/T)
RKAMAM = AAMAM*DEXP(-EAAMAM/1.987*(1/T - 1/298))
RKAMTA = AAMTA*DEXP(-EAAMTA/1.987*(1/T - 1/298))
RKAMWC = AAMWC*DEXP(-EAAMWC/1.987*(1/T - 1/298))
```

CALCULATE THE EQUILIBRIUM CO2 ACTIVITY. THE CO2 ACTIVITY IN EQUILIBRIUM WITH BICARBONATE IS REPRESENTED WITH ABCO2E. THE CO2 ACTIVITY IN EQUILIBRIUM WITH CARBAMATE IS ACCO2E. THE OVERALL EQUILIBRIUM CONSTANTS FOR BICARBONATE AND CARBAMATE ARE OBTAINED BY COMBINING...
THE APPROPRIATE CONSTANTS CALCULATED IN SUBROUTINE USRCON.

\[ \text{ACCO2E} = \text{ACT}(3+\text{IMOL}+\text{ICAT})\times\text{EKW}/\text{EKCO2}/\text{ACT}(1+\text{IMOL}+\text{ICAT}) \]

IF (ISYS.EQ.4) THEN
  ACCO2E = 0.0
ELSE
  ACCO2E = \text{ACT}(1)\times\text{ACT}(2+\text{IMOL}+\text{ICAT})\times\text{EKW}/\text{EKCARB}/\text{EKCO2}/
  & \text{ACT}(1+\text{IMOL}+\text{ICAT})/\text{ACT}(3)
ENDIF

CALCULATE THE RATE OF BICARBONATE AND CARBAMATE FORMATION. THESE VALUES ARE MULTIPLIED BY THE LIQUID HOLDUP TO GIVE APPROPRIATE UNITS (KMOL/S).
ALSO CHECK TO BE SURE RATE ISN'T TOO LARGE

\[ \text{RTHCO3} = (\text{ACT}(4) - \text{ACCO2E})\times(\text{RKTMW}+\text{ACT}(2)\times\text{ACT}(1) + \text{RKAMWB} + \text{ACT}(3)\times\text{ACT}(1) + \text{RKAMOH}\times\text{ACT}(2)\times\text{ACT}(1+\text{IMOL}+\text{ICAT}) + \text{RKOH}\times\text{ACT}(1+\text{IMOL}+\text{ICAT}))\times\text{TIMLIQ}*/\text{TOTVOL} \]
WRITE (52,*) 'RTHCO3=',RTHCO3

\[ \text{RTCARB} = \text{ACT}(3)\times(\text{ACT}(4) - \text{ACCO2E})\times(\text{RKPM} + \text{RKAMAM}\times\text{ACT}(3) + \text{RKAMTAM}\times\text{ACT}(2) + \text{RKAMWC}\times\text{ACT}(1)\times\text{TOTLIQ}*/\text{TOTVOLZ} \]
WRITE (52,*) 'RTCARB=',RTCARB

CALCULATE THE RATES OF INDIVIDUAL COMPONENTS. AS A REMINDER: 1 = H2O, 2 = MDEA, 3 = DEA(MEA,DGA), 4 = CO2, 5 = H2S, 6 = H2CO3, 7 = AMCOOH
THE RATES CALCULATED ABOVE HAVE TO BE MULTIPLIED BY THE LIQUID HOLDUP TO OBTAIN THE APPROPRIATE UNITS FOR ASPEN PLUS.

\[ \text{RATES}(1) = -\text{RTHCO3} \]
\[ \text{RATES}(2) = 0.0 \]
\[ \text{RATES}(3) = -\text{RTCARB} \]
\[ \text{RATES}(4) = -\text{RTHCO3} - \text{RTCARB} \]
\[ \text{RATES}(5) = 0.0 \]
\[ \text{RATES}(6) = \text{RTHCO3} \]
\[ \text{RATES}(7) = \text{RTCARB} \]

CLOSE UNIT=51
CLOSE UNIT=52

RETURN
END

SUBROUTINE USRCON ( T )

THIS SUBROUTINE CALCULATES THE EQUILIBRIUM CONSTANTS NEEDED TO SPECIATE THE LIQUID PHASE USING THE SUBROUTINE USREQ. THE NATURAL LOG OF THE ACTIVITY COEFFICIENTS IS PASSED THROUGH THE COMMON /GAMMA/. 
THESE VALUES ARE CALCULATED FROM THE ASPEN FLASH.

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 MDEA, MDEAH, MEA, MEAH

COMMON /GAMMA/ GAMMA(I)
COMMON /USREK/ EKW, EKMDEA, EKDEA, EKMEA, EKDGA, EKCO2,
EKHZS, EKCARB, EKHC03
COMMON /USRFLG/ ISYS, IMOL, ICAT, IAN
COMMON /USRACT/ ACTCOF(I)

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. 100.0 OR. ACTCOF(I) .LT. 1D-6) THEN
      WRITE (52,*) 'ACTCOF OUT OF RANGE'
      ACTCOF(I) = 1.0
   ENDIF
10 CONTINUE

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(I))
   ELSE IF (ISYS .EQ. 2) THEN
      EKMEA = DEXP(2.1211 - 8189.38/T - 0.007484*T)
& 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(I))
   ELSE IF (ISYS .EQ. 3) THEN
      EKDGA = DEXP(1.6957 - 8431.65/T - 0.005037*T)
& 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(I))
   ENDIF
EKHZS = DEXP(214.582 - 12995.4/T - 33.5471*DLOG(T)/
& (ACTCOF(1+IMOL)*ACTCOF(4+IMOL+ICAT)/ACTCOF(5)/
& ACTCOF(1))
EKHC03 = 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)

RETURN
SUBROUTINE USRSEC ( GUESS1, GUESS2, FLOW )

THIS SUBROUTINE USES THE SECANT METHOD TO DIRECT CONVERGENCE OF THE USER FLASH ROUTINE.

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION FLOW(1)

ITER = 0
XOLOD = GUESS1
X = GUESS2

DELTA = X - XOLOD
CALL USREQ (ITER,XOLOD,FLOW,BULK)
FOLD = BULK

CALL USREQ (ITER,X,FLOW,BULK)
F = BULK
DELTA = -DELTA*F/(F-FOLD)
X = X + DELTA
IF (X .LT. 0.0) X = DABS(X)

ITER = ITER + 1
IF (ITER .GT. 100) THEN
  WRITE (52,*) 'SECANT DID NOT CONVERGE IN 100 ITERATIONS.'
  RETURN
ENDIF

IF (DABS(DELTA/X) .GT. 0.0005) THEN
  FOLD = F
  GOTO 10
ENDIF

WRITE (52,*) 'SECANT CONVERGED IN ',ITER,' ITERATIONS.'
WRITE (52,*) 'SECANT CONVERGED. BULK = ',BULK

RETURN

END

SUBROUTINE USREQ ( ITER, OH, FLOW, BULK )

THIS SUBROUTINE SPECIATES THE APPARENT COMPONENT COMPOSITION.

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 MDEAH, MDEAH, MEA, MEA

C COMMON /USREK/ EKW, EKMDEA, EKDEA, EKMEA, EKDOI, EKCO2, 
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
  DEA = TOTFLO(3)/(1.0 + EFACT)
  DEA = EFACT*DEA
ELSE
  DEA = 0.0
ENDIF
IF (ISYS .EQ. 2 ) THEN
  EFACT = EKMEA*OH/EKW/H2O
  MEA = TOTFLO(3)/(1.0 + EFACT)
  MEA = EFACT*MEA
ELSE
  MEA = 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$_2$S 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$_2$S 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$_2$S 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$_2$S 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 CO₂ and H₂S equilibrium constants were fit to an empirical expression with six adjustable parameters. Finally, the CO₂-MDEA rate constant expression was updated. The extended model continues to use an analytical expression for the CO₂ 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 H₂S in the absorber off-gas (H₂S 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 H₂S equilibrium constant, the H₂S heat of reaction, the mass transfer coefficients, and the CO₂-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 H₂S 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 H₂S leak. Using the same solvent circulation rate while adding acid improves performance to 25 ppm; however, the H₂S 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 H₂S equilibrium in the stripper, thus H₂S was more easily removed when acid is present.

Figure D.2 shows that reducing the stripper pressure also improves H₂S leak. As the stripper pressure is reduced, the CO₂ lean loading increases because the CO₂-MDEA reaction rate constant is reduced in the stripper. This extra CO₂ acts as an acid and causes the H₂S equilibrium to be linearized in the stripper. However, examination of Figure D.2 shows that the CO₂ 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 H₂S equilibrium, the gas phase mass transfer coefficient and number of gas phase transfer units are increased when the pressure is reduced. Because H₂S absorption is partially gas phase controlled and CO₂ absorption is totally liquid phase controlled, an increase in these gas phase mass transfer parameters also helps to improve H₂S 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 H₂S leak, CO₂ lean loading, and percent CO₂ removed to changes in the H₂S equilibrium constant, the H₂S heat of reaction, the liquid phase mass transfer coefficient (k₁'), the gas phase mass transfer coefficient (k₉), and the CO₂-MDEA rate constant. These results show that the estimated H₂S leak is very sensitive to the value of the H₂S equilibrium constant and heat of reaction in the stripper which suggests that determination of these values at high temperatures is warranted. The H₂S leak is sensitive to both the liquid and gas mass transfer coefficient because H₂S absorption is partially liquid and gas phase controlled; however, the selectivity, as indicated by the percent CO₂ removed, is only sensitive to k₁' because CO₂ absorption is totally liquid phase controlled. Finally, the H₂S leak is sensitive to the CO₂-MDEA rate constant because the CO₂ lean loading changes with values of this constant. As found in the case of stripper pressure
reduction, increases in \(\text{CO}_2\) lean loading can result in dramatic changes in the \(\text{H}_2\text{S}\) 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 \(\text{CO}_2\) in the mixed amine systems MEA-MDEA and DEA-MDEA. The experimental data is reported as the \(\text{CO}_2\) partial pressure versus the \(\text{CO}_2\) loading (moles of \(\text{CO}_2\) absorbed per mole of MDEA); therefore, for a given \(\text{CO}_2\) loading, the ASPEN PLUS™ equilibrium flash calculated the \(\text{CO}_2\) partial pressure. Figures D.3 and D.4 compare the model results to the experimental data for \(\text{CO}_2\) 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 \(\text{CO}_2\).
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% H₂S, 10% CO₂, 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% H₂S, 0.028 lb steam/SCF feed gas).
Table D.1: Base Case Sensitivity of System Responses to Various Parameters.

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

<table>
<thead>
<tr>
<th>Adjusted Parameter</th>
<th>H\textsubscript{2}S Leak (ppm)</th>
<th>CO\textsubscript{2} Lean Loading</th>
<th>Percent CO\textsubscript{2} Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}S equilibrium constant in both columns</td>
<td>0.33</td>
<td>-0.96</td>
<td>-0.20</td>
</tr>
<tr>
<td>H\textsubscript{2}S equilibrium constant in only the stripper</td>
<td>1.72</td>
<td>-1.05</td>
<td>0.0</td>
</tr>
<tr>
<td>H\textsubscript{2}S heat of reaction</td>
<td>-1.29</td>
<td>0.78</td>
<td>0.0</td>
</tr>
<tr>
<td>$k_\text{g}$</td>
<td>-0.27</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$k_1^*$</td>
<td>-0.48</td>
<td>0.14</td>
<td>0.57</td>
</tr>
<tr>
<td>CO\textsubscript{2}-MDEA rate constant</td>
<td>0.17</td>
<td>-0.60</td>
<td>0.11</td>
</tr>
</tbody>
</table>
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 CO₂ 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\(_2\)O)

\( C_P \)
- 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\(_2\)O/mole)

\( \Delta H \)
- stream enthalpy (cal/mole)

\( \Delta H_{rxn} \)
- 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)

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\( N_g \) 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**

\( \Theta \) enhancement factor dimensionless driving force
\( \phi \) froth density
\( \kappa \) thermal conductivity (cal/cm/K/s)
\( \rho \) density (kg/L)
\( \mu \) viscosity (cp)

**Superscripts**

\( o \) unloaded solution
\( \infty \) 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
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Vita

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