SIMULATION OF REACTIVE ABSORPTION COLUMN

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

By

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CANDIDATE'S DECLARATION

I hereby certify that the work presented in this dissertation entitled "**SIMULATION OF REACTIVE ABSORPTION COLUMN**," in partial fulfilment of the requirements for the award of the degree of **MASTER OF ENGINEERING** in **CHEMICAL ENGINEERING** with specialisation in **COMPUTER AIDED PROCESS PLANT DESIGN**, at University of Roorkee, Roorkee, is an authentic record of my own work carried out between July 1999 and January 2000 under the guidance of Dr. V. K. Agarwal, Assistant Professor, Department of Chemical Engineering University of Roorkee, Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other University.

Dated: January 31, 2000

(Nelson Ashok D'Silva)
Signature of the candidate

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The present investigation pertains to a theoretical study on the simulation of reactive absorption column. It basically deals with the development of a mathematical model for these absorbers. It also includes the solution technique for the solution of the model. In the end, studies of the effect of different operating parameters viz. gas pressure, gas and liquid temperatures, gas concentrations and liquid molarity on the model behaviour has been done.

Using the basic principles of mass conservation, energy conservation and gas-liquid equilibrium a mathematical model of a reactive absorption column has been developed. These balance equations include component material balance, phase equilibrium, sum equations and enthalpy balance equations. The relation for phase equilibrium for a reactive absorption process has been developed from the principles of chemical thermodynamics to give the "Thermodynamic model." The balance equations, which are non-linear in nature, are linearized using Taylor Series expansions and then transformed into a tri-diagonal matrix system. The resulting system of equations are solved using "Thomas Algorithm" to get the component flow rates and temperatures of both the streams.

The model developed is tested for the absorption of H_2S *into aqueous Diethanolamine (DEA). The results of the simulation have been compared with those due to DeLeye and Froment (1986). An examination of the results shows, that the model has been successful in representing the reactive absorption column for the above system, as has been found for the different profiles of temperature, pressure and the molar flow* *rates of gas and liquid. The maximum deviation between the profiles obtained by this simulation with those obtained by DeLeye and Froment (1986) was found to be around 5%. This simulation technique as has been found here requires lesser number of iterations for the solution of the same problem as compared with those by DeLeye and Froment (1986).*

The effect of operating variables e.g., pressure of the gas, temperature of gas and liquid and the gas and liquid compositions has been made. The results show that the model and its solution technique have been successful in showing the behaviour of the column with a change in the operating variables. A sensitivity analysis of the process shows that for a particular composition of the incoming streams the Pressure of gas plays an important part in deciding the height of the column required for a particular level of separation. Temperatures of the liquid and gaseous streams have been found to be the next in importance in deciding the height of the column

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x	*Fraction of gas in the liquid in chemically combined form*
$\bar{x}$	*Total fractional saturation*
γ	*Factor multiplied with temperature change*
λ	*Factor multiplied with component flow rate change*
ν	*Stoichiometric coefficients for reactions*
θ	*Correction factor for component flow rates*
ρ	*Density of the solution (kg/m^3)*
$\Delta\xi$	*Variation of the extent of reaction*

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NOMENCLATURE

A	*Absorbing component*
A_j	*Absorption factor for stage j*
a	*concentration of physically dissolved A (kmol/m^3)*
at	*total concentration of A (kmol/m^3)*
ap	*concentration of physically dissolved A (kmol/m^3)*
ac	*concentration of chemically combined A (kmol/m^3)*
B_j	Species present in the liquid phase
b_j	Concentration of species B_j *(kmol/m^3)*
Ha	*Henry's law constant (mm Hg)*
H	*Enthalpy of gas (kJ/kmol)*
h	*Enthalpy of liquid (kJ/kmol)*
ΔH	*Heat of reaction (kJ/kmol)*
K	*Equilibrium constant of the reaction*
L	*Liquid total flow rate (kmol/h)*
l	*Liquid component flow rate (kmol/h)*
N	*Number of stages*
M	*Number of reactions*
NN	*Number of reacting components*
P	*Pressure (mm Hg)*
V	*Gas total flow rate (kmol/h)*

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Chapter - 1

INTRODUCTION

Reactive Absorption: It is a process by which component(s) are separated from a gaseous mixture by absorbing them into a liquid solvent. This is done using the reaction properties of the gaseous component(s) and component(s) present in the solvent. This may also be referred to as gas treating with chemical solvents. The products of the reaction are usually carried with the liquid phase where from they are separated using the desorption process.

Reactive absorption is primarily used to separate gaseous impurities of acidic nature (CO_2, H_2S, SO_2, etc.), organic sulphur impurities and certain other impurities from gases. Acid gas removal generally refers to removal of CO_2 and H_2S. Apart from these uses, reactive absorption shows excellent use in olefin/paraffin separation [*Safarik et al(1998)*] and also in the removal of mercury vapours by the use of aqueous permanganate [*Zhao et al.(1996)*].

The acid gas impurities (CO_2, H_2S, etc.) occur in large concentrations (5-50%) in industrial process such as hydrogen manufacture, ammonia production, and natural gas purification. The removal of these and other impurities is important. as high purity is the primary demand of several catalytic processes. These impurities are poisons for many industrial catalysts.

The cleanup target required varies markedly from process to process and with the nature of the acid impurity; the cleanup targets for H_2S is particularly stringent, e.g., 4 ppm by volume for pipe line gas at 1000 psi and 0.1 ppm for chemical applications such as ammonia synthesis. A stringent target is necessary for H_2S to avoid catalyst poisoning, corrosion, and environmental release. CO_2 specifications are also very low for ammonia synthesis and LNG manufacture.

When such impurities are to be removed from the system economically satisfying the required standards, reactive absorption is used. Selective absorption of the acidic impurities from the parent gas into a liquid solvent may be by physical absorption (based on difference in solubility) or on absorption with reaction using a chemical base. The chemical approach takes advantage of the relative acidity of the impurities. Such an approach is able to remove the gas and bring it to very low concentrations.

1.1 TYPES OF GAS TREATING PROCESSES

Absorption of gaseous components into a liquid agent either by physical or chemical absorption into the solution of a chemical base is the most widely used approach. This process is used most widely for bulk removal of acid gas contaminants. By bulk removal it means removing of majority of acid gas present in high concentrations down to a level amount 0.1-2percent in the treated gas.

Other types of treating processes for gaseous separation are also in use among them are pressure swing adsorption (PSA) and cryogenic distillation. PSA is generally used for such an application in relatively small capacity plants, with cryogenic methods representing a very small fraction of commercial applications owing to their cost.

A variety of solvents are being developed and are in use for the gas creating processes among which are MEA, DEA, DGA, DIPA, promoted hot potassium carbonate solution, organic solvent alkanolamines, etc. of these the most widely used chemical solvents have been aqueous alkanolamine (amino alcohols) and promoted potassium carbonate solvents. As new additives to these solvents, like MDEA, etc. are used the efficiency of the process is further enhanced.

The use of physical solvents is less as compared to chemical solvents but may rise as energy costs further rise, and energy saving becomes a necessity. Chemical solvents are particularly useful for low-pressure gas treating (<50 psi) and for higher pressure gas treating applications where regeneration of the scrubbing solvent represents an attractive utilization of low level waste heat.

Loading of chemical solvents for gas absorption is determined in the limit by considering the vapour-liquid equilibrium. At any temperature, for a given solvent, there is a definite relationship between the loading of acid gas in the solvent x and the equilibrium vapour pressure p^* over the liquid, which may be expressed as:

$$p^* = f\ (T,x) \tag{1.1}$$

Considering figure 1.1, the vapour-liquid equilibrium for CO_2 at 313K in a physical (propylene carbonate) and a chemical solvent (aqueous DEA). CO_2 solubility (loading) is small at low pressure, but it becomes larger at higher pressure. The chemical solvent (aqueous DEA), on the other hand exhibits quite high loading at low CO_2 pressures but quickly becomes chemically saturated at moderate pressures.

Thus when removing acid gas with low partial pressures in feed gas,

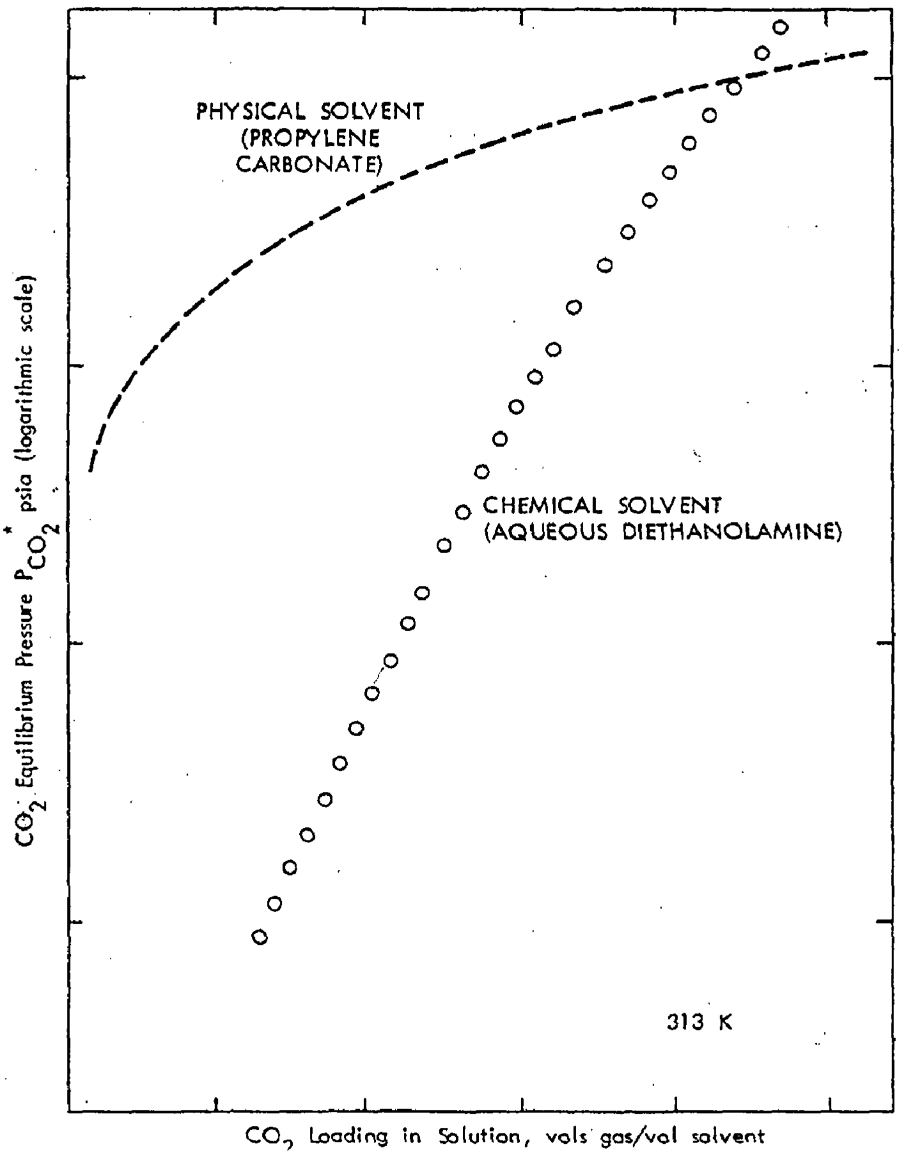


Fig. 1.1 - Vapour-Liquid equilibrium curves for CO_2 at 313 K

chemical solvents are generally preferred, while physical solvents are preferred and may be advantageous for high partial pressures. In chemical solvents after chemical equilibrium has once reached further absorption is due to physical absorption. An interesting way is to use such solvents, which have a good physical solubility for acid gas when being used for gas loading so that physical absorption takes place after the solvent is chemically saturated used.

1.2 PHYSICAL VS CHEMICAL SOLVENTS :

The principal difference between physical and chemical solvents one as in table-1.1. Both type of solvents are capable of reducing acid gas to low levels in the treated gas, but chemical solvents can do this with fewer number of contacting stages, owing to the different shape of VLE curve as shown in figure 1.2. Physical solvents require much taller towers to achieve high degree of acid cleanup, which requires higher capital investment.

Table 1.1 - Comparison of Physical and Chemical solvent use for absorption

Physical	Chemical
Capacity (solubility) proportional to acid gas partial pressure in feed gas	Capacity not highly sensitive to acid gas partial pressure
Low heat of absorption	High heat of absorption
Desorb by flashing	Need low-level steam for desorption
Difficulty to remove acid gas completely (need many stages)	Easily reduces acid gas to low level in treated gas

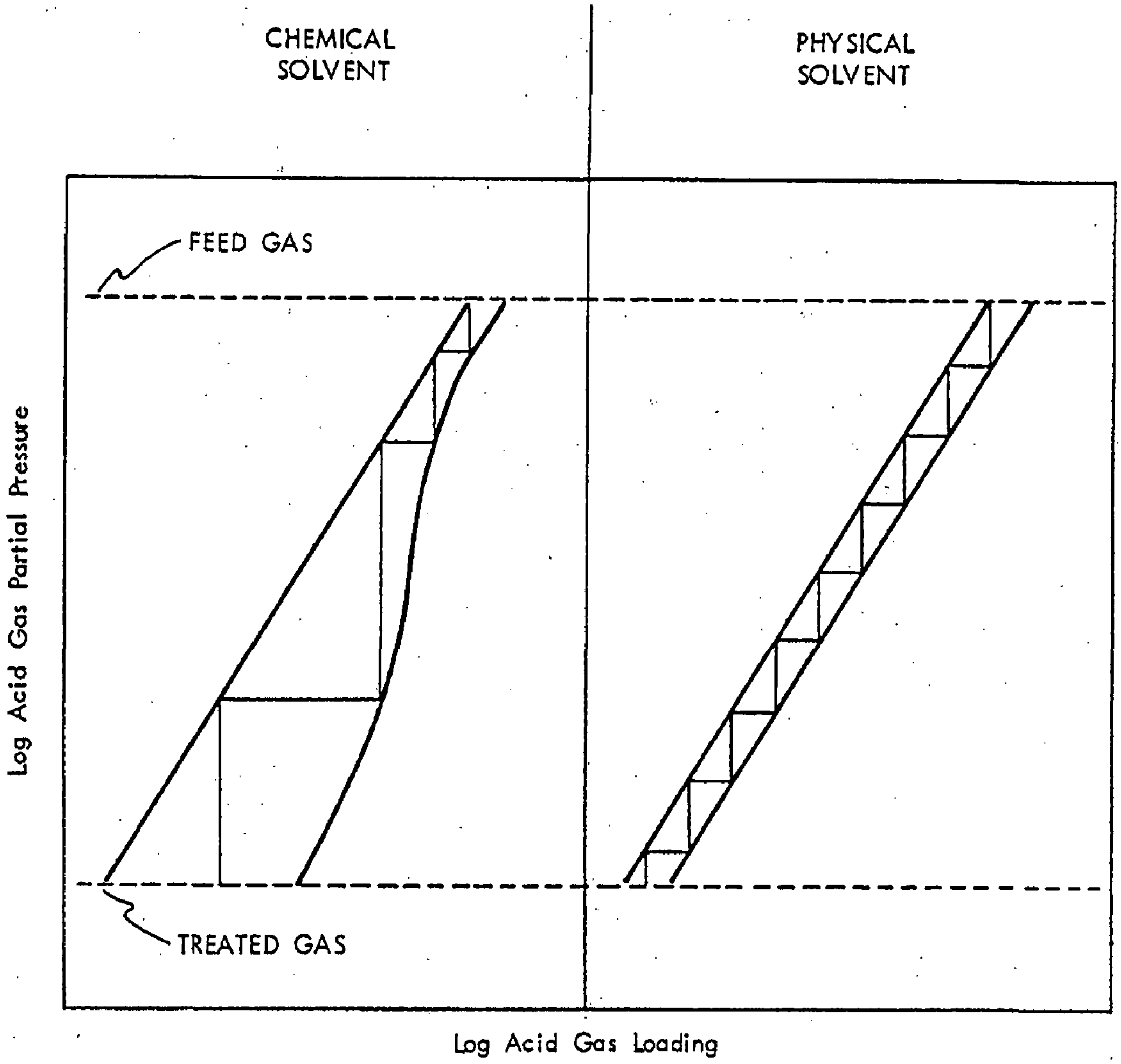


Fig. 1.2 - Absorber theoretical stage requirement for Physical and Chemical solvent

The main problem with chemical solvents comes in dealing with corrosion of the column and precipitation, which limits the molarity of the absorbing liquid to a certain extent. Apart from these shortcomings, the advantages of chemical solvents can be listed as follows:

- Increased capacity, especially, when removing acid gases having low partial pressure
- High degree of removal
- Higher value of absorption mass transfer coefficient (if the reaction is fast enough to occur at the interface).
- Desorption mass transfer coefficient increased.
- Potential for selectively absorbing one reacting gas over another based on the difference in the rates of absorption (called kinetic selectivity).

1.3 CONTACTOR TYPE

The different types of gas-liquid contractors used in gas treating are packed column, tray column and spray towers. Majority of applications are those of packed and tray columns. Although packed towers have many advantages over tray columns due to the advent of novel packing materials, which make it a better contractor type, tray columns are especially used when fluctuating loads are expected for liquid and gas. Use of plate towers is also required for a slow reaction system since trays with high weirs can be used to provide long liquid hold-up and residence time. These towers are especially convenient when cooling is necessary thoroughout the column. These are also helpful when future increase in plant capacity is anticipated.

This process has been under study by different investigators and a wide range of work has been done in this field some of which has been discussed in the next chapter. The simulation of a reactive absorption column has been done by very few workers in the past, using the theories of mass transfer. As work on the equilibrium simulation has not been done, an effort has been made here to use the equilibrium modelling for the reactive absorber. The present work has been planned to use the concept of "Thermodynamic Model" (*Astarita et al (1983)*] in the equilibrium simulation of a reactive absorption column. The thermodynamic model which is based on the thermochemical equilibrium is used for the determination of equilibrium compositions of the liquid and gas phase in the column. This work has been planned with the following objectives.

1. To model an absorption column with equilibrium stages based on the concept of "thermodynamic model".
2. To check the model with an industrially well known system.
3. To check the effect of the various parameters on the model and the operation of the column.
4. To find the variable(s), to which the column operation is most sensitive.

Chapter - 2

LITERATURE REVIEW

Reactive absorption has been in use since the 1920's when very high purity carbon dioxide was produced using the absorption of carbon dioxide into aqueous carbonate solutions. This product was required by the beverage industry. A large number of patents have been obtained in gas treating which specialise in different aspects of the process like the type of contractor, solvent additives, solvents, and their compositions, etc. The main applicability of reactive absorption is where the gas concentrations in the feed is very low i.e. less than 2percent *[Astarita et al. (1983)]*.

In past years a lot of work has been done on the simulation of reactive absorption process by different theories of mass transfer and some of the work is being described below:

Cornelisse et al (1980) describe a discretization technique which makes it possible to calculate numerically mass transfer behaviour. In their work, which was one of the first ones to study the simultaneous mass transfer of CO_2 and H_2S an industrially well known system. They considered the simultaneously occurring and strongly interfering chemical reactions. They paid special attention on the reversibility of the reactions. They found the discretization technique to be applicable to the absorption and the desorption of the gas, and the mass transfer behaviour could be accurately calculated for complex reacting system, thus avoiding the linearisation technique.

Glasscock and Rochelle (1989) have also considered the CO_2-H_2S-MDEA system to model the process using steady-and unsteady-state theories of interfacial mass transfer. The theories used by them are the film theory, simplified eddy diffusivity theory, and an approximation of surface renewal theory. They reviewed Danckwerts surface renewal theory and Higbie's penetration theory as the unsteady-state theories. Orthogonal collocation on finite elements was used to solve the diffusion and reaction equations in ionic systems. The applicability of approximate methods has also been discussed.

Asai (1990) has presented a general approximation formula applicable for any value of the bulk concentration based on the Hikita-Asai linearisation technique for m^{th} order reaction with respect to a solute transferring across the interface between the two phases. Some of the assumptions and shortcomings of the Hikita-Asai linearisation technique have been modified. They found the proposed approximation yields remarkably accurate results by analysing few diffusion problems under steady-and unsteady-state conditions.

Landau (1990) has described the simultaneous interface mass transfer and zero-order reactions by the film model of mass transfer. The results show that this case involves some features particular for zero-order reactions and not in other reactions. He found that at low rates of absorption the reaction goes to completion somewhere within the film and proceeds as an instantaneous reaction when the reaction proceeds in the bulk and goes to completion there.

Littel et al. (1991) used numerical models based on Higbie's penetration theory and studied the effects of coupled diffusion of ions and that of parallel and consecutive chemical reactions on the mass transfer rate for the H_2S-CO_2 alkanolamine system.

Suchak et al. (1991) developed a mathematical model for the absorption of nitrogen oxides in a series of packed columns, as an adiabatic operator. The gas phase reactions and equilibria, gas phase mass transfer, inter phase equilibria and liquid phase reactions have been considered in the model. The heterogeneous gas-liquid equilibrium being included for the first time.

Hagewiesche et al (1995) made an experimental and theoretical investigation of the absorption of carbon dioxide into aqueous blends of MEA and MDEA. A mathematical model capable of predicting gas absorption rates and enhancement factors for chemical reaction kinetics, system hydrodynamics and physical properties has been developed, on the basis of Higbie's penetration theory.

Rinker et al (1995) conducted experiments on a wetted sphere absorber to acquire kinetic data for CO_2-MDEA system and compared three different models on Higbie's penetration theory and used to estimate the forward rate coefficients of MDEA-catalysed hydrolysis of CO_2 reaction.

Kenig et al (1997) modelled reactive absorption based on a theoretical description of reaction and mass transport in multi component systems. The multicomponent nature, and the adjoining complex behaviour due to the superposition of many driving forces-multi component diffusion, chemical interactions, convective flows, multi component thermodynamic interplay, etc. They found Maxwell-Stefan equations useful for describing such a system and modelled a two-phase gas-liquid system for NO_X absorption and showed good agreement of results with experimental.

Brinkmann et al (1998) used the film renewal theory for gas-liquid mass transfer which is more realistic for turbulent conditions. They have proposed numerical schemes employing this theory which is capable of calculating mass transfer rates, conversion, and remaining gas holdup from system and operating parameters. They found that no assumptions, as those required in the modelling on the basis of enhancement factor method are required, for the hydrodynamics of operations, and non-linear phase equilibria can also be considered. Simulations for reversible and irreversible second order reactions was done to show the parametric sensitivity.

Cadours and Bouallou (1998) used a general model based on the film theory to setup the diffusion/reaction partial differential equations, which describe the absorption of gases with multiple reactions. This model, they have shown, is capable of calculating mass transfer of a typical, highly complicated chemical absorption reaction system without a stability or convergence problem. They show their model to be useful for estimating scrubber efficiency for this process.

Pacheco and Rochelle (1998) have used the Maxwell-Stefan and enhancement factor theories to model the transport processes that take place during reactive absorption when both rate and equilibrium controlled reactions occur in the liquid phase. They used RATEFRAC, the rate-based distillation module of Aspen Plus.

Rascol et al (1998) have presented a general simulation model able to represent mass transfer in the presence of chemical reactions. A set of equations describing the film has therefore been developed, and the problems encountered in the index reduction of the differential algebraic equations (DAE) has been discussed.

The above work has been done mainly the simulation of the mass-transfer theories for reactive absorption to get the mass transfer properties of process and the applicability of their model. Prior to *De Leye and Froment (1986)* no simulation of a reactive absorption column had been done as has been claimed by them. In a series of two papers they modelled the column on the basis of film theory of mass transfer. The equations for the determination of flux of the absorbed components at the gas-liquid interface at any stage has been developed. They have simulated the column for a wide range of reactions and side reactions to give the concentration profiles in liquid and gaseous phase at any height of column or stage for packed and plate columns respectively. Their work accounts for any non-isothermal and non-isobaric conditions.

The present work on the equilibrium simulation of a reactive absorption column is based on the thermodynamic model as described by *Astarita et al.*

Such a model has the following advantages:

1. They allow easy interpolation and smoothing of vapour-liquid equilibrium data and provide a basis for the calculation of both the limiting liquid circulation rate and the minimum steam requirement at the regenerator reboiler.
2. They allow extrapolation when experimental accuracy is hard to obtain.
3. They can be used to classify categories of chemical solvents in a logical way, thus making the preliminary choice of possible chemical solvents easier.

The problems encountered in the case of thermodynamic modelling are that of determining the various equilibrium constants, which are determined by experimental procedures *[Astarita et al. (1983), Danckwerts (1970)]* or through theoretical chemistry (calculation based on bond strength, inter molecular forces, etc.) *[Danckwerts (1970)].* In the development of a thermodynamic model only the order of magnitude of several of these constants suffice.

2.1 THERMODYNAMIC MODEL

Development of the model is based on concepts of chemical thermodynamics *[Astarita et al (1983)].* Initially considering a single phase reaction in a liquid phase, the density of which is independent of composition, so that the number of moles and molar concentration are proportional to each other. When only one chemical reaction takes place, the components present in the liquid B_j $(j = 1,2,3,....,NN)$ of molar concentrations b_j the equilibrium reaction can be represented as

$$\bar{\nu}_1, B_1 + \bar{\nu}_2 B_2 + \ldots\ldots <\!\!=\!\!=\!\!> \bar{\nu}_3 B_3 + \bar{\nu}_4 B_4 + \ldots\ldots \tag{2.1}$$

where all the stoichiometric coefficients $\bar{\nu}_j$'s are positive.

If a new set of stoichiometric coefficients $\bar{\nu}_j$*'s* are taken such that they are positive for reactants and negative for products the reaction can be represented in the following equivalent form.

$$\sum_j \nu_j B_j = 0 \tag{2.2}$$

The conditions for chemical equilibrium can be written as

$$\mathrm{K} = \prod_j b_j^{-n_j} \tag{2.3}$$

where the symbol $\prod$ has the meaning of product of all the j components. As long as the composition of the considered phase changes only as a result of the chemical reactions, the variation of the number of moles of the individual components B_j and hence their concentrations are not independent of each other but are related by the following stoichiometric condition:

$$\frac{\Delta b_1}{\nu_1} = \frac{\Delta b_2}{\nu_2} = \frac{\Delta b_3}{\nu_3} = \ldots\ldots\ldots = -\Delta\xi \tag{2.4}$$

with $\Delta\xi$ a variable independent of the index j.

The variable $\Delta\xi$ is usually referred to as the "variation of the extent of reaction." Now defining a base composition or the "admissible composition" b_j^o for each of the components such that the change in concentration with respect to it can be measured for the system. The admissible composition of the phase considered may be the actual composition of the phase at a particular time, or any other stoichiometrically compatible with the actual one. Once the admissible compositions have been decided the extent of reaction at this composition could be set to zero so that eq. (2.4) becomes

$$b_j = b_j^o - \nu_j\xi \tag{2.5}$$

where $j = 1,2,3,\ldots\ldots, NN$

Thus the equilibrium compositions of the base under consideration can be calculated of the use of equation (2.2) and (2.2).

Substitution of equation (2.5) into equation (2.2) gives

$$K = \prod_j \left(b_j^o - \nu_j\xi\right)^{-\nu_j} \tag{2.6}$$

Now considering the case when more than one chemical reactions are taking place (a set of M independent chemical reactions). This set of M chemical reactions may be said independent if no one of them is a linear combination of the others. A set of M chemical reactions may thus be written as

$$\sum_j \nu_{jk} B_j = 0 \qquad (k=1,2,3,\ldots\ldots, M) \tag{2.7}$$

The equilibrium condition may be written as

$$K_k = \prod_j b_j^{-\nu_{jk}} \tag{2.8}$$

The generalisation of eq. (2.5) to the case of several chemical reactions gives :

$$b_j = b_j^0 - \sum_k \nu_{jk} \xi_k \tag{2.9}$$

ere ξ_k is the extent of the Kth reaction.

On the basis of the above relations considering the gas treating system with one volatile component A to be removed from the gas under the following assumptions:

1. Only one component is to be removed from the gaseous phase.
2. All other components are non-condensable.
3. Liquid phase is non-volatile.

Thus in this case only component. A will be present in both the phases. Defining the total content of A in the liquid phase α

$$\alpha = a + xm = \bar{x}m \tag{2.10}$$

where m is the molarity of the solution,

x is the degree of saturation.

a is the concentration of physically absorbed A.

$\bar{x}$ is the total saturation.

The molarity m of the solution is defined as the equivalent concentration of species that may react equimolarly with component A. The degree of saturation x is defined such that xm is the total concentration of chemically combined A in the liquid phase. When we use a chemical solvent there may be more than one chemical reaction taking place between A and the liquid phase components B_j. In this case a set of reactions taking place between the components with the stoichiometric coefficients of A taken as unity in more than one reaction may be written as:

$$A + \sum_{j} \nu_j B_j = 0 \qquad (2.11)$$

$$\sum_{j} \nu_{jk} B_j = 0 \quad (k=1,2,3,\ldots,M) \qquad (2.12)$$

After defining the reactions the thermodynamic problem is that of knowing the composition of the liquid phase at equilibrium, as well as the equilibrium partial pressure of A when m and x are known. Both m and xm can be expressed as a linear combination of b_j's as:

$$m = \sum_{j} \lambda_j b_j \qquad (2.13)$$

$$xm = \sum_{j} \mu_j b_j \qquad (2.14)$$

The coefficients λ_j are the number of atoms in B_j of some element that is not present in component A and μ_j are the number of moles of component A chemically combined in component B_j. Satisfying eq. (2.13) and eq. (2.14) a set of b_j^o can be found for any given values of m and x the choice is obtained by assuming that all chemically combined a is present in one particular form B_j; if the form is B_2 then we can write

$$b_2^o = \frac{xm}{m_2} \tag{2.15}$$

while $b_j^o = 0$ for all other B_j^o's characterised by non-zero μ_j. The equilibrium composition can then be found from these set of admissible composition (b_j^o) as follows :

$$b_j = b_j^o - \sum_j \nu_{jk} \xi_k \tag{2.16}$$

The equilibrium relation will give a set of M polynomial equations for the reaction, given by eq. (2.12) as follows:

$$K_k = \prod_j \left(b_j^o - \nu_{jk} \xi_k\right)^{-\nu_{jk}} \tag{2.17}$$

which when solved simultaneously will give the b_j's. Once all the b_j's have been calculated, the value of a is calculated from the equilibrium condition for reaction (2.12) as follows:

$$K = \left[\frac{\prod_j b_j^{-\nu_j}}{a}\right] \tag{2.18}$$

with these equations the complete composition of the liquid phase is calculated. The equilibrium partial pressure of A, p^*, can be calculated from the requirements, that the equilibrium must prevail between the gaseous and the physically dissolved forms of A i.e. from the equilibrium condition the above reaction also depicted by fig. 3. will be

$$A(g) \quad <==> \quad A\ (l) \tag{2.19}$$

We can write this physical equilibrium between the physically dissolved form of the component a into the liquid with its partial pressure in the gas by the Henry's law as

$$p^* = Ha \tag{2.20}$$

where H is the Henry's law constant.

Thus knowing the values of x and m the value of both $\bar{x}$ and p^* can be calculated from the above equations. Using the Henry's coefficients. The determination of Henry's law coefficient presents difficulties in the case of chemical solvents. In many cases $\bar{x}$ and p^* data would be generated at different conditions and from this the Henry's coefficient could be evaluated.

Danckwerts (1970) shows the use of the method of Van Krevelen and Hoftijzer for the calculation of Henry's law coefficient for electrolytic solution where in the ionic strength and other properties are used. It has been shown that as these data are also not easily available, these can be approximated to the similar species.

Apart from this, data for many of the industrial systems has been published; for the system under consideration; the absorption of H_2S into aqueous alkanolamine system by *Atwood et al (1957), Quwerkerk (1978) and Kent and Eisenberg (1976).*

Studies on various systems for reactive separation techniques, and particularly absorption are underway with the recent once which have been proposed one the Olefin/Paraffin separation *[Safarik et al (1998)]* by the use of Copper (I) and Silver (I) based complexing solutions. The process has been found to use less energy as compared to conventional cryogenic distillation process.

Hg vapour absorption in aqueous permanganate *[Zhao and Rochelle (1996)]* is one such field where reactive absorption takes place. The process being important because of the toxicity of mercury and the environmental standards becoming more stringent. Their work gives the rate of reaction of permanganate with mercury.

2.2 AVAILABLE COMPUTATIONAL TECHNIQUES

Burmingham and Qtto (1967) have compared the various design procedures to check the suitability of the procedures. The following procedures have been tested.

- Bubble point using Thiele-Geddes with theta convergence.
- Bubble point using Tri-Diagonal Matrix.
- Sun rates using Thiele-Geddes.
- Sun rates using Tri-Diagonal matrix.

The computer program problems encountered with these and many other methods have also been discussed.

Tomich (1970) presents a new general method for mathematical simulation of equilibrium stage operations. The procedure solves component material balance equation with tri-diagonal matrix algorithm. Broyden's method has been proposed for this technique.

Naphtali and Sandholm (1971) have specified an approach to separation calculations for non-linear systems by linearisation. The energy and material balance equations and the equilibrium are used used in this method. The resulting set of equation have a block. Tri-diagonal structure which permits solution by a simple technique. Newton-Raphson technique is used to linearise the equation for calculation.

Holland (1975) also gives the methods for the equilibrium simulation of absorbers which is more or less a compilation of the above methods.

Chapter - 3

MATHEMATICAL MODELLING

This chapter describes the formulation of mathematical model and its simplification for an absorption column. Based on the principles of physical and thermodynamic equilibrium alongwith material and energy balances, a model for the column is developed in the following sections.

For the equilibrium simulation of a reactive absorption column we need to convert the reaction and absorption part into some function of the physical equilibrium concentration. This is done using a thermodynamic model, thus we develop the thermodynamic model for the particular case of H_2S absorption into aqueous alkanolamine solution and use it to model the column. The equilibrium on the on the basis of which the present work is being undertaken is as in figure 3.1.

3.1 CASE STUDY OF THERMODYNAMIC MODELLING

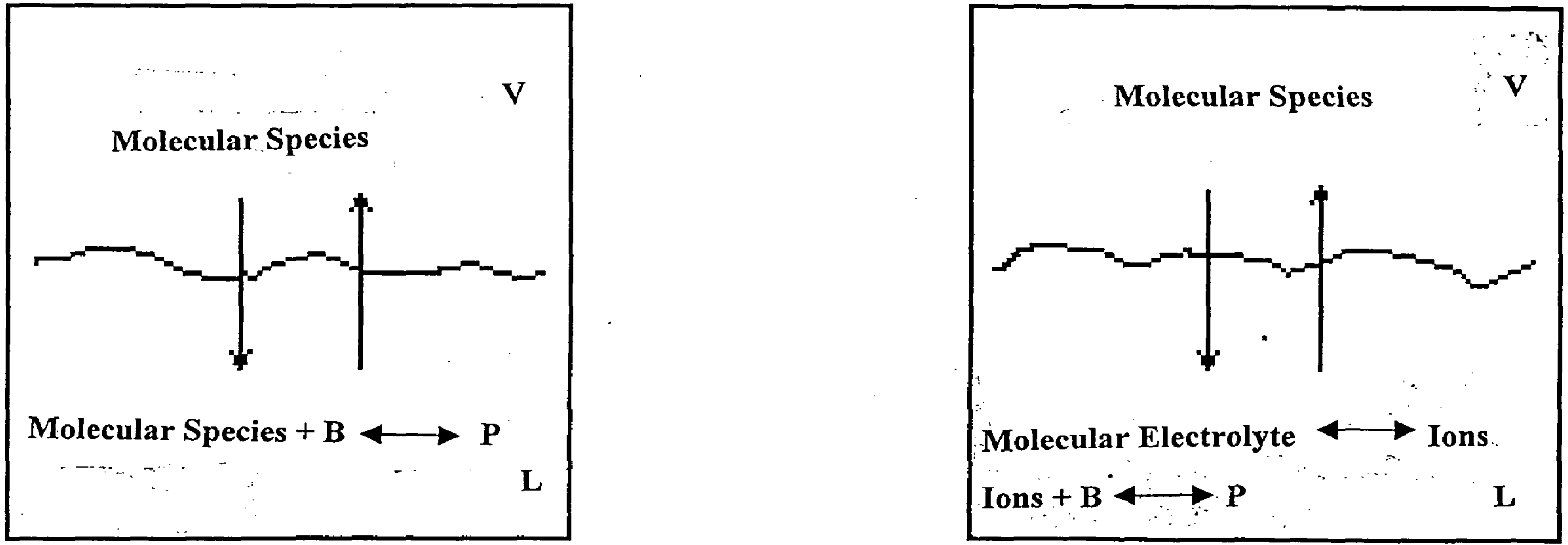
Considering the absorption of H_2S into an aqueous solution of an alkanolamine. The equilibrium reaction taking place in the liquid phase on the absorption of H_2S is as follows:

$$H_2S + R_2NH \xleftrightarrow{K} R_2NH_2^+ + HS^- \tag{3.1}$$

In this case there are only three non-volatile species to be considered.

They are

$$B_1 = R_2NH \tag{3.2}$$



(a) When the species absorbs and reacts with B without ionising

(b) When the species ionises before reacting with B

Fig. - 3.1 Equilibrium considered for thermodynamic modelling

$$B_2 = HS^- \tag{3.3}$$

$$B_3 = R_2NH_2^+ \tag{3.4}$$

The liquid phase also contains other species as well i.e., H^+, OH^+ and water. The presence of these do not help in defining the saturation as well molarity of the solution which are defined as :

$$m = b_1 + b_2 \tag{3.5}$$

$$xm = b_2 \tag{3.6}$$

$$xm = b_3 \tag{3.7}$$

As the reaction is unimolecular with respect to both H_2S and the amine. It can be seen that at $x = 0$ when only amine is present in the solution and its concentration is then the molarity of the solution. As there are only three species to be considered in this case the solution of equation (3.5) and equation (3.6) will give the concentration of the described as :

$$b_1 = m(1 - x) \tag{3.8}$$

$$b_2 = xm \tag{3.9}$$

$$b_3 = xm \tag{3.10}$$

The matrix of the coefficients λ_j, μ_j and ν_j is as follows :

$$\begin{array}{cccc} & \lambda_j & \mu_j & \nu_j \\ B_1 & 1 & 0 & 1 \\ B_2 & 1 & 1 & -1 \\ B_3 & 1 & 1 & -1 \end{array} \tag{3.11}$$

The equilibrium constant for the reaction 3.21 is given by

$$K = \frac{b_2\, b_3}{b_1 a} \tag{3.12}$$

which gives on substitution for b_1, b_2 and b_3

$$K = \frac{mx^2}{(1 - x)\, a} \tag{3.13}$$

and subsequently a is obtained as

$$a = \frac{mx^2}{K(1-x)} \tag{3.14}$$

The values of α and $\bar{x}$ are obtained as :

$$\alpha = mx \left[1 + \frac{x}{K(1 - x)}\right] \tag{3.15}$$

$$\bar{x} = x \left[1 + \frac{x}{K(1 - x)}\right] \tag{3.16}$$

The equilibrium partial pressure p^* can thus be obtained as

$$p^* = \frac{Hm}{K} \frac{x^2}{(1 - x)} \tag{3.17}$$

A plot of p^* vs. $\frac{x^2}{1-x}$ should be a straight line and the experimental data and the above model have been found to agree well [*Astarita et al. (1983)]*, such a plot should give a straight line on a log-log scale which is evident from figure 3.2.

Using equation 3.17 the modelling of the absorption column is to be done in the coming sections.

3.2 MODELLING OF A REACTIVE ABSORPTION COLUMN

Considering a reactive absorption column of N numbers of theoretical stages as shown in figure 3.3. The present model is developed under the following assumptions:

1. Gas-liquid equilibrium is achieved on each stage, i.e., the stages are

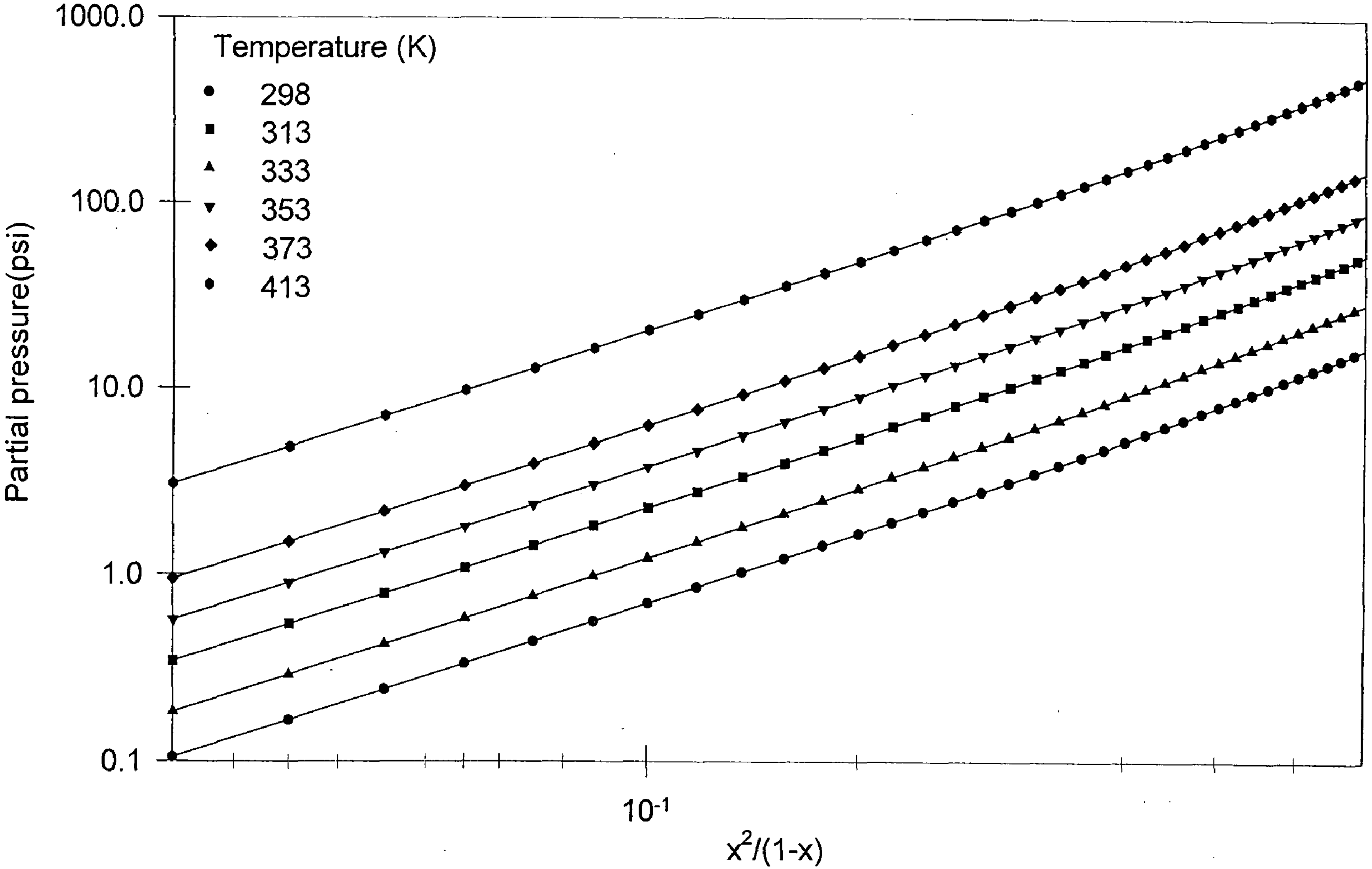


Fig.- 3.2 H_2S loading in gas vs partial pressure over aqueous DEA at different temperatures

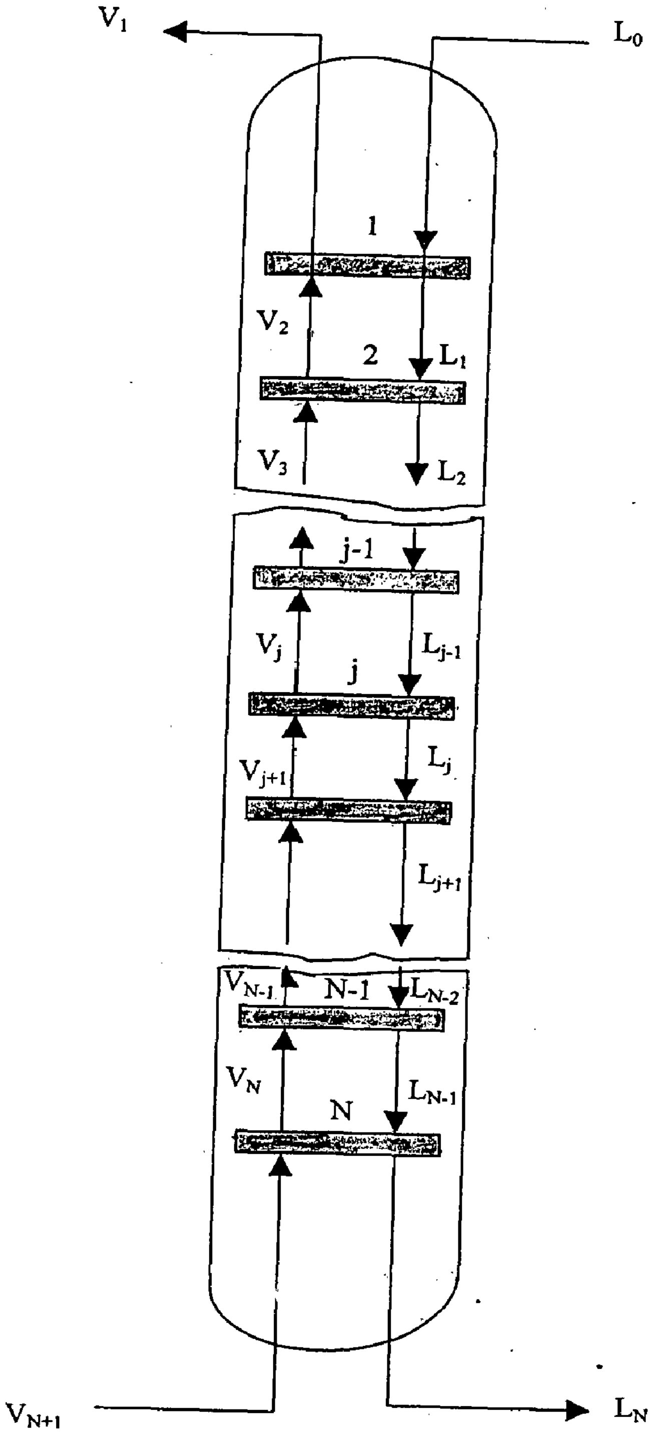


Fig. 3.3 Schematic diagram of an absorber

ideal in nature.

2. Only one component from the gaseous phase is absorbed to the liquid phase, all other components remain unabsorbed.
3. No component from the liquid phase diffuses to the gaseous phase.
4. The reaction between the absorbed component and the component from the liquid phase proceeds in the liquid phase.
5. The heat losses from the column walls is negligible.
6. No side streams enter or leave the column.
7. The volume change on the absorption of the gas to the liquid is negligible.
8. The heat of reaction is independent of temperature.

Considering the example of the absorption of H_2S into aqueous alkanolamine solution of molarity *m* the applicability of the thermodynamic model will be shown for the equilibrium simulation of the column.

There are generally four sets of equations which must be satisfied in the simulation for an equilibrium stage *[Holland (1975)]*. Considering a jth stage and writing the material balance equations, the gas-liquid equilibrium relations, the mole fraction summation equations and the enthalpy balance equations which will include the heat of reaction for the case of reactive absorption.

* *Component material balance*

$$l_{j-1} - v_j - l_j + v_{j+1} = 0 \qquad 1 \leq j \leq N \qquad (3.18)$$

where l_j and v_j are the component flow rate of the gas leaving the jth stage. The liquid component flow rate considers both the physical and the chemically absorbed amount of gas, which when represented in terms of total fractional saturation will be

$$l_j = \bar{x}_j L_j \tag{3.19}$$

where $\bar{x}_j$ is the total fractional saturation as defined in the development of the thermodynamic model equation (3.16).

* *Phase equilibrium*

$$y_j = \frac{H_{aj}\, x_{pj}}{P_j} \qquad 1 \le j \le N \tag{3.20}$$

where x_{pj} is the physically absorbed amount of the gas in the liquid phase, represented in the units of concentration in the thermodynamic model by a H_{aj} is the Henry's law constant in units of pressure

P_j is the stage pressure

* *Summation equations of the fractions of all the components present in both the phases for the gas phase*

$$\sum_{i=1}^{c} y_{ij} - 1 = 0 \qquad (1 \le j \le N) \tag{3.21}$$

for liquid phase

$$\sum_{i=1}^{c} x_{ij} - 1 = 0 \qquad (1 \le j \le N) \tag{3.22}$$

where c is the number of components in the system.

The equations are important and their effect appreciable when more than one component is being transferred between the two phase.

* *Enthalpy balance*

$$V_{j+1} H_{j+1} + L_{j-1} h_{j-1} - V_j H_j - L_j h_j + \Delta H_{Rj} l_{cj} = 0 \qquad (1 \le j \le N) \quad (3.23)$$

where H_j's are the enthalpy of the gaseous phase h_j's are the enthalpy of liquid phase at the j^{th} stage.

The above balance equations are written ignoring the kinetic and potential energy changes.

The component flow rate l_{cj} is that of chemically absorbed gas in the liquid which is also equal to rate of reaction. Is product with the heat of reaction will give the rate of heat generation.

The variable H_a, H_j and h_j are functions of temperature which have been duly considered in the present work. Apart from these the dependency of the reaction equilibrium constant on temperature has also been considered.

Thus for the simulation of an absorber with only one component absorbing can be represented by N material balance equations N phase equilibrium relation, 2N summation equations and N enthalpy balance equations. Thus making up a set of 5N equation which have to be solved to determine the component flow rates, total flow rates, temperature profile and column pressure profile thus, 4N variables.

The degree of freedom for this case thus will be N(=5N-4N). We choose the pressure profile of the column as the design variables. The stage pressures being calculated from the physics of the problem for an average liquid and gas flow rate, giving the pressure drop per stage. Thus the system is now a fully defined one.

The material balance equations of a reactive absorption column are non-linear in nature, the non-linearity arising due to the ongoing chemical reaction. These equations have to be linearised before any simultaneous equation solving technique could be applied.

An analysis of the arising non-linearity can be made as follows:

$$a_t = a_s + a_c \tag{3.24}$$

where

a_t is the total concentration of absorbed species

a_p is the concentration of physically absorbed species

a_c is the concentration of chemically absorbed species

Applying the above to the thermodynamic model for the particular case of H_2S-alkanolamine solution we have

$$a_p = \frac{a_c^2}{K(m - a_c)} \tag{3.25}$$

Multiplying the above equation with the liquid volumetric flow rate on both sides we get the thermodynamic model in terms of the component flow rates of the absorbed species and that of the solute in the solution as follows:

$$l_{pj} = \frac{l_{cj}^{2}}{K\,(C - l_{cj})} \tag{3.27}$$

where $$C = m\,L_0/\rho \tag{3.27}$$

L_0 is the molar flow rate of the feed liquid

ρ is the molar density of the feed liquid

The physically absorbed amount of the absorbing component can be determined by the Henry's law, and this has to be used to know the amount of the chemically absorbed gas we simplify equation to get l_{cj} as follows :

$$l_{cj} = \frac{-l_{pj}\, K + \sqrt{l_{pj}^{2}\, K^{2} + 4 l_{pj} K C}}{2} \tag{3.28}$$

the negative root is rejected l_{cj} being a real quantity.

The above relation between l_{cj} and l_{pj} will thus give

$$l_j = l_{pj} - \frac{1}{2}\, l_{pj} K + \frac{1}{2} \sqrt{l_{pj}^{2}\, K^{2} + 4 l_{pj} K C} \tag{3.29}$$

This non-linear relation makes the system non linear.

Using the Henry's law and the absorption factor, the above equation becomes

$$l_j = A_j v_j - \frac{1}{2}\, A_j v_j K + \frac{1}{2} \sqrt{A_j^{2}\, K^{2} v_j^{2} + 4 A_j K C v_j} \tag{3.30}$$

where
$$A_j = \frac{P_j L_j}{H_{aj} V_j} \tag{3.31}$$

is the absorption factor

v_j is the component flow rate of the absorbing component in the gaseous phase.

The solution of these equations is done using the computation techniques as in the next chapter.

Chapter - 4

COMPUTATIONAL TECHNIQUE

This chapter presents a method for solution of the model equations which have been discussed in the preceding chapter, for a single component reactive absorption column.

The material balance, the thermodynamic equilibrium and the physical equilibrium provide a set of equations, which have to be solved along with the enthalpy balances to get an improved set of variables. The set of equations which make up to a tri-diagonal form are solved by Thomas Algorithm to get a change in the previous value of the variable.

DeLeye and Forment (1986) identify this simulation problem as the calculation of the molar flow rates, composition profiles temperature profiles, extent of reaction and pressures on each plate when the total number of plates, the compositions, flow rates, temperatures and pressures of the gas and the liquid feed streams and the flow rates of intermediate gas and liquid withdrawn is given. Here also these outputs will be determined by calculation procedure explained in the coming sections.

4.1 FORMULATION OF TRI-DIAGONAL MATRIX SYSTEM

A tri-diagonal matrix can be formed from the component material balance and the enthalpy balance equations by suitable mathematical simplifications.

Writing equation (3.18) for the j^{th} stage as

$$f_j = l_{j-1} - v_j\, l_j + v_{j+1} \qquad (1 \le j \le N) \tag{4.1}$$

Substituting equation (3.30) for the j-1th stage in the respective form we have

$$f_j = g(v_{j-1}) - g'\left(v_j\right) + v_{j+1} \qquad (1 \le j \le N) \tag{4.2}$$

where
$$g(v_{j-1}) = l_{j-1}$$
$$g'(v_j) = v_j l_j$$

Thus the component material balance equation has been transformed into a non-linear function which is a function of only three component flow rates which helps in the formulation of a tri-diagonal matrix system. As functions f_j are non-linear function (g and g' being non-linear functions), they have to be linearised using Newton-Raphson technique to get the Jacobian J_n as follows:

$$J_n\left(\frac{f}{v}\right) \Delta v_n = - f_n \tag{4.3}$$

where n is the iteration number and

$$J_n \left[\frac{f}{v}\right] = \begin{bmatrix} \frac{\partial f_1}{\partial v_1} & \frac{\partial f_1}{\partial v_2} & & & \\ \frac{\partial f_2}{\partial v_1} & \frac{\partial f_2}{\partial v_2} & \frac{\partial f_2}{\partial v_3} & & \\ & \ddots & \ddots & \ddots & \\ & & \frac{\partial f_{N-1}}{\partial v_{N-2}} & \frac{\partial f_{N-1}}{\partial v_{N-1}} & \frac{\partial f_{N-1}}{\partial v_N} \\ & & & \frac{\partial f_N}{\partial v_{N-1}} & \frac{\partial f_N}{\partial v_N} \end{bmatrix} \tag{4.4}$$

All other elements other than those on the tri-diagonal are zero.

$$f_n = \left[f_1\, f_2\, f_3 \,\cdots\cdots f_N\right]^T \tag{4.5}$$

$$\Delta v_n = \left[\Delta v_1\ \Delta v_2\ \Delta v_3 \ldots\ldots \Delta v_N\right]^T \tag{4.6}$$

$$\Delta v_j = v_{j,n} - v_{j,n-1} \tag{4.7}$$

The above system of simultaneous equations can now be solved by using Thomas Algorithm for tri-diagonal matrix system. A similar treatment can be done with the enthalpy balance equations.

The enthalpy balance equations (Eq. 3.23) could be written as

$$G_j = V_{j+1} H_{j+1} + l_{j-1} h_{j-1} - V_j H_j - l_j h_j + \Delta H_{Rj} l_{cj} \quad (1 \le j \le N) \tag{4.8}$$

As per the assumption that the gas and liquid phase leaving are in equilibrium with each other, they would be at the same temperature, and under the assumptions that the flow rates are independent of temperature changes we have on application of Newton-Raphson method to enthalpy balances, the Jacobian J_n of Newton-Raphson equations

$$J_n \begin{bmatrix} G \\ T \end{bmatrix} \Delta T_n = - G_n \tag{4.9}$$

A modification of equation (4.8) will give

$$G_j = e \left(T_{j-1}\right) + e' \left(T_j\right) + e'' \left(T_{j+1}\right) + \Delta H_{Rj} l_{cj} \qquad (1 \leq j \leq N) \tag{4.10}$$

where

$$e \left(T_{j-1}\right) = L_{j-1} H_{j-1}$$

$$e'\left(T_j\right) = - V_j H_j - l_j h_j \tag{4.11}$$

$$e'' \left(T_{j+1}\right) = V_{+1} H_{j+1}$$

are the functions of the respective temperatures and thus give

$$G_n = \left[G_1 \; G_2 \; \ldots\ldots\ldots\ldots G_N\right]^T \tag{4.12}$$

$$\Delta T_n = \left[\Delta T_1 \; \Delta T_2 \; \ldots\ldots\ldots \Delta T_N\right]^T \tag{4.13}$$

$$\Delta T_j = \mathrm{T}_{j,n} - \mathrm{T}_{j,n-1} \tag{4.14}$$

and

$$J_n\left(\frac{G}{T}\right) = \begin{bmatrix} \frac{\partial G_1}{\partial T_1} & \frac{\partial G_1}{\partial T_2} & & & \\ \frac{\partial G_2}{\partial v_1} & \frac{\partial G_2}{\partial v_2} & \frac{\partial G_2}{\partial v_3} & & \\ & \ddots & \ddots & \ddots & \\ & & \frac{\partial G_{N-1}}{\partial v_{N-2}} & \frac{\partial G_{N-1}}{\partial v_{N-1}} & \frac{\partial G_{N-1}}{\partial v_N} \\ & & & \frac{\partial G_N}{\partial v_{N-1}} & \frac{\partial G_N}{\partial v_N} \end{bmatrix} \qquad (4.15)$$

A new set of component flow rates and temperatures can thus be obtained for further calculations as per the following algorithm.

4.2 ALGORITHM FOR ABSORBER CALCULATIONS :

1. Average pressure drop per stage in the column is calculated from column design and from it the pressure on each stage of the column is estimated.
2. A set of temperatures $\left[T_j\right]$ and a set of vapour flow rates $\left[V_j\right]$ is assumed. The corresponding sets of liquid flow rates are calculated by

   the total material balance equations:

   $$l_{j-1} - V_j - l_j + V_{j+1} = 0 \qquad (1 \leq j \leq N) \qquad (4.16)$$

   l_0 and V_{N+1} being known, all others can be calculated.
3. A set of gas component flow rates are assumed for the initialisation for

the calculation of Netwon-Raphson Jacobian elements. From these gas component flow rates the sets of corresponding liquid component flow rates are calculated using eq. (3.30).

4. From these gas component flow rates the elements of the Jacobian and the functions are calculated. The matrix is then solved to get the new sets of the component flow rates as

$$v_{jn+1} = v_{jn} + \lambda_j \, \Delta v_j \tag{4.17}$$

The factor λ_j for a j^{th} is found such that the value of function $\left(f_j\right)^2$ is minimized. For this, in this work the function at three different values of λ_j i.e. 1, 0.5 and 0.001 has been calculated. If the minima occurs at 0.5 a parabola is fitted through these points and the minima of the parabola is taken as λ; else if the minima lies at 0.001 or 1.0 they are taken as λ_j for that particular stage and iteration.

This is somewhat like the "Globally Convergent Method for Non-linear equations" [*Press et al (1997)*] to reach the required convergence. The iterations are continued till the required convergence criteria for v_j is achieved.

The convergence criteria for these calculations has been taken as 0.0001. The convergence is taken reached when $(\Delta v_j / V_j)$ has met the required criteria.

5. With the new set of gas component flow rates the corresponding liquid flow rates are calculated by the use of equation 3.30.

6. From these new set of component flow rates, corrected values of the component flow rates are obtained so as the total balance for the component is applied. A balance on the component on the entire column,

can be written as:

$$v_{N+1} + l_o = l_N + v_1 \tag{4.18}$$

The correction by the "single theta convergence" method *[Holland (1976)]* specifies

$$\frac{l_N}{v_1} = \theta \left(\frac{l_N}{v_1}\right)_{ca} \tag{4.19}$$

where the factor θ is close to unity and *ca* represents the calculated values.

Equation (4.18) and (4.19) may be solved for v_1 to give

$$v_{1,c} = \frac{v_{N+1} + l_o}{1 + \theta \left(\frac{l_N}{v_1}\right)_{ca}} \tag{4.20}$$

Here θ has been taken to be unity for all

Thus a new corrected value for $v_{1,c}$ is obtained.

Other component flow rates are corrected using this corrected $v_{1,c}$ as

$$l_{j,c} = \left(\frac{l_j}{v_1}\right)_{c1} v_{1,c} \tag{4.21}$$

$$v_{j,c} = \left(\frac{v_j}{v_1}\right)_{c1} v_{1,c} \tag{4.22}$$

7. From these corrected component flow rates the new set of total flow rates calculated by summing the flow rates of all the absorbing and the non-absorbing components for both the liquid and the gas phase respectively. These new total flow rates are used for further calculations.

8. From the temperatures assumed or obtained from the last iteration the enthalpy balance functions and the Newton-Raphson Jacobian is calculated and solved to get the change in temperatures at each stage ΔT_j.
9. These changes are used for getting the new sets of temperatures as

$$T_{j,n+1} = T_{j,n} + \gamma_j \Delta T_j \tag{4.23}$$

The values of γ_j being calculated in the same way as described in step 4 but for the minimizing the enthalpy balance functions. The required convergence criteria of 0.0001 for temperature is checked. The convergence is applied with the value of $(\Delta T_j / T_j)$. If the required convergence is obtained it is reached then the iterations are stopped here, but if the required convergence criteria is not met all the steps from step - 1 are repeated for the new set of temperatures throughout the column.

4.3 PROPERTIES CALCULATION

The properties like density, specific heat, etc. have been determined from correlations and the data available.

The density of the liquid phase has been taken equivalent to water due to unavailability of the proper data. Under the assumptions of that the solution is a perfect mixture this could be justified, it has also been seen that the alkanol amines have the density around close to that of water at NTP and hence the solution density was approximated by the density of water.

The gas density was determined from the compressibility factor method by using method given for the gaseous mixtures, from Perry's Chemical Engineer's Handbook(1997). The virial coefficients for the compressibility factor determination were also determined from the relations given here and have been incorporated into the computer program.

The enthalpy of the component gases was taken at the reference temperature of 273.15 K. The enthalpy relations were taken from HYSYS simulation software and were added up in proper fractions to give the total enthalpy of the gaseous mixture. The liquid enthalpy has been approximated to that of water at that temperature because of inadequate data and correlations. The base temperature for enthalpy calculations has been taken as 273.15 K.

The *Henry's law* coefficient and the equilibrium constant for the reaction have been taken from *Kent and Eisenberg (1976)*.

The correlations and the correlation coefficients used have been tabulated in appendix A.

4.4 PRESSURE DROP CALCULATION

The pressure drop per plate has been calculated based on the weir height, weir length, tower diameter, number of holes, etc. for a *Glitsch Ballast* tray for the design used by *De Leye and Froment (1986)*, using the pressure drop correlations from *Glitsch Ballast tray design manual(1981)*. The pressure drop being calculated on the basis of average flow rate of gas and liquid throughout the column and has been taken constant at each stage.

The computer program, written for these absorber calculations with subroutines and the calculation technique used for solving the reactive absorber simulation, written in FORTRAN visual workbench has been given in appendix I.

Chapter - 5

RESULTS AND DISCUSSIONS

In this chapter an analysis of the results obtained by solving the model developed in chapter 3 by the technique as explained in chapter 4 is being done. In the following sections, the model validity and the parametric sensitivity of the process is analysed, using this model and the solution technique. The parameters considered for this study are gas and liquid concentrations, their temperatures and gas pressures.

In this investigation the system chosen is of H_2S absorption into aqueous Diethanolamine(DEA). This is well known system and has also been used by *DeLeye and Froment(1986)*, which makes the comparison easy.

5.1 VALIDITY OF THE MODEL

For testing the model, the column considered is a Glitsch Ballast tray column (V-1 type). The column has 18 number of value trays. The feed gas at 7.6 bar is fed to the 18th tray.

The average molecular weight of the feed gas is 24.44. The composition of the feed gas is so taken that it is near that used by *DeLeye and Froment (1986)*. For this the following components with respective compositions in mole fractions have been used

H_2S	0.195
Methane	0.445
Ethane	0.35

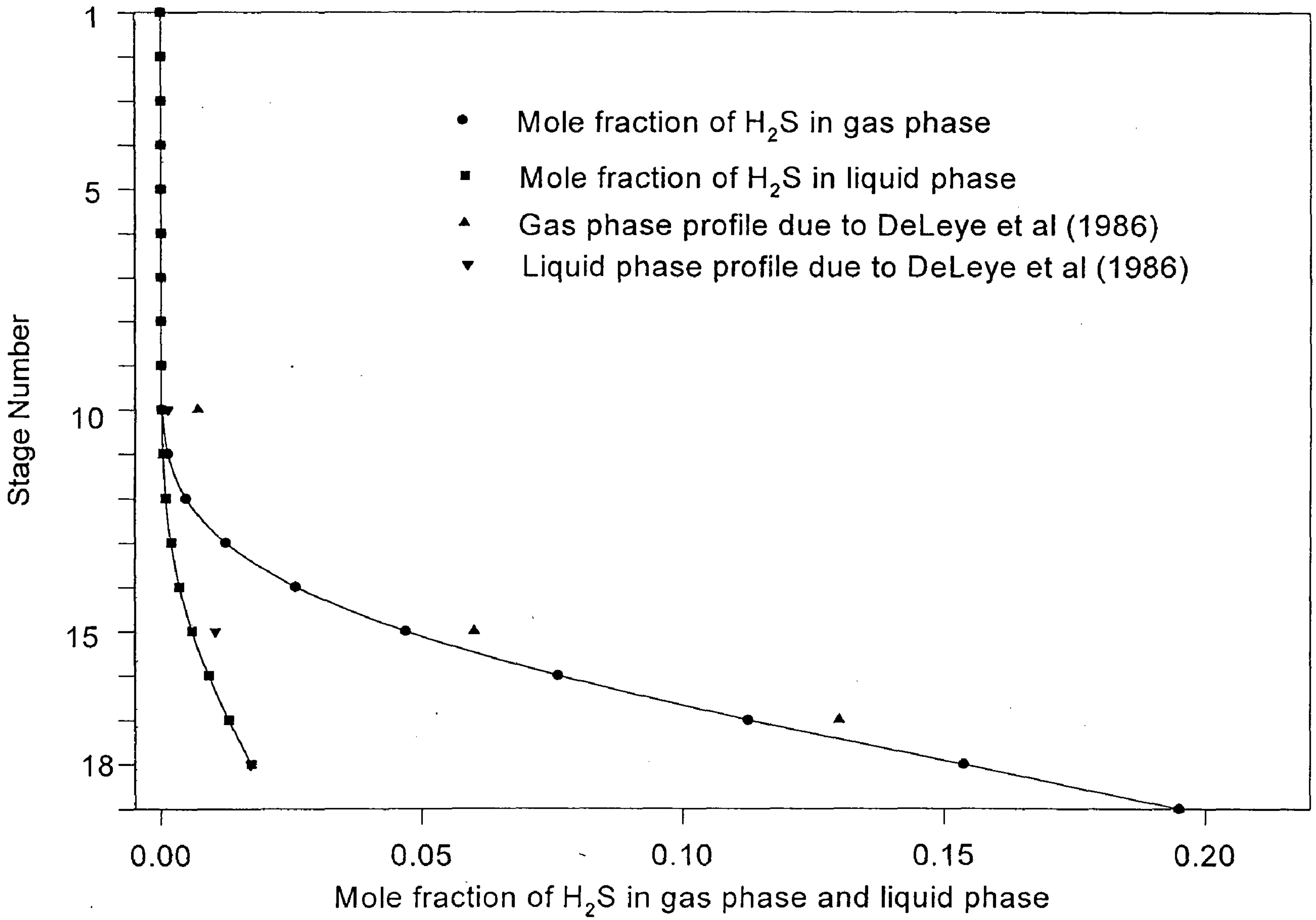


Fig.- 5.1 Concentration profile of the column

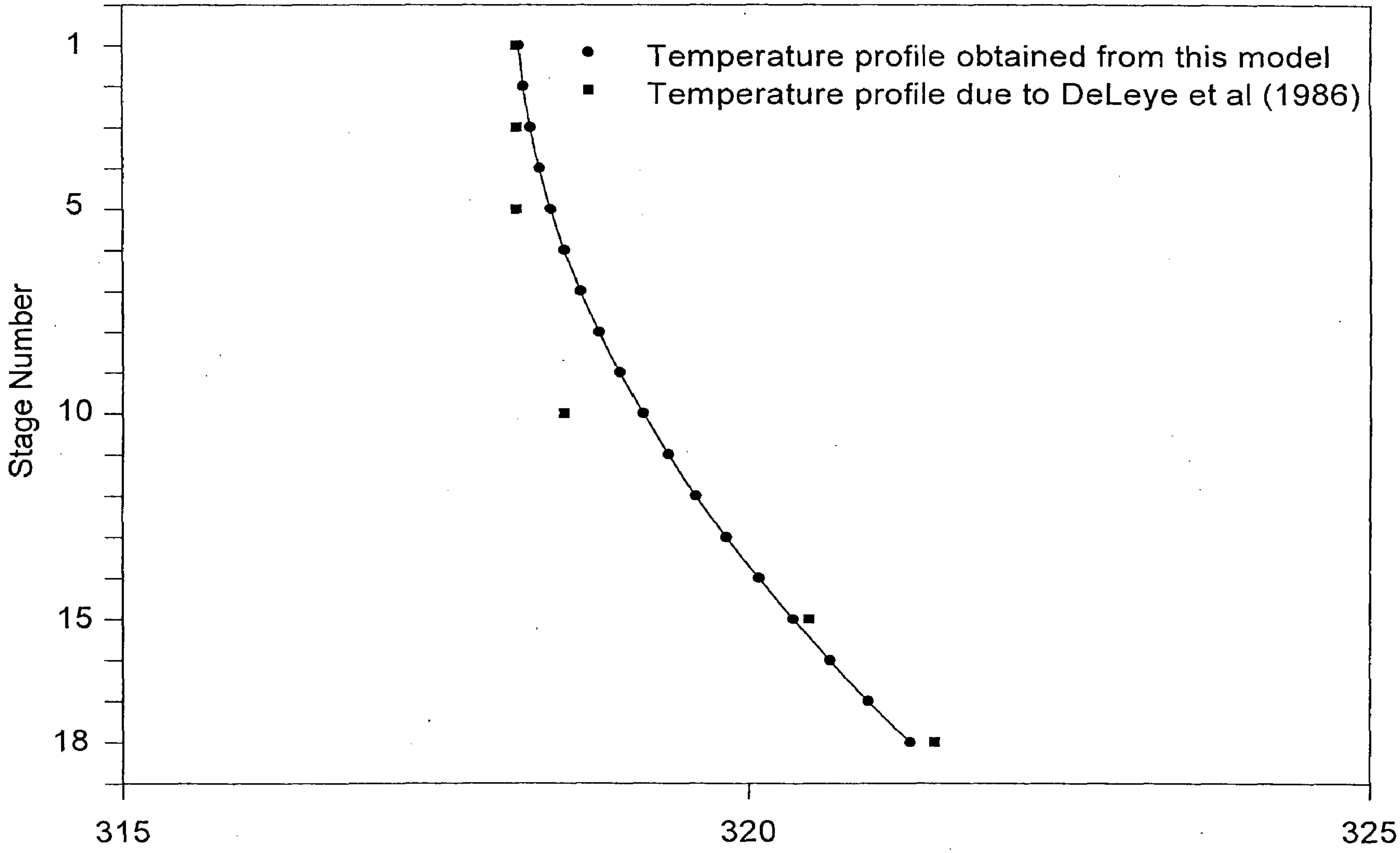


Fig.- 5.2 Temperature profile of the column

The gas flow rate is taken as 200.85 kmol/h. The solvent liquid flows at 2208.8 kmol/h, having 15% by weight of DEA. Other details of the column are as in the appendix B.

The results from the simulation program as well as those by *DeLeye and Froment (1986)* are as given in appendix C. Figure 5.1 to 5.4 depict these results in the graphical form for better interpretation.

Figure 5.1 shows the concentration profiles as obtained by this simulation with that due to *DeLeye and Froment (1986)* for the system under consideration. This figure shows a good agreement between the curves at the ends of the column. Deviation is seen at the middle section of the column, this is because equilibrium has been assumed at every stage in column.

The gas concentrations as they go up the column decrease and become very very less which makes even a slight deviation look appreciably large. The purity of gas obtained from this model is found to be much more than that due to *DeLeye and Froment (1986)* because of equilibrium consideration.

Figure 5.2 shows a comparison between the temperature profiles obtained with that due to *DeLeye and Froment(1986)*. There has been fairly good agreement between the two with maximum deviation around 5percent. The reasons for this may be the approximation of enthalpy data, with the assumptions gas mixture and the liquid solutions behaving as ideal mixtures.

Figure 5.3 depicts the total flow rates of the gas and liquid, the results of *DeLeye and Froment (1986)* have not been shown as the gas concentration being very low in the gas phase and the liquid phase any deviation between the two was not evident. The total flow rate profile thus matches excellently, with the total flow rates of the outlet gas and liquid as

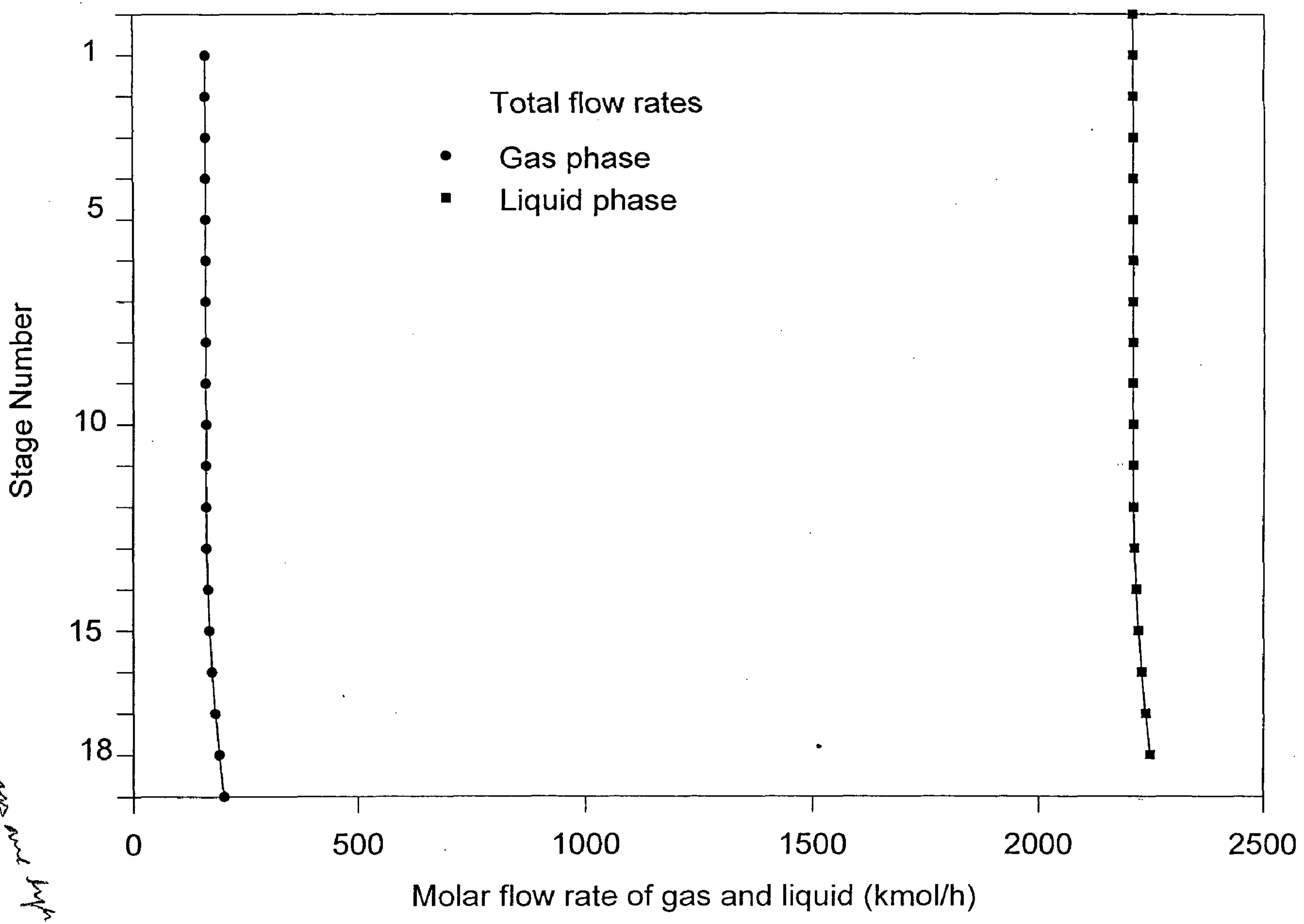


Fig.- 5.3 Change in the total flow rate throughout the column

both liq & gas are high at stage 18

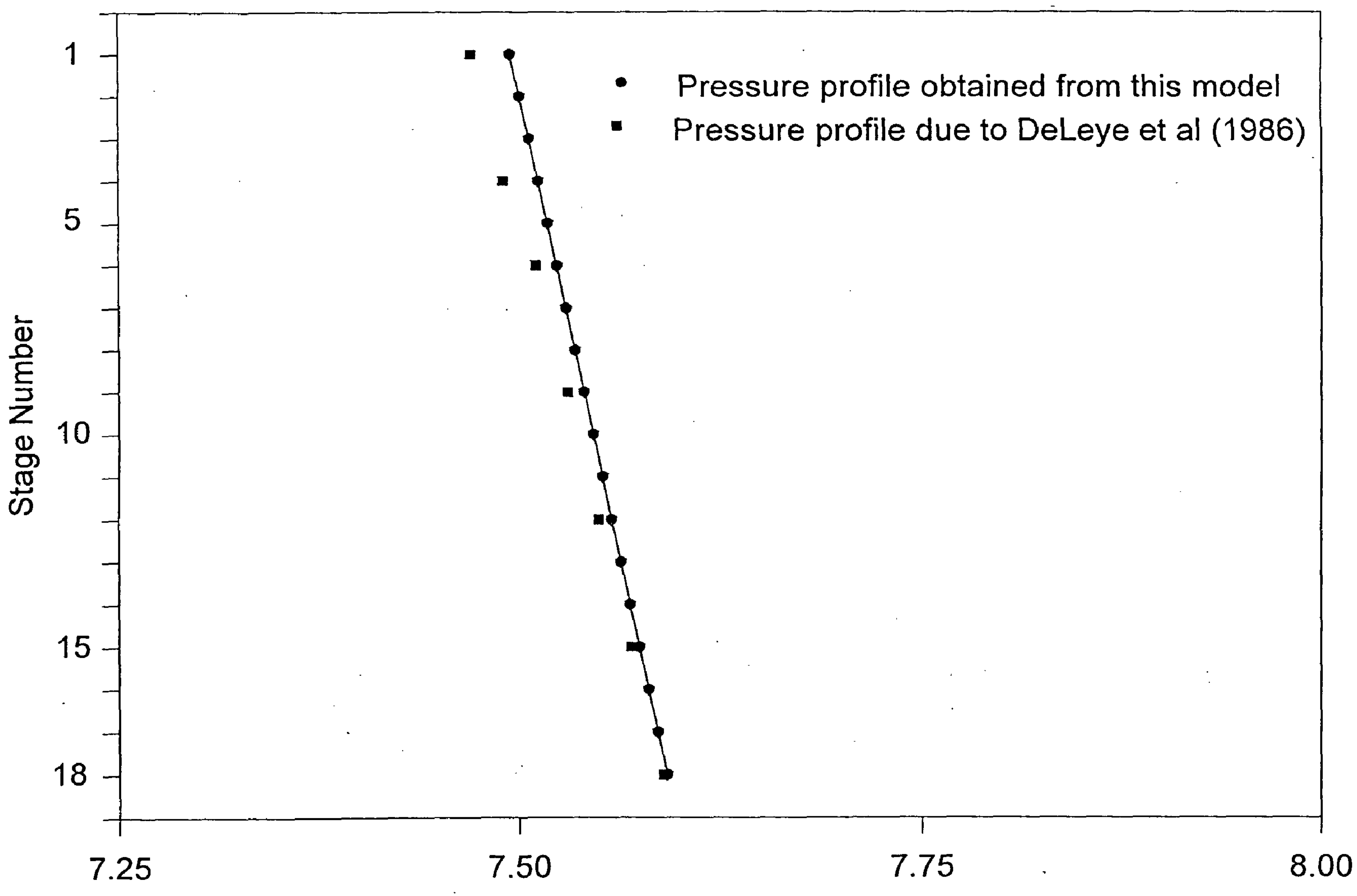


Fig.-5.4 Pressure profile of the column

given in appendix D.

In figure 5.4 a comparison of the pressure profile between the two results have been given, here the deviation (max 2percent) can be attributed to the calculation of pressure drop based on an average liquid and gas flow rate and density.

The most important feature of this work as compared to *DeLeye and Froment (1986)* is that it requires only two number of iterations to solve for the same system as compared to four number of iterations required by *DeLeye and Froment(1986)*. A comparison of the computation time has not been done as this program being only for a single component absorption, may be much simpler than the variety of subroutines used by them, and also over these years lesser computation times are required by faster processors.

Thus this model and computational technique can be said on the basis of the above results and explanations to have been successful in simulating a reactive absorption column.

In the following section which shows the effect of the operating variables for an absorption column would further identify the validity of the model.

5.2 EFFECT OF OPERATING VARIABLES

In this section an effect of the operating variables for a reactive absorption process, which for this process are the composition of the liquid and gas, their temperatures and the gas pressure has been studied. Liquid and Gas flow rates are also important design parameters but they have not been changed in this analysis as the computer program developed for this case does nt check for the flooding of the column. The variables on which the **analysis** has been done have been varied in the range as given below

Pressure	6-10 bar
Temperature	300-330 K
Gas concentration	0.1-0.3 mole fraction
Liquid composition	
DEA(Molarity)	1-5 kmol/m^3
Absorbing gas(H_2S) presence	0-0.0001 mole fraction

5.2.1 Effect of pressure

Figure 5.5 and 5.6 shows the concentration profile of gas with chance in gas pressure when there is no H_2S present in the feed liquid and for 0.0001 mole fraction of H_2S in the feed liquid respectively. The pressure for this study has been varied from 6 to 10 bar with all the other inputs to the column and the corresponding output obtained are as in appendix E.

For an increase in gas pressure in the column figure 5.5 shows that the same degree of separation is achieved at a lower stage than when at a lower pressure. The reason for this is that at high pressure the equilibrium reaches early in the column due to an increase in the value of the absorption factor of the system for all other inputs being constant.

A similar trend is shown when the feed liquid contains some amount of gas dissolved in it, with the only difference that greater height is required for same degree of separation as shown in figure 5.6.

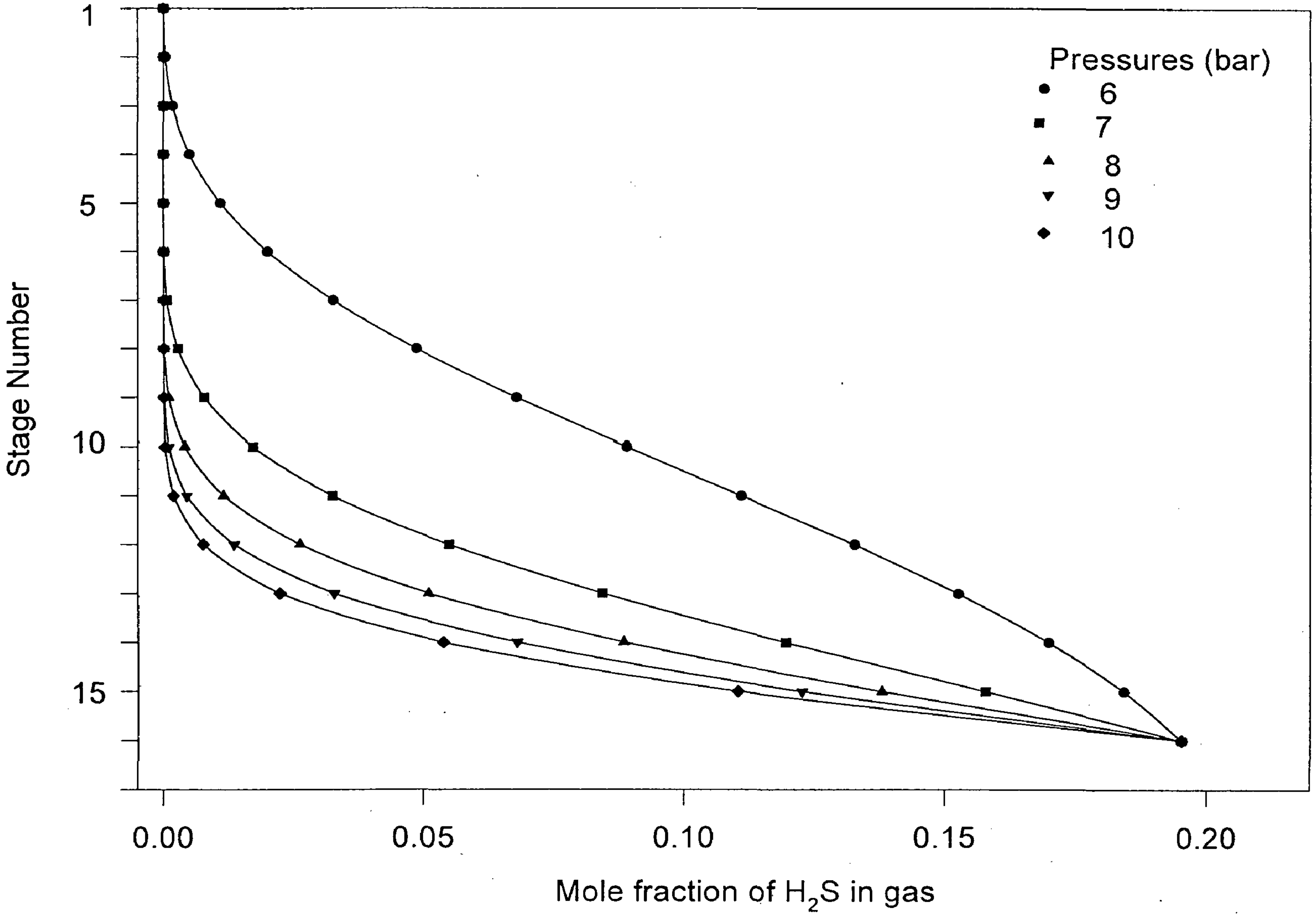


Fig.- 5.5 Variation of mole fraction in gas with gas pressure, at 315 K

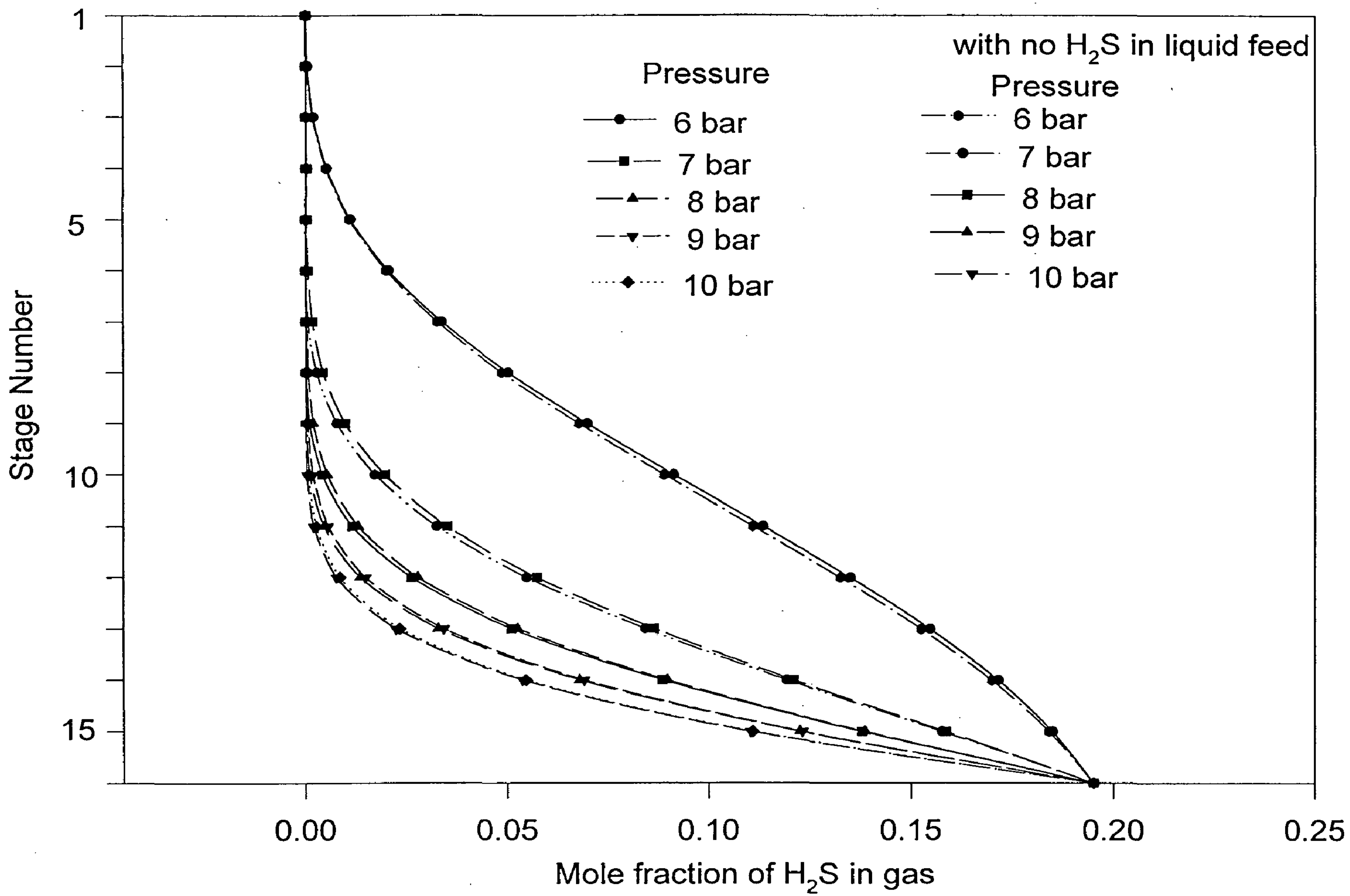


Fig.- 5.6 Variation of mole fraction in gas with gas pressure, at 315 K, with 0.0001 mole fraction of H2S in liquid feed

5.2.2 Effect of feed temperature

Figure 5.7 and 5.8 are plotted to find the effect of temperature change on the mole fraction of H_2S in the gaseous phase. The two figures are respectively for no presence of H_2S in the feed the feed liquid and for 0.0001 mole fraction of H_2S in the liquid. The feed temperatures were taken as 300K, 310K, 320K and 330K, other variables and the corresponding outputs from the computer program are as in appendix F.

Figure 5.7 shows that the same degree of separation is achieved at greater height when temperature is increased than at a less temperature. This can be attributed to an increase in the value of Henry's law coefficient at increased temperature and thus a reduction in the absorption factor, and thus the results. This pattern obtained is like that as would be expected for a change in temperature.

A similar trend is obtained when the solvent contains 0.0001 mole fraction of H_2S, with the difference that a greater height is required at same temperature and for the same degree of separation as shown in figure 5.8.

5.2.3 Effect of feed gas composition

Figure 5.9 and 5.10 show the observed behaviour of the model to changing feed compositions. The plots were obtained for no H_2S present in the feed liquid and 0.001 mole fraction of H_2S in absorbing liquid respectively. The fraction of H_2S in the feed gas being varied as 0.05, 0.10,. 0.20, 0.25, 0.30, mole fraction. Other inputs to the system and corresponding outputs have been tabulated in appendix G.

Figure 5.9 shows that an increase in the fraction of H_2S in the feed gas

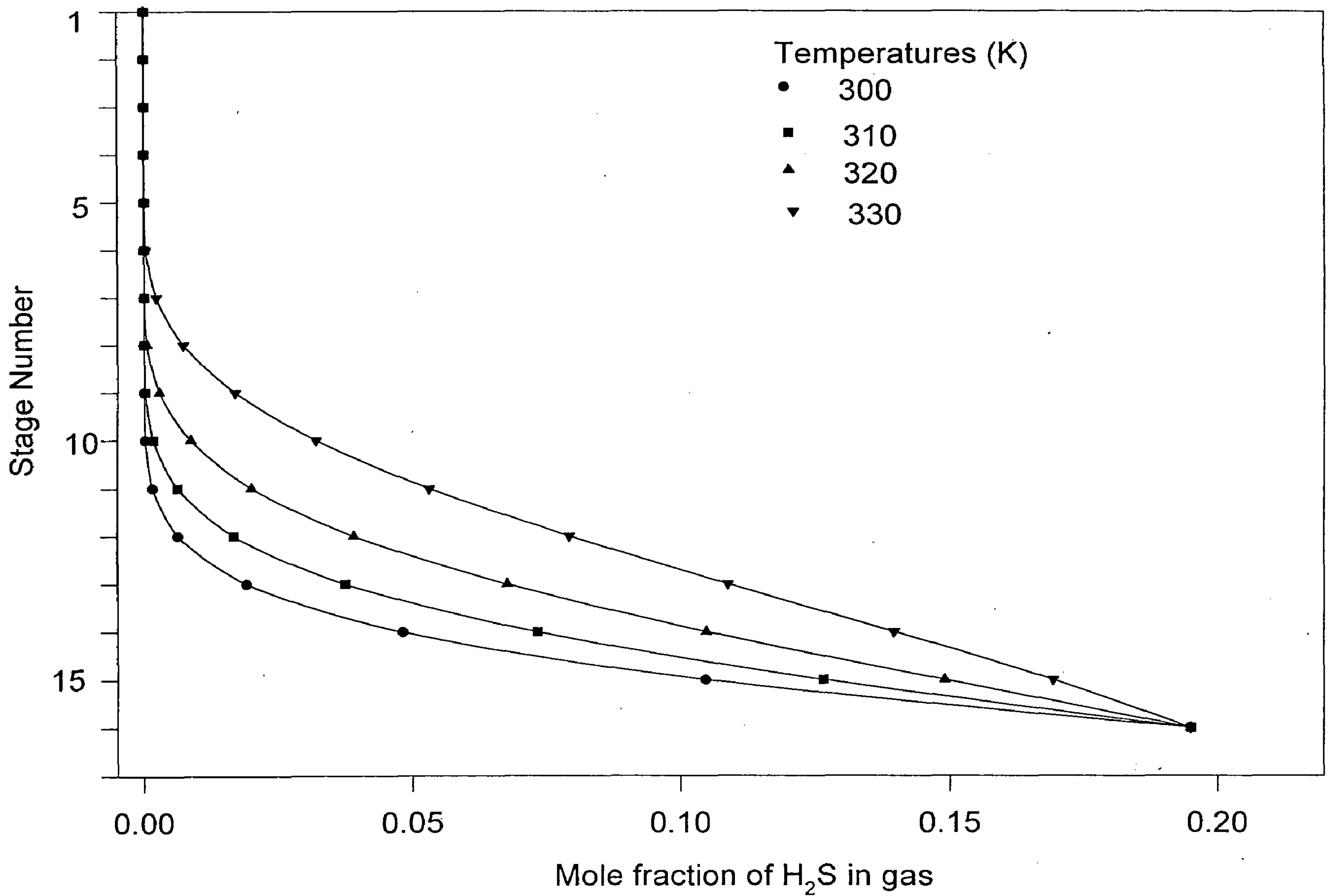


Fig.- 5.7 Variation of mole fraction in gas with feed gas and liquid temperature, at 8 bar

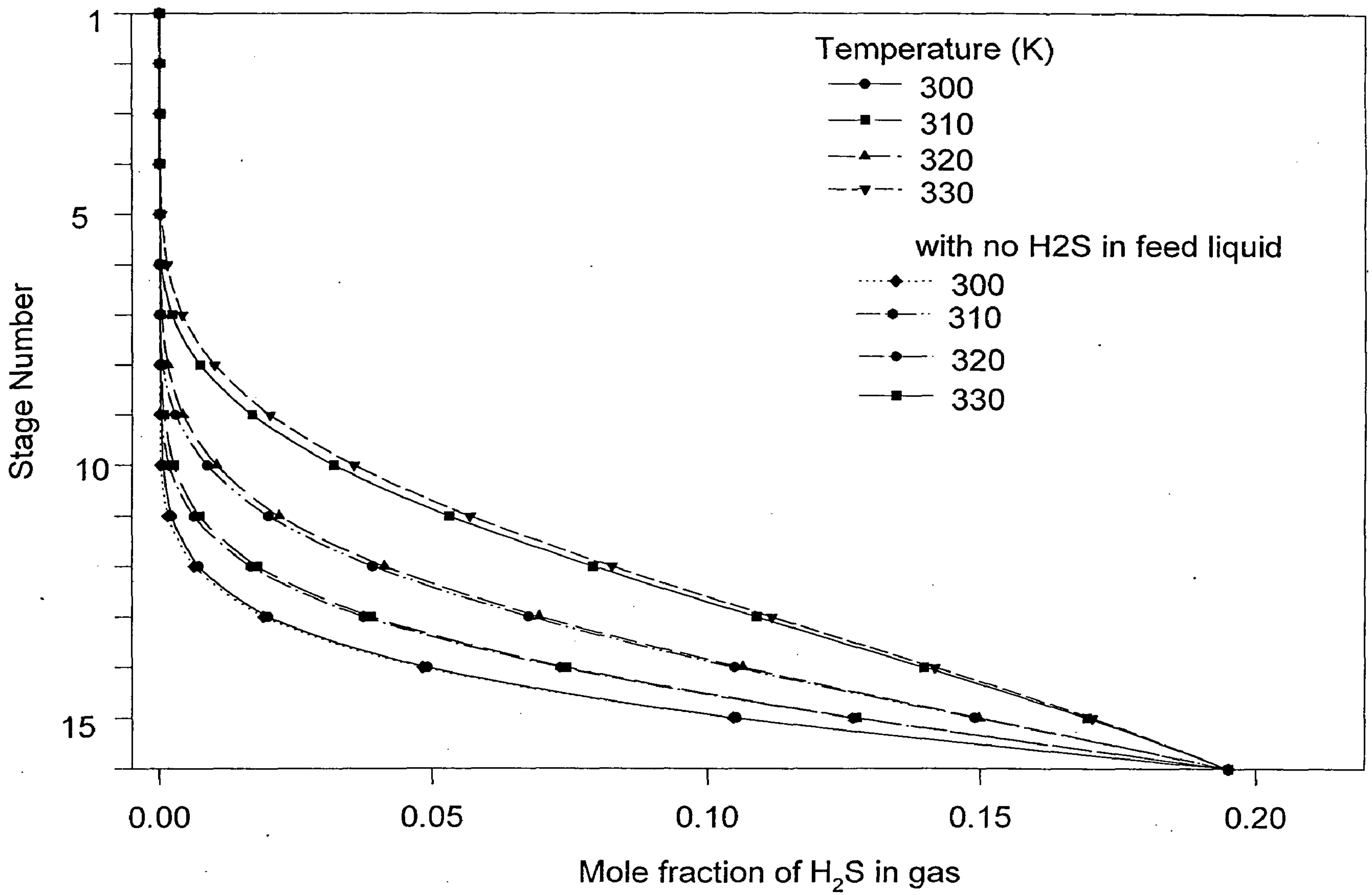


Fig.- 5.8 Variation of mole fraction in gas with feed gas and liquid temperature, at 8 bar, with 0.0001 mole fraction of H_2S in liquid

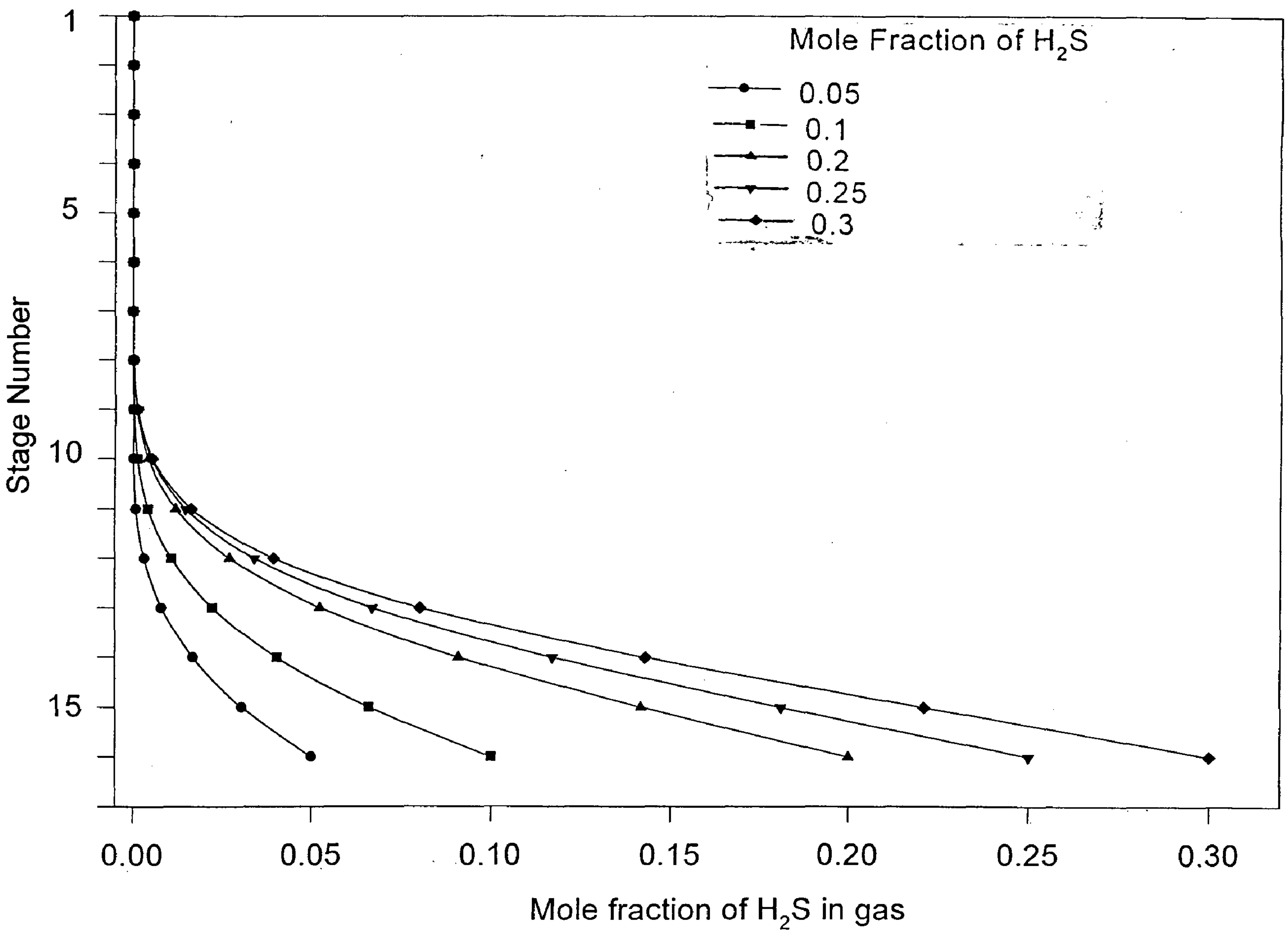


Fig.- 5.9 Variation of mole fraction in gas with fraction of H_2S in the feed gas

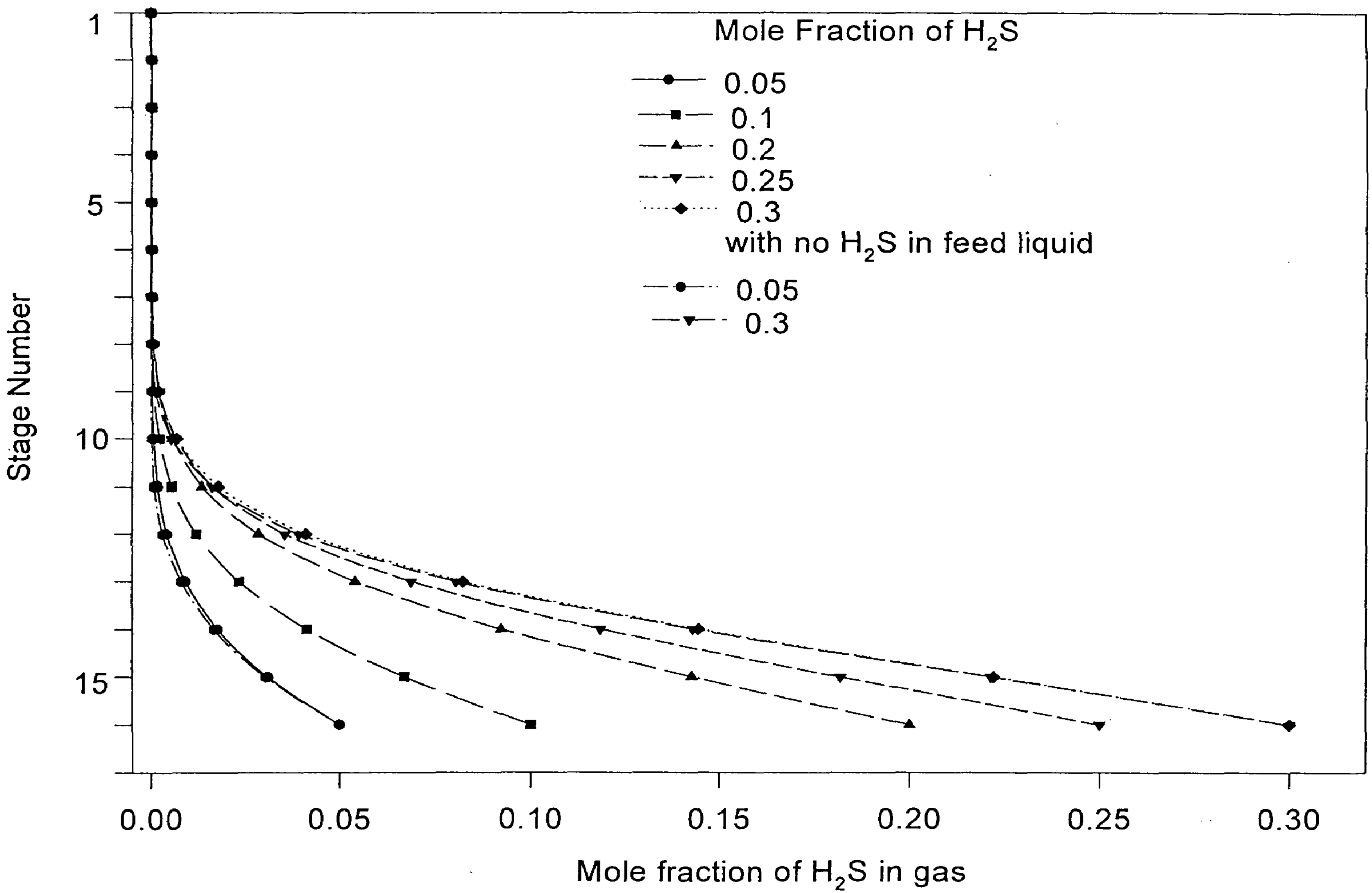


Fig.- 5.10 Variation of mole fraction in gas with fraction of H_2S in the feed gas with 0.0001 mole fraction of H_2S in liquid

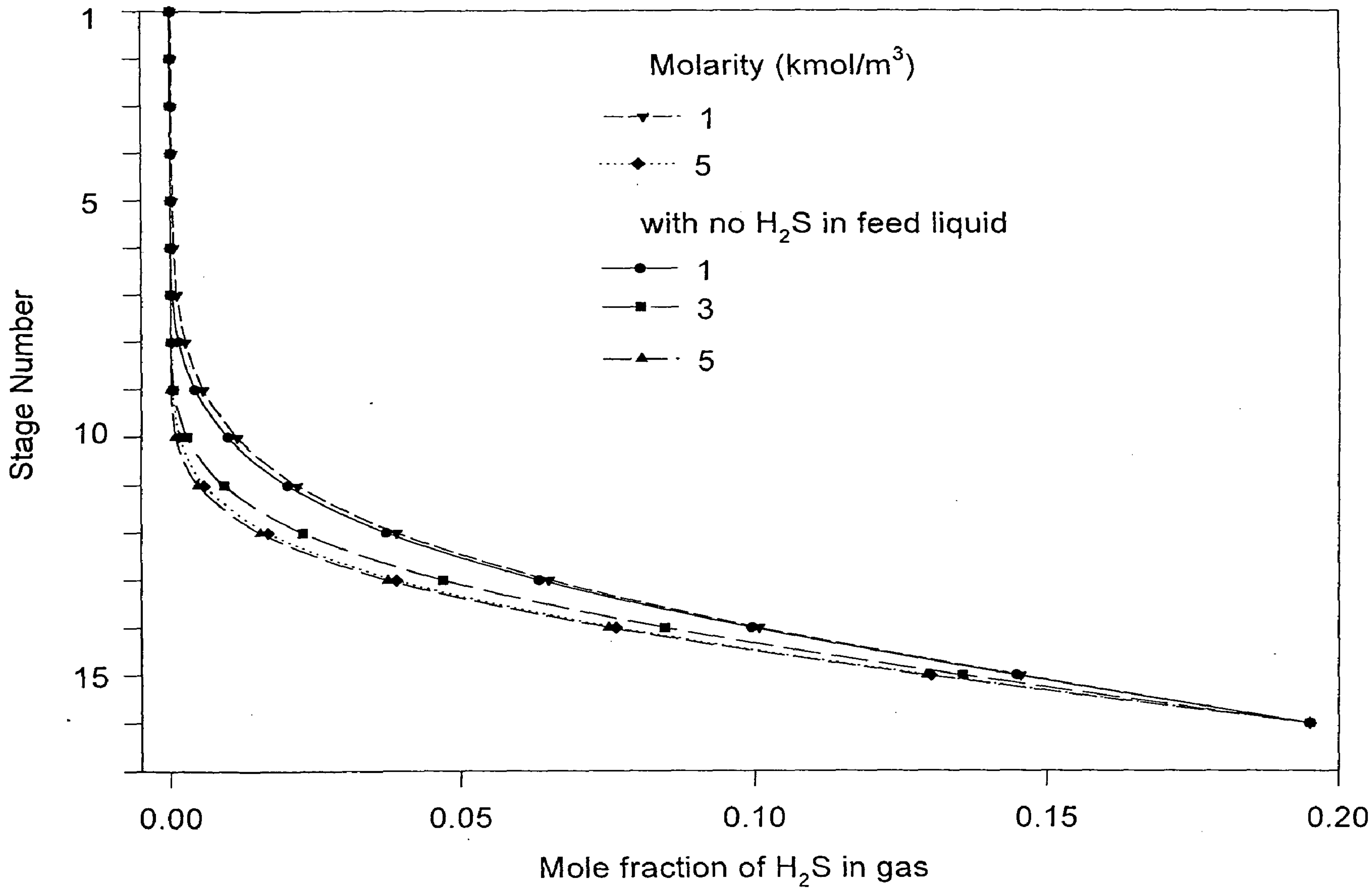


Fig.- 5.12 Variation of mole fraction in gas with change in molarity of solution, at 315 K, with 0.0001 mole fraction of H2S in liquid feed

The above discussions show that this model and computational technique has been able to satisfactorily predict the behaviour of a reactive absorption column within the range of variables on which the studies have been undertaken.

5.3 Sensitivity Analysis

Sensitivity analysis of this system (figures 5.5-5.12) shows that, within the range of studies the pressure of the gas feed plays a very important role on the number of stages orequired for separation. At low pressure pressure the height of the column required for at which a certain degree of separation is reached is much more than at high pressure. The other variable which has been found to be having a major effect is the temperature of the gas and liquid feed.

Thus for the separation of these gases effectively and for the proper operation of the column the temperature of the feed streams and most importantly the pressure of the column has to be controlled.

Chapter - 6

CONCLUSIONS AND RECOMMENDATIONS

The testing of the model and the computational technique helps us to draw the following conclusions:

1. This model has been satisfactory in simulating a reactive absorption column for the system under consideration. The results have been found to agree well with those of *DeLeye and Froment (1986)*; the temperature profile the molar flow rates and the pressure profiles match excellently, within the error range of 5percent for each.
2. This model and computational technique have also been successful in determining the effect of the various parameters in reactive absorption, with the results which could be well interpreted with theoretical explanations.
3. Using this computational technique for equilibrium absorber simulation results were obtained with only two number of iterations as compared to 4 iterations required by *DeLeye and Froment (1986)*.
4. The system has been found most sensitive to pressure and temperature changes of the feed. The major effect of these being due to pressure changes.

Although this model and computational technique has been able to simulate the reactive absorption column within satisfactory limits, still many of the simplifications which exist now could be rectified and are henceforth being recommended here for further analysis:

1. This model has been used only for single component absorption with all the other components being neutral in the system. This simplification can

be rectified by considering multicomponent absorbing system, with only one absorbing component.

2. Here only one acid gas has been absorbed from the system. This model could be used for study of selective absorption of one acidic component over other.
3. Here only the Newton-Raphson's technique has been used for the solution of the tri-diagonal matrix system. Other techniques could also be used for the solution of system of equations using Broyden's technique given by *Tomich (1970)*.
4. The Murphree plate efficiency of the column can also be considered as given by *Naphtali and Sandholm (1971)* so that the equilibrium stage assumption made here would give much better results.

Appendix B

Glitsch Ballast Tray Column Details

Design taken from DeLeye and Froment (1986)

Property	
Tray Diameter (m)	0.98
Active area(m^2)	0.4225
Weir Length (mm)	872
Weir Height (mm)	66
Valve thickness (mm)	1.88
Valve unit type	V-1

Pressure Drop correlation coefficients[*Glitsch Ballast tray design manual(1981)*]
Specific to this particular unit and valve thickness

$k1=0.2$
$k2=1.05$

$$\Delta P_{dry}=1.35t_m D_m/D_L+k1(V_h)^2 D_v/D_L$$

$$\Delta P_{dry}=k2(V_h)^2 D_v/D_L$$

where ΔP_{dry} = inches liquid
t_m =valve thickness, inches
D_m = valve metal density, lb/cu ft
D_v = gas density, lb/cu ft
D_L = liquid density, lb/cu ft
k1,k2 =pressure drop coefficients
V_h =hole velocity, ft/sec

$$\Delta P=\Delta P_{dry}+0.4(gpm/Lwi)^{2/3}+0.4Hw$$

where ΔP = total pressure drop, inches liquid
gpm = gallons per minute of liquid
Lwi = weir length, inches
Hw = weir height, inches

Appendix-C

RESULTS OBTAINED FROM MODEL SIMULATION

TableC-1: Concentration profile

Stage No.	gas	liquid
	0.195	
18	0.153711	0.017423
17	0.112587	0.013118
16	0.076006	0.009198
15	0.046844	0.005982
14	0.02592	0.003581
13	0.012455	0.001942
12	0.004826	0.000921
11	0.001269	0.000353
10	0.000151	9.3E-05
9	2.89E-06	1.11E-05
8	1.10E-07	2.1E-07
7	1.85E-08	8.60E-08
6	1.37E-08	2.33E-08
5	1.34E-08	7.29E-09
4	1.31E-08	7.20E-09
3	1.29E-08	7.14E-09
2	4.58E-09	1.34E-09
1	1.27E-09	7.08E-10
		0

TableC-2: Temperature profile

Stage No.	Temp.
18	321.30033
17	320.95792
16	320.64597
15	320.3529
14	320.07803
13	319.82131
12	319.58279
11	319.3625
10	319.16052
9	318.97685
8	318.81153
7	3.19E+02
6	3.19E+02
5	3.18E+02
4	3.18E+02
3	3.18E+02
2	3.18E+02
1	3.18E+02

Table C-3: Total flow rate profiles

Stage No.	gas	liquid
	200.85	
18	191.0509	2247.966
17	182.1972	2238.167
16	174.9841	2229.313
15	169.6304	2222.1
14	165.9866	2216.746
13	163.7235	2213.102
12	162.4684	2210.839
11	161.8897	2209.584
10	161.7087	2209.005
9	161.6847	2208.824
8	1.62E+02	2208.8
7	1.62E+02	2.21E+03
6	1.62E+02	2.21E+03
5	1.62E+02	2.21E+03
4	1.62E+02	2.21E+03
3	1.62E+02	2.21E+03
2	1.62E+02	2.21E+03
1	1.62E+02	2.21E+03
		2208.8

Table C-4: Pressure profile

Stage No.	Pressure
18	7.592366
17	7.58661
16	7.580853
15	7.575096
14	7.56934
13	7.563583
12	7.557826
11	7.55207
10	7.546313
9	7.540556
8	7.5348
7	7.53E+00
6	7.52E+00
5	7.52E+00
4	7.51E+00
3	7.51E+00
2	7.50E+00
1	7.49E+00

Appendix E

Effect of gas pressure on the gas phase concentration profile

Table E-1: Inputs to the column

Stages	15	15	15	15	15
gas flow rate (kmol/h)	200.85	200.85	200.85	200.85	200.85
Liquid flow rate (kmol/h)	2208.8	22.8.8	2208.8	2208.8	2208.8
Gas composition (mole fraction) H_2S Ethane Methane	 0.195 0.35 0.455	 0.195 0.35 0.455	 0.195 0.35 0.455	 0.195 0.35 0.455	 0.195 0.35 0.455
Temperature (K)	315	315	315	315	315
Molarity of DEA (kmol/m^3)	2.4	2.4	2.4	2.4	2.4
Gas Pressure (bar)	6	7	8	9	10

Table E-2: When the liquid feed contains no H_2S

Pressure	6 bar	7 bar	8 bar	9 bar	10 bar
Stage No.					
15	0.183936	0.157671	0.13795	0.122605	0.110345
14	0.169742	0.119449	0.088365	0.067794	0.053697
13	0.152478	0.084148	0.050966	0.032843	0.022381
12	0.132577	0.054712	0.026195	0.013591	0.007659
11	0.11095	0.032453	0.011548	0.004453	0.001899
10	0.088838	0.017179	0.004059	0.000949	0.000231
9	0.067627	0.007773	0.000939	7.7E-05	5.34E-06
8	0.048569	0.002702	9.02E-05	7E-07	4.3E-09
7	0.032583	0.000579	9.96E-07	0	0
6	0.020016	4.19E-05	1.85E-08	0	0
5	0.010968	2.65E-07	1.45E-08	0	0
4	0.005019	1.65E-07	0	0	0
3	0.001722	1E-07	0	0	0
2	0.000319	7.54E-08	0	0	0
1	1.5E-05	2.42E-09	0	0	0

Table E-3: When the liquid contains 0.0001 mole fraction of H_2S

Pressure	6 bar	7 bar	8 bar	9 bar	10 bar
Stage No.					
15	0.184764	0.158498	0.138685	0.123276	0.110949
14	0.171352	0.12106	0.089652	0.068939	0.054572
13	0.15468	0.086349	0.05255	0.034167	0.023329
12	0.135093	0.057228	0.027786	0.014872	0.008529
11	0.113518	0.03502	0.013065	0.005557	0.002583
10	0.09124	0.019581	0.005326	0.001735	0.00068
9	0.069672	0.009818	0.001853	0.000509	0.000231
8	0.050185	0.004317	0.000605	0.000217	0.000148
7	0.033664	0.001661	0.000263	0.00016	0.000135
6	0.020594	0.000621	0.000186	0.000149	0.000133
5	0.011266	0.000298	0.00017	0.000148	0.000133
4	0.005235	0.000216	0.000167	0.000148	0.000133
3	0.001918	0.000196	0.000166	0.000148	0.000133
2	0.000511	0.000192	0.000166	0.000148	0.000133
1	0.000206	0.000191	0.000167	0.000148	0.000132

All the values of the order of 10^{-10} and lower have been given as zero

Appendix F

Effect of temperature on the gas phase concentration profile

Table F-1: Inputs to the column

Stages	15	15	15	15
gas flow rate (kmol/h)	200.85	200.85	200.85	200.85
Liquid flow rate (kmol/h)	2208.8	22.8.8	2208.8	2208.8
Gas composition (mole fraction) H_2S Ethane Methane	 0.195 0.35 0.455	 0.195 0.35 0.455	 0.195 0.35 0.455	 0.195 0.35 0.455
Temperature (K)	300	310	320	330
Molarity of DEA (kmol/m^3)	2.4	2.4	2.4	2.4
Gas Pressure (bar)	8	8	8	8

Table F-2: when the liquid feed is free of H_2S

Temp.	300 K	310 K	320 K	330 K
Stage No.				
15	0.10467	0.12669	0.14896	0.16908
14	0.04827	0.07322	0.10488	0.1397
13	0.01925	0.03758	0.06748	0.10887
12	0.00641	0.01686	0.03925	0.07919
11	0.00158	0.00632	0.02019	0.05308
10	0.00021	0.00171	0.00877	0.03218
9	0.00001	0.00024	0.00288	0.01708
8	0	0.00001	0.00056	0.00742
7	0	0	0.00003	0.00229
6	0	0	0	0.00036
5	0	0	0	0.00001
4	0	0	0	0
3	0	0	0	0
2	0	0	0	0
1	0	0	0	0

Table F-3: when the gas contains 0.0001-mole fraction of H_2S

Temp.	300 K	310 K	320 K	330 K
Stage No.				
15	0.105221	0.127363	0.149774	0.17004
14	0.049077	0.074327	0.106353	0.141646
13	0.020118	0.038872	0.06939	0.111666
12	0.007217	0.018142	0.041321	0.082637
11	0.002245	0.007427	0.022199	0.056834
10	0.000662	0.002615	0.010525	0.03587
9	0.000265	0.000832	0.004268	0.020379
8	0.000182	0.000318	0.001463	0.010108
7	0.000165	0.000199	0.000487	0.00419
6	0.000162	0.000174	0.000231	0.001411
5	0.000162	0.000169	0.000175	0.000442
4	0.000161	0.000168	0.000163	0.000201
3	0.000161	0.000168	0.000161	0.000152
2	0.000161	0.000168	0.000161	0.000143
1	0.000161	0.000168	0.000145	0.000109

All the values of the order of 10^{-10} and lower have been given as zero

Appendix G

Effect of gas concentration on the gas phase concentration profile

Table G-1: Inputs to the column

Stages	15	15	15	15	15
gas flow rate (kmol/h)	200.85	200.85	200.85	200.85	200.85
Liquid flow rate (kmol/h)	2208.8	22.8.8	2208.8	2208.8	2208.8
Gas composition (mole fraction) H_2S Ethane Methane	 0.05 0.45 0.5	 0.1 0.4 0.5	 0.2 0.4 0.4	 0.25 0.35 0.4	 0.195 0.3 0.4
Temperature (K)	315	315	315	315	315
Molarity of DEA (kmol/m^3)	2.4	2.4	2.4	2.4	2.4
Gas Pressure (bar)	8	8	8	8	8

Table G-2: When the feed liquid contains no H_2S

Mol fr.	0.05	0.1	0.2	0.25	0.3
Stage No.					
15	0.030312	0.066106	0.141828	0.181099	0.221145
14	0.016657	0.040159	0.090939	0.11696	0.142915
13	0.007965	0.022076	0.05244	0.067005	0.080412
12	0.003058	0.010626	0.026875	0.033806	0.039239
11	0.000786	0.004183	0.011856	0.014639	0.016237
10	8.91E-05	0.001153	0.004162	0.005069	0.005292
9	1.33E-06	0.000154	0.000964	0.00118	0.00111
8	0	3.62E-06	9.02E-05	0.000114	8.67E-05
7	0	2.24E-09	1.05E-06	1.45E-06	6.56E-07
6	0	0	0	0	0
5	0	0	0	0	0
4	0	0	0	0	0
3	0	0	0	0	0
2	0	0	0	0	0
1	0	0	0	0	0

Table G-3: When the liquid contains 0.0001-mole fraction of H_2S

Mol fr.	0.05	0.1	0.2	0.25	0.3
Stage No.					
15	0.030981	0.066824	0.142567	0.181857	0.221926
14	0.017694	0.041275	0.09225	0.118318	0.144381
13	0.009157	0.023392	0.054057	0.068677	0.082237
12	0.004217	0.01197	0.028549	0.035514	0.04108
11	0.001688	0.005395	0.013402	0.016195	0.017882
10	0.000635	0.002096	0.005452	0.006373	0.00662
9	0.000289	0.000743	0.001889	0.002102	0.002042
8	0.000195	0.000306	0.000613	0.000642	0.000588
7	0.000172	0.000193	0.000265	0.000264	0.000246
6	0.000166	0.000166	0.000186	0.000185	0.00018
5	0.000165	0.00016	0.00017	0.000169	0.000168
4	0.000165	0.000159	0.000167	0.000167	0.000166
3	0.000165	0.000159	0.000166	0.000166	0.000166
2	0.000165	0.000159	0.000166	0.000166	0.000166
1	0.000142	0.000112	0.000167	0.000163	0.000155

All the values of the order of 10^{-10} and lower have been given as zero

Appendix H

Effect of liquid molarity on the gas phase concentration profile

Table H-1: Inputs to the column

Stages	15	15	15
gas flow rate (kmol/h)	200.85	200.85	200.85
Liquid flow rate (kmol/h)	2208.8	22.8.8	2208.8
Gas composition (mole fraction) H_2S Ethane Methane	 0.195 0.35 0.455	 0.195 0.35 0.455	 0.195 0.35 0.455
Temperature (K)	315	315	315
Molarity of DEA (kmol/m^3)	1	3	5
Gas Pressure (bar)	8	8	8

Table H-2: When the liquid feed contains no H_2S

Molarity	1	3	5
Stage No.			
15	0.14478	0.135566	0.129401
14	0.099472	0.084561	0.075191
13	0.063261	0.046926	0.037541
12	0.037223	0.022732	0.015449
11	0.020128	0.009153	0.004659
10	0.009805	0.002722	0.000775
9	0.004112	0.000443	3.4E-05
8	0.001334	1.82E-05	7.03E-08
7	0.000273	3.48E-08	0
6	1.89E-05	0	0
5	1.11E-07	0	0
4	0	0	0
3	0	0	0
2	0	0	0
1	0	0	0

Table H-3: When liquid contains 0.0001-mole fraction of H_2S

Molarity	1	5
Stage No.		
15	0.145495	0.130144
14	0.100744	0.076397
13	0.06488	0.038957
12	0.038979	0.016772
11	0.021864	0.005756
10	0.011415	0.001465
9	0.005525	0.00032
8	0.002498	0.000124
7	0.001113	9.85E-05
6	0.000562	9.54E-05
5	0.000367	9.52E-05
4	0.000304	9.53E-05
3	0.000284	9.54E-05
2	0.000278	9.56E-05
1	0.000218	9.57E-05

All the values of the order of 10^{-10} and lower have been given as zero

Appendix I

Fortran Program simulating the absorber

```
***********************************************************************
C     THIS PROGRAM WILL SIMULATE THE REACTIVE ABSORPTION COLUMN
C     FOR THE ABSORPTION OF H2S INTO AQUEOUS DEA SOLUTION WITH H2S AS
C     THE ONLY ABSORBING COMPONENT WITH NO OTHER COMPONENT BEING
C     ABSORBED IN THE LIQUID. THE SIMULATION IS DONE ASSUMING THE
C     COLUMN TO BEHAVE AS EQUILIBRIUM STAGES
***********************************************************************
C     THE INPUT REQUIRED ARE THE FOLLOWING
C     NUMBER OF STAGES-----------------------NN
C     THE TOTAL GAS FLOW RATE-----------------GTF      (MOL/HR)
C     THE GAS INLET PRESSURE------------------P(NN+1)  (BAR)
C     THE INLET GAS TEMPERATURE---------------T(NN+1)  (K)
C     THE ABSORBING GAS FRACTION--------------Y(NN+1)  (MOLES/MOLE)
C     SOLVENT FLOW RATE-----------------------ELO     (MOLES/HR)
C     SOLVENT INLET TEMPERATURE---------------T(0)    (K)
C     MOLALITY OF THE SOLVENT-----------------CM
C     AMOUNT OF H2S PRESENT IN THE SOLVENT----X(0)    (MOLES/MOLE)
***********************************************************************

      REAL*8 GTF,P,T,Y,ELO,CM,X,VG,VLIJ,EL,ELIJ,GVIJ,A,PK,TO,AA,BB,CC
      REAL*8 DD,CHAG,DV,DL,GG,AE,BE,CE,GH,CHAT,CONVOB,TD
      REAL*8 DGF,DTV,CONVT,CH,DHR,GHG,GVJC,DEN,CONCT
      REAL CV,CL,CHS
      INTEGER IN,NN,OUT
      COMMON NN,IN,OUT,DHR

      DIMENSION P(800),TO(800,800),Y(800),X(800),VLIJ(800),GHG(1000)
      DIMENSION EL(800,800),ELIJ(800,800),DL(800,800),GVIJO(800,800)
      DIMENSION A(800,800),PK(800),VG(800,800),CONV(800),CV(6,800)
      DIMENSION AA(800,800),BB(800,800),CC(800,800),DD(800,800)
      DIMENSION THETA(3),GG(800,800),DTV(800,800),THI(800),CHS(3,6)
      DIMENSION CL(6),GH(800,800),CHAT(800,800),AE(800,800),CHK(800)
      DIMENSION CE(800,800),CONVT(800),CH(800,800),GVJC(800,800)
      DIMENSION TD(800,800),CPC(3),GVIJ(800,800),CHAG(800,800),PH(800)
      DIMENSION DV(800,800),T(800),DGF(800),BE(800,800),THE(800)
      OPEN(10,FILE='n1tT.DAT')
      OPEN(11,FILE='n2tT.DAT')
      OPEN(12,FILE='n3tT.DAT')
      OPEN(13,FILE='n4tT.DAT')
      OPEN(14,FILE='n5tT.DAT')
      RCONV=1E-4
      TCONV=1E-4
      DHR=41.905167E3
      DATA(THETA(I),I=1,3)/0.9,0.5,0.001/
```

```
      DATA(CHS(1,I),I=1,4)/-9156.30348,34.0289,-6.28094E-3,18.98515E-6/
      DATA(CHS(1,I),I=5,6)/10.827421E-9,2.169746E-12/
      DATA(CL(I),I=1,4)/-35918.447,2.7637E2,-1.04505,2.70833E-3/
      DATA(CL(I),I=5,6)/-3.529E-6,1.874E-9/
      DATA(CHS(2,I),I=1,3)/-10.7339551e+3,34.367003,-9.730652e-3/
      DATA(CHS(2,I),I=4,6)/127.590017e-6,-102.032321e-9,26.5246267e-12/
      DATA(CHS(3,I),I=1,3)/-9.34681893e+3,37.9280236,-34.2048188e-3/
      DATA(CHS(3,I),I=4,6)/90.8152720e-6,-59.7451504e-9,13.8087718e-12/

      WRITE(*,*)'GIVE THE NUMBER OF STAGES'
      READ(*,*)NN
      WRITE(10,*)'NUMBER OF STAGES',NN
      WRITE(*,*)'GIVE THE TOTAL GAS FLOW RATE (MOLES/HR)'
      READ(*,*)GTF
      WRITE(10,*)'THE TOTAL FLOW RATE',GTF
      WRITE(*,*)'GIVE THE GAS PRESSURE (BAR)'
      READ(*,*)P(NN+1)
      WRITE(10,*)'GAS PRESSURE',P(NN+1)
      WRITE(*,*)'GIVE THE GAS TEMPERATURE (K)'
      READ(*,*)T(NN+1)
      WRITE(10,*)'GAS TEMPERATURE',T(NN+1)
      WRITE(*,*)'GIVE THE CONCENTRATION OF GAS IN FEED GAS'
      READ(*,*)Y(NN+1)
      WRITE(10,*)'GAS CONCENTRATION',Y(NN+1)
      WRITE(*,*)'GIVE THE FRACTION OF ETHANE AND METHANE RESPECTIVELY'
      CPC(1)=Y(NN+1)
      DO 239 I=2,3
      READ(*,*)CPC(I)
239   CONTINUE
      WRITE(*,*)'GIVE THE SOLVENT FLOW RATE (MOLES/HR)'
      READ(*,*)ELO
      WRITE(10,*)'SOLVENT FLOW RATE',ELO
      WRITE(*,*)'GIVE LIQUID TEMPERATURE (K)'
      READ(*,*)T(0)
      WRITE(10,*)'SOLVENT TEMP.',T(0)
      WRITE(*,*)'GIVE MOLARITY OF SOLUTION'
      READ(*,*)CM
      WRITE(*,*)'SOLVENT MOLARITY',CM
      WRITE(*,*)'GIVE THE FRACTION OF GAS IN LIQUID'
      READ(*,*)X(0)
      WRITE(10,*)'FRACTION OF GAS IN LIQUID',X(0)
      WRITE(*,*)'GIVE THE AVERAGE MOLECULAR WEIGHT OF THE SOLUTION'
      READ(*,*)FMOL
      WRITE(10,*)'AVERAGE MOLECULAR WEIGHT OF THE SOLUTION',FMOL
**********************************************************************
C     CALCULATION OF LIQUID AND GAS DENSITY
**********************************************************************
      TIN=T(0)
      CALL LIQDEN(TIN,DEN)
      CONCT=CM*FMOL*ELO/DEN
```

```
      AVGM=CPC(1)*34.04+CPC(2)*30.07+CPC(3)*16.04
      PIN=P(NN+1)*100
      CALL DENGM(CPC,TIN,PIN,DENMOL)
      DENG=DENMOL*AVGM
************************************************************************
C     CALCULATION OF ENTHALPY OF THE FEED GAS
************************************************************************
      GA1=GTF*CPC(2)
      GA2=GTF*CPC(3)
      CPP=0
      DO 33 J=1,6
      CPP=CPP+CL(J)*T(NN+1)**(J-1)
33    CONTINUE
      HIN=CPP
************************************************************************
C     CALLING THE SUBROUTINE FOR CALCULATION OF PRESSURE
************************************************************************
      P(NN+1)=P(NN+1)*100/1.333224E-1
      CALL PRESS(AVGM,GTF,DENG,DEN,PDROP)
      DO 1 I=NN,1,-1
      P(I)=P(I+1)-PDROP
1     CONTINUE
      VLIJ(NN+1)=Y(NN+1)*GTF
      CONSTV=(1.-Y(NN+1))*GTF
************************************************************************
C     ASSUMING THE TOTAL FLOW RATES OF THE GAS THROUGHOUT THE COLUMN
************************************************************************

      DVD=(VLIJ(NN+1)-0.1*VLIJ(NN+1))/FLOAT(NN)
      OUT=1
      IN=1

      GVIJ(NN+1,IN)=VLIJ(NN+1)

      DO 2 I=NN,1,-1

      GVIJ(I,IN)=GVIJ(I+1,IN)-DVD*FLOAT(I)/FLOAT(NN)

2     CONTINUE

      DELT=DHR*VLIJ(NN+1)/(FLOAT(NN)*74.46*ELO)

      TO(0,OUT)=T(0)
      TO(NN+1,OUT)=T(NN+1)
      DO 3 I=1,NN
      TO(I,OUT)=TO(I-1,OUT)+DELT*FLOAT(I)/FLOAT(NN)
3     CONTINUE

      LUT=0
      MUT=0
```

```
2000  OUT=OUT
1000  IN=IN

      TO(0,OUT)=TO(0,OUT)
      TO(NN+1,OUT)=TO(NN+1,OUT)

      DO 45 I=0,NN+1
      TD(I,OUT)=TO(I,OUT)/T(NN+1)
45    CONTINUE

      VG(NN+1,IN)=GTF
      EL(0,IN)=ELO
      GVIJ(NN+1,IN)=VLIJ(NN+1)
      ELIJ(0,IN)=ELO*X(0)

      DO 4 I=1,NN
      VG(I,IN)=CONSTV+GVIJ(I,IN)
4     CONTINUE

      EL(1,IN)=ELO+VG(2,IN)-VG(1,IN)

      DO 5 I=2,NN-1
      EL(I,IN)=VG(I+1,IN)-VG(I,IN)+EL(I-1,IN)
5     CONTINUE

      EL(NN,IN)=GTF-VG(NN,IN)+EL(NN-1,IN)

      CALL THER(NN,IN,OUT,TO,P,EL,VG,PK,A)

      DL(0,IN)=ELIJ(0,IN)/GTF

      DO 6 I=1,NN+1
      DV(I,IN)=GVIJ(I,IN)/GTF
6     CONTINUE

      CALL DLL(CONCT,DV,A,PK,GTF,NN,IN,OUT,DL)
      CALL THOMEL(CONCT,GTF,DV,NN,IN,OUT,A,PK,AA,BB,CC)
      CALL FUNC(DL,DV,NN,IN,DD)
      CALL THOMAS(AA,BB,CC,DD,IN,CHAG)
     IN=IN+1
    DO 8 I=1,NN
      AIT=CHAG(I,IN-1)
      IF((AIT.LT.0).AND.(ABS(AIT).GT.DV(I,IN-1)))THEN
      FACT=ABS(DV(I,IN-1)/CHAG(I,IN-1))*AIT
      ELSEIF((AIT.LE.0).AND.(ABS(AIT).LT.DV(I,IN-1)))THEN
      FACT=AIT
      ELSEIF(AIT.GT.0)THEN
      FACT=AIT
      ENDIF
```

```
        DGF(I)=FACT
8       CONTINUE

        DO 11 I=1,3
        CALL GAS(DGF,DV,I,NN,THETA,IN,DTV)
        DO 15 J=1,NN
15      CONTINUE

        CALL CALC(CONCT,DTV,A,PK,GTF,NN,I,OUT,GG)

11      CONTINUE

        CALL THET(GG,THETA,NN,THI)

        DO 17 I=1,NN
        CHK(I)=THI(I)*DGF(I)*GTF
        IF((CHK(I).LT.0).AND.(ABS(CHK(I)).LT.GVIJ(I,IN-1)))THEN
        THETAM=THI(I)

        ELSEIF((CHK(I).LT.0).AND.(ABS(CHK(I)).GT.GVIJ(I,IN-1)))THEN
        THETAM=1.

        ELSEIF(THI(I).GT.0)THEN
        THETAM=THI(I)

        ELSE
        THETAM=1.
        ENDIF
        GVIJ(I,IN)=GVIJ(I,IN-1)+THETAM*DGF(I)*GTF
17      CONTINUE

        DO 129 I=1,NN
        CONV(I)=ABS(CHAG(I,IN-1))
129     CONTINUE

        CONVOB=RCONV

        DO 281 I=1,NN
        IF(CONV(I).GT.CONVOB)THEN
        CONVOB=CONV(I)
        ELSE
        ENDIF
281     CONTINUE

        IF(CONVOB.GT.RCONV)THEN
        GOTO 1000

        ELSE
        ENDIF
```

```
      GVIJ(NN+1,IN)=GTF*Y(NN+1)

      DO 231 I=1,NN
      VG(I,IN)=CONSTV+GVIJ(I,IN)
231   CONTINUE
      EL(1,IN)=ELO+VG(2,IN)-VG(1,IN)

      DO 234 I=1,NN-1
      EL(I,IN)=VG(I+1,IN)-VG(I,IN)+EL(I-1,IN)
234   CONTINUE

      EL(NN,IN)=GTF-VG(NN,IN)+EL(NN-1,IN)

      DO 206 I=1,NN+1
      DV(I,IN)=GVIJ(I,IN)/GTF
206   CONTINUE

      CALL DLL(CONCT,DV,A,PK,GTF,NN,IN,OUT,DL)

      DO 256 I=1,NN
      ELIJ(I,IN)=DL(I,IN)*GTF
256   CONTINUE

      GVIJO(1,IN)=GVIJ(1,IN)
      ELIJ(0,IN)=ELO*X(0)
      GVJC(1,IN)=(GVIJ(NN+1,IN)+
     +ELIJ(0,IN))/(1+(ELIJ(NN,IN)/GVIJ(1,IN)))

      DO 264 I=1,NN
      GVIJ(I,IN)=(GVIJ(I,IN)/GVIJO(1,IN))*GVJC(1,IN)
      ELIJ(I,IN)=(ELIJ(I,IN)/GVIJO(1,IN))*GVJC(1,IN)
      VG(I,IN)=CONSTV+GVIJ(I,IN)
264   CONTINUE

      EL(1,IN)=ELO+VG(2,IN)-VG(1,IN)

      DO 415 I=2,NN-1
      EL(I,IN)=VG(I+1,IN)-VG(I,IN)+EL(I-1,IN)
415   CONTINUE

      EL(NN,IN)=GTF-VG(NN,IN)+EL(NN-1,IN)
      IF(LUT.EQ.1)THEN
      MUT=1
      ELSE
      MUT=0
      ENDIF
      DO 263 I=1,NN
      DL(I,IN)=ELIJ(I,IN)/GTF
      DV(I,IN)=GVIJ(I,IN)/GTF
```

```
263    CONTINUE

       DL(0,IN)=ELIJ(0,IN)/GTF

       CALL CLL(CONCT,DV,A,PK,GTF,NN,IN,OUT,CH)

       DO 363 I=1,NN
       GHG(I)=VG(I,IN)
363    CONTINUE

       CALL GCP(NN,GA1,GA2,DV,IN,GTF,GHG,CHS,CV)
       CALL ENTH(ELO,T,TD,VG,CV,CL,NN,IN,OUT,EL,CH,HIN,DHR,GH)
       CALL THOMENT(ELO,HIN,VG,EL,T,TD,CL,CV,IN,NN,OUT,AE,BE,CE)
       CALL THOMAS(AE,BE,CE,GH,OUT,CHAT)

       DO 125 I=1,NN
       CHAT(I,OUT)=CHAT(I,OUT)

125    CONTINUE
       DO 185 I=1,NN
       CONVT(I)=CHAT(I,OUT)
185    CONTINUE

       OUT=OUT+1
       CALL THETAE(ELO,T,TD,THETA,CHAT,VG,EL,CV,CL,CH,HIN,DHR,THE)

       DO 200 I=1,NN
       TO(I,OUT)=TO(I,OUT-1)+THE(I)*CHAT(I,OUT-1)*T(NN+1)
200    CONTINUE

       DO 77 I=1,NN
       GVIJ(I,1)=GVIJ(I,IN)
77     CONTINUE

       DO 127 I=1,NN
       CONVT(I)=ABS(CHAT(I,OUT-1))
127    CONTINUE

       CONVOBT=TCONV
       DO 128 I=1,NN

       IF(CONVT(I).GT.CONVOBT)THEN
       CONVOBT=CONVT(I)
       ELSE
       ENDIF
128    CONTINUE
       IF(CONVOBT.GT.TCONV)THEN
       IN=1
       T(NN+1)=T(NN+1)
```

```
      LUT=0
      GOTO 2000

      ELSE
      LUT=1
      IF(MUT.EQ.1)THEN
      GOTO 5000
      ELSE
      GOTO 1000
      ENDIF
      ENDIF
      CALL CLL(CONCT,DV,A,PK,GTF,NN,IN,OUT,CH)
5000  WRITE(11,*)'GVIJ'
      WRITE(12,*)'ELIJ'

      DO 210 I=NN,1,-1
      PH(I)=A(I,OUT-1)*DV(I,IN)*GTF
      WRITE(14,*)TO(I,OUT),GVIJ(I,IN)/VG(I,IN),ELIJ(I,IN)/EL(I,IN)
      WRITE(11,80)GVIJ(I,IN)/VG(I,IN)
      write(12,80)ELIJ(I,IN)/EL(I,IN)
      WRITE(14,*)VG(I,IN),EL(I,IN)
      write(*,80)P(I)
80    FORMAT(1X,F10.5)
210   CONTINUE
      STOP
      END
***************************************************************************
C     SUBROUTINE FOR CALCULATING THE PROPERTIES DEPENDENT ON TEMP.
***************************************************************************
      SUBROUTINE THER(NN,IN,OUT,TO,P,EL,GV,PK,A)
      REAL*8 TO,P,EL,GV,PK,A,TT,AK,AKL,AKK,AAA,XY,XX,H,XL,Z
      INTEGER NN,OUT,IN
      DIMENSION TT(800),XY(800),XX(800),H(800),AAA(800),P(800)
      DIMENSION AKK(800),XL(800),Z(800),AKL(800),AK(800)
      DIMENSION PK(800),A(800,800),TO(800,800),EL(800,800)
      DIMENSION GV(800,800)
      DO 1 I=1,NN
      TT(I)=(TO(I,OUT)-273.15)*9./5.+32.+459.69
      XY(I)=-((1.01898E11)/(TT(I)**3))+
     +((1.59734E13)/(TT(I)**4))
      XX(I)=104.518-((24.6254E4)/TT(I))+
     +((2.39029E8)/(TT(I)**2))+XY(I)
      H(I)=DEXP(XX(I))
      AAA(I)=-2.5510-(1.0174E4)/TT(I)
      AKK(I)=DEXP(AAA(I))
      XL(I)=(2.5551E11/(TT(I)**3))-(3.91757E13/(TT(I)**4))
      Z(I)=-304.689+(69.6979E4/(TT(I)))+
     +(-(6.31007E8/(TT(I)**2)))+XL(I)
      AKL(I)=DEXP(Z(I))
```

```
      AK(I)=H(I)/P(I)
      PK(I)=AKK(I)/AKL(I)
      A(I,OUT)= EL(I,IN)/(AK(I)*GV(I,IN))
1     CONTINUE

      RETURN
      END
************************************************************************
C     SUBROUTINE FOR CALCULATION OF ELEMENTS OF THOMAS ALGORITHM FOR
C     CALCULATING THE FLOW RATES
************************************************************************
      SUBROUTINE THOMEL(ELCON,GTF,GIJ,NN,IN,OUT,A,PK,AA,BB,CC)
      REAL*8 A,GIJ,PK,YY,GTF,AA,BB,CC,C,SA,SA1,SA2,ELCON
      INTEGER OUT
      DIMENSION A(800,800),GIJ(800,800),PK(800)
      DIMENSION AA(800,800),BB(800,800),CC(800,800)

       DO 1 I=1,NN
      DO 2 J=1,NN
      GTF=GTF
      IF(J.EQ.(I-1))THEN
      GOTO 5
      ELSEIF (J.EQ.I) THEN
      GOTO 6
      ELSEIF (J.EQ.(I+1))THEN
      GOTO 7
      ELSE
      GOTO 2
      ENDIF
5     GTF=GTF
      C=4*PK(J)*A(J,OUT)*ELCON/GTF+2*GIJ(I,IN)*(PK(J)*A(J,OUT))**2
      SA=(((4*ELCON/GTF)+
     +A(J,OUT)*PK(J)*GIJ(I,IN))*PK(J)*A(J,OUT)*GIJ(I,IN))**0.5
      AA(I,IN)=A(J,OUT)-PK(J)*A(J,OUT)*0.5+0.25*(1/(SA))*C
      GOTO 2
6     GTF=GTF
      C=4*ELCON*PK(J)*A(J,OUT)/GTF+2.*GIJ(I,IN)*(PK(J)*A(J,OUT))**2
      SA1=(4*ELCON/GTF)+A(J,OUT)*GIJ(I,IN)*PK(J)
      SA2=PK(J)*A(J,OUT)*GIJ(I,IN)
      SA=(SA1*SA2)**0.5
      YY=1+A(J,OUT)-PK(J)*A(J,OUT)*0.5+0.25*(1/(SA))*C
      BB(I,IN)=-YY
      GOTO 2
7     CC(I,IN)=1
      GOTO 2
2     CONTINUE
1     CONTINUE
      RETURN
      END
```

```
************************************************************************
C     SUBROUTINE FOR FUNCTION EVALUATION FOR FLOW RATE CALCULATION
************************************************************************
      SUBROUTINE FUNC(DL,DV,N,NOM,DD)
      REAL*8 DL,DV,DD
      DIMENSION DL(800,800),DV(800,800),DD(800,800)

      DO 1 I=1,N
      DD(I,NOM)=-(DV(I+1,NOM)+DL(I-1,NOM)-DV(I,NOM)-DL(I,NOM))
1     CONTINUE

      RETURN
      END
************************************************************************
C     SUBROUTINE FOR TRIDIAGONAL MATRIX CALCULATIONS (THOMAS ALGORITHM)
************************************************************************
      SUBROUTINE THOMAS(ATH,BTH,CTH,DTH,K,THC)
      COMMON NN
      REAL*8 ATH,BTH,CTH,DTH,PTH,QTH,THC

      DIMENSION ATH(800,800),BTH(800,800),CTH(800,800)
      DIMENSION PTH(800),QTH(800),THC(800,800),DTH(800,800)

      PTH(1)=BTH(1,K)

      DO 7 I=2,NN
      PTH(I)=BTH(I,K)-(ATH(I,K)*CTH(I-1,K)/PTH(I-1))
7     CONTINUE

      QTH(1)=DTH(1,K)/BTH(1,K)
      DO 8 I=2,NN
      QTH(I)=(DTH(I,K)-(ATH(I,K)*QTH(I-1)))/PTH(I)
8     CONTINUE
      THC(NN,K)=QTH(NN)
      DO 9 I=NN-1,1,-1
      THC(I,K)=QTH(I)-CTH(I,K)*THC(I+1,K)/PTH(I)
9     CONTINUE
      RETURN
      END
************************************************************************
C     SUBROUTINE FOR CALCULATION OF DIMENTIONLESS LIQUID COMP FLOW RATE
************************************************************************
      SUBROUTINE DLL(ELCON,DGV,A,PK,GTF,NM,NUM,MUM,DTTL)
      REAL*8 DGV,A,PK,GTF,DTTL,ELCON
      DIMENSION PK(800),A(800,800),DGV(800,800),DTTL(800,800)
      DO 2 I=1,NM
      DTTL1=A(I,MUM)*DGV(I,NUM)
      DTTL2=-PK(I)*A(I,MUM)*DGV(I,NUM)*0.5+0.5*((4*ELCON/GTF+
     +A(I,MUM)*DGV(I,NUM))*PK(I)*A(I,MUM)*DGV(I,NUM))**0.5
```

```
      DTTL(I,NUM)=DTTL1+DTTL2

2     CONTINUE
      RETURN
      END
**********************************************************************
C     THESE ARE SUBROUTINES FOR GETTING THE OPTIMUM VALUE OF FACTOR
**********************************************************************
C     SUBROUTINE GAS SOLVES THE GAS COMP. FLOW RATE FOR THREE VALUES
C     THETA I.E. 1,0.5 AND 0.01, SUCCESSIVELY
**********************************************************************
      SUBROUTINE GAS(DGF,DV,NUMB,NN,THETA,IN,DTV)
      REAL*8 DGF,DV,DTV
      DIMENSION DGF(800),DV(800,800),DTV(800,800),THETA(800)

      DO 2 I=1,NN
      DTV(I,NUMB)=DV(I,IN-1)+DGF(I)*THETA(NUMB)
2     CONTINUE

      RETURN
      END
**********************************************************************
C     SUBROUTINE SOLVES TO GIVE THE FUNCTION VALUE SQUARED
**********************************************************************
      SUBROUTINE CALC(ELCON,DTV,A,PK,GTF,NN,NUM,OUT,GG)
      INTEGER OUT
      REAL*8 DTV,A,PK,GG,DTL,GTF,FF,ELCON
      DIMENSION DTV(800,800),A(800,800),PK(800),GG(800,800)
      DIMENSION FF(800,800),DTL(800,800)

      CALL DLL(ELCON,DTV,A,PK,GTF,NN,NUM,OUT,DTL)
      CALL FUNC(DTL,DTV,NN,NUM,FF)
      DO 1 I=1,NN
      GG(I,NUM)=ABS(FF(I,NUM))**2
1     CONTINUE
      RETURN
      END
**********************************************************************
C     SUBROUTINE GIVING THE OPTIMUM VALUE OF THETA BY FITTING A
C     QUADRATIC TO THE VALUES OF FUNCTION CORRESPONDING TO
C     THETA 1,0.5 & 0.01
**********************************************************************
      SUBROUTINE THET(GG,THT,NN,THI)
      REAL*8 GG,THTAA,THTB,THTA
      DIMENSION GG(800,800),THT(800),THI(800)
      DO 2 I=1,NN
      IF((GG(I,2).LT.GG(I,1)).AND.(GG(I,2).LT.GG(I,3)))THEN
      THTAA=(THT(1)-THT(2))
```

```
      THTAB=(GG(I,2)-GG(I,3))-(THT(2)-THT(3))*(GG(I,1)-GG(I,2))*THTAA
      THTA=THTAB/((THT(2)-THT(3))*(THT(1)-THT(2))*(THT(3)-THT(1)))
      THTB=(GG(I,1)-GG(I,2)-THTA*(THT(1)**2-THT(2)**2))/(THT(1)-THT(2))
      THI(I)=-THTB/(2*THTA)

      ELSEIF((GG(I,1).LT.GG(I,2)).AND.(GG(I,1).LT.GG(I,3)))THEN
      THI(I)=THT(1)
      ELSEIF((GG(I,3).LT.GG(I,1)).AND.(GG(I,3).LT.GG(I,2)))THEN
      THI(I)=THT(3)
      ELSE
      THI(I)=1
      ENDIF

2     CONTINUE

      RETURN
      END
***********************************************************************
C     SUBROUTINE FOR CALCULATION OF ENTHALPY BALANCE FUNCTION
***********************************************************************
      SUBROUTINE ENTH(ELO,TI,TD,VG,CV,CL,NN,IN,OUT,EL,CH,HIN,DHR,GH)

      INTEGER OUT
      REAL*8 TD,GH,EL,HL,HV,GHH,GHL,CH,TI,VG,DHR,ELO,CTC
      REAL CV,CL
      DIMENSION TD(800,800),VG(800,800),GH(800,800),CL(6)
      DIMENSION HV(800),HL(800),EL(800,800),CV(6,800),GHH(800)
      DIMENSION TI(800),CH(800,800),GHL(800)

      CTC=TI(NN+1)

      DO 2 I=1,NN
      HV(I)=0
      HL(I)=0
      DO 3 J=1,6
      HV(I)=CV(J,I)*(TI(NN+1)**(J-1))*(TD(I,OUT)**(J-1))/HIN+HV(I)
      HL(I)=CL(J)*(TI(NN+1)**(J-1))*(TD(I,OUT)**(J-1))/HIN+HL(I)
3     CONTINUE
2     CONTINUE

      DO 1 I=1,NN
      GHH(I)=VG(I+1,IN)*HV(I+1)+DHR*CH(I,IN)/HIN+
     +EL(I-1,IN)*HL(I-1)-VG(I,IN)*HV(I)
      GHL(I)=-HL(I)*(-VG(I,IN)+VG(I+1,IN)+EL(I-1,IN))
      GH(I,OUT)=-(GHH(I)+GHL(I))/ELO
1     CONTINUE

      RETURN
      END
```

```
************************************************************************
C     SUBROUTINE FOR CALCULATION OF THOMAS ALGORITHM ELEMENTS FOR
C     ENTHALPY BALANCE
************************************************************************
      SUBROUTINE THOMENT(ELO,HIN,VG,EL,T,TD,CL,CV,IN,NN,OUT,AE,BE,CE)
      INTEGER OUT
      REAL*8 VG,EL,TD,AE,BE,CE,PDH,PDV,VL,T,ELO
      REAL CV,CL
      DIMENSION VG(800,800),EL(800,800),TD(800,800),CL(6)
      DIMENSION CV(6,800),AE(800,800),BE(800,800),CE(800,800)
      DIMENSION T(800)
      DO 1 I=1,NN
      DO 2 J=1,NN
      IF(J.EQ.I-1)THEN
      GOTO 3
      ELSEIF(J.EQ.I)THEN
      GOTO 4
      ELSEIF(J.EQ.I+1)THEN
      GOTO 5
      ENDIF
3     PDH=0

      DO 7 K=0,4
      PDH=PDH+(CL(K+2)*(TD(J,OUT)**K)*(K+1))*(T(NN+1)**(K+2))/HIN
7     CONTINUE
      AE(I,OUT)=EL(J,IN)*PDH/ELO
      GOTO 2
4     VL=(VG(I,IN)-VG(I+1,IN)-EL(I-1,IN))/ELO
      PDH=0
      PDV=0
      DO 8 K=0,4
      PDH=PDH+(CL(K+2)*(TD(J,OUT)**K)*(K+1))*(T(NN+1)**(K+2))/HIN
      PDV=PDV+(CV(K+2,I)*(TD(J,OUT)**K)*(K+1))*(T(NN+1)**(K+2))/HIN
8     CONTINUE

      BE(I,OUT)=VL*PDH-VG(J,OUT)*PDV/ELO
      GOTO 2
5     PDV=0

      DO 9 K=0,4
      PDV=PDV+(CV(K+2,I)*(TD(J,OUT)**K)*(K+1))*(T(NN+1)**(K+2))/HIN
9     CONTINUE
      CE(I,OUT)=VG(J,IN)*PDV/ELO
      GOTO 2
2     CONTINUE
1     CONTINUE
      RETURN
      END
```

```
*************************************************************************
C     SUBROUTINE FOR CALCULATION OF CHEMICALLY ABSORBED GAS
*************************************************************************
      SUBROUTINE CLL(ELCON,DG,A,PK,GTF,NM,NU,MU,CH)
      REAL*8 DG,A,PK,GTF,CH,ELCON
      DIMENSION PK(800),A(800,800),DG(800,800),CH(800,800)

      DO 2 I=1,NM

      CH(I,NU)=-0.5*DG(I,NU)*PK(I)*A(I,MU)+0.5*((4*ELCON/GTF+
     +A(I,NU)*PK(I)*DG(I,NU))*PK(I)*A(I,MU)*DG(I,NU))**0.5
2     CONTINUE

      RETURN
      END
*************************************************************************
C     SUBROUTINE FOR OPTIMUM VALUE OF THETA FOR TEMPETRATURE CHANGE
*************************************************************************
      SUBROUTINE THETAE(ELO,T,TD,THETA,CHAT,VG,EL,CV,CL,CH,HIN,DHR,THE)
      INTEGER OUT
      COMMON NN,IN,OUT
      REAL*8 TD,CHAT,CH,VG,EL,TTD,DHR,T,GGH,GGL,ELO
      DIMENSION TD(800,800),THETA(3),CHAT(800),CH(800,800)
      DIMENSION VG(800,800),EL(800,800),THE(800),CL(800)
      DIMENSION TTD(800,800),GGL(800,800),GGH(800,800)
      DIMENSION T(1000)

      DO 1 I=1,NN
      DO 2 J=1,3
      TTD(I,J)=TD(I,OUT-1)+THETA(J)*CHAT(I)
2     CONTINUE
1     CONTINUE
      DO 3 J=1,3
      CALL ENTH(ELO,T,TTD,VG,CV,CL,NN,IN,J,EL,CH,HIN,DHR,GGL)
      GGH(I,J)=GGL(I,J)**2
3     CONTINUE
      CALL THET(GGH,THETA,NN,THE)
      RETURN
      END

*************************************************************************
C     SUBROUTINE FOR CALCULATION OF THE GAS ENTHALPY COEFFICIENTS
C     COMPRESSIBILITY FACTOR METHOD PERRY'S HANDBOOK 7TH EDN.
*************************************************************************
      SUBROUTINE GCP(NN,GA1,GA2,DV,IN,GTF,GVGG,CHS,CV)
      REAL*8 DV,GTF,GVGG
      DIMENSION DV(1000,1000),GVGG(1000),CV(6,800)
      DIMENSION CHS(3,6)
```

```
      DO 4 K=1,NN
      DO 31 I=1,6
      CV(I,K)=CHS(1,I)*DV(K,IN)*GTF/GVGG(K)+CHS(2,I)*GA1/GVGG(K)+
     +CHS(3,I)*GA2/GVGG(K)
31    CONTINUE
4     CONTINUE
      RETURN
      END
***********************************************************************
C     SUBROUTINE FOR CALCULATION OF LIQUID DENSITY
C     TAKEN FROM PERRY'S HANDBOOK 7TH EDN.
***********************************************************************
      SUBROUTINE LIQDEN(T,DEN)
      REAL*8 DEN
      C1=5.459
      C2=0.30542
      C3=647.13
      C4=0.081

      DEN=18*C1/C2**(1+(1-T/C3)**C4)

      RETURN
      END
***********************************************************************
C     SUBROUTINE FOR PRESSURE DROP CALCULATION
C     DPD'S ARE THE DRY TRAY PRESSURE DROP
C     WL IS THE WEIR LENGTH (mm)
C     WH IS THE WEIR HEIGHT (mm)
C     VFR IS THE VOLUMETRIC FLOW RATE OF THE LIQUID (l/hr)
C     VH IS THE HOLE VELOCITY (ft/s)
C     PRESSD IS THE PRESSURE DROP (mm Hg)
C     DENG AND DENL ARE THE DENSITY OF GAS AND LIQUID (kg/m3)
C     AH IS THE HOLE AREA
C     VFR IS THE GAS FLOW RATE (m3/hr)
C     NU IS THE NUMBER OF VALVES PER TRAY
***********************************************************************
      SUBROUTINE PRESS(AVGM,GTF,DENG,DENL,PRESSD)
      REAL*8 DENL,GTF,k1,k2

      WRITE(*,*)'GIVE THE NUMBER OF VALVE UNITS'
      READ(*,*)NU
      WRITE(*,*)'GIVE THE METAL THICKNESS (mm)'
      READ(*,*)TM
      TM=TM/25.4
      WRITE(*,*)'GIVE THE VALVE METAL DENSITY (Kg/m3)'
      READ(*,*)DENM
      WRITE(*,*)'GIVE THE BALLAST TRAY PRESSURE DROP COEFFICIENTS'
      WRITE(*,*)'GIVE K1'
      READ(*,*)K1
```

```
      WRITE(*,*)'GIVE K2'
      READ(*,*)K2
      WRITE(*,*)'GIVE THE WEIR LENGTH (mm)'
      READ(*,*)WL
      WL=WL/25.4
      WRITE(*,*)'GIVE THE WEIR HEIGHT (mm)'
      READ(*,*)WH
      WH=WH/25.4
      VFR=GTF*AVGM/(DENG*2.271247E-1)
      AH=NU/78.5
      VH=GTF*AVGM*35.315/(DENG*3600)
      DPD1=1.35*TM*DENM/DENL+K1*(VH**2)*DENG/DENL
      DPD2=K2*(VH**2)*DENG/DENL
      IF(DPD1.GT.DPD2)THEN
      DPD=DPD1
      ELSE
      DPD=DPD2
      ENDIF
      PRESSD=(DPD+0.4*(VFR/WL)**(2/3)+0.4*WH)*DENL/(33.3*1.601846E1)
      RETURN
      END
************************************************************************
C     SUBROUTINE FOR THE CALCULATION OF GAS DENSITY
************************************************************************
      SUBROUTINE DENGM(CPC,T,P,DENMOL)
      DIMENSION PCC(3),TCC(3),OHMC(3),CPC(3)
      DATA(PCC(I),I=1,3)/9.00E3,4.85E3,4.59E3/
      DATA(TCC(I),I=1,3)/373.53,305.32,190.564/
      DATA(OHMC(I),I=1,3)/0.096,0.098,0.011/
      R=8.314
      PC=0
      TC=0
      OHM=0
      DO 1 I=1,3
      PC=CPC(I)*PCC(I)+PC
      TC=CPC(I)*TCC(I)+TC
      OHM=CPC(I)*OHMC(I)+OHM
1     CONTINUE
      TR=T/TC
      PR=P/PC
      B0=0.1445-(0.330/TR)-(0.1385/TR**2)-(0.0121/TR**3)-
     +(0.000607/TR**5)
      B1=0.0637+(0.0331/TR**2)-(0.423/TR**3)-(0.008/TR**8)
      B=(B0+OHM*B1)*8.3140*TC/PC
      GMV=(R*T+SQRT((R*T)**2+4*P*R*T*B))/(2*P)
      DENMOL=1/GMV
      RETURN
      END
```

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ERRATA FOR EQUATIONS

Equations	To be read as	Page
Eq. 3.24	a_s to be read as a_p	31
Eq. 4.1	$f_j=l_{j-1}-v_j-l_j+v_{j+1}$	34
Eq. 4.2	$g'=v_j+l_j$	34
Eq. 4.11	$e(T_{j-1})=L_{j-1}h_{j-1}$ $e'(T_j)=-V_jH_j-L_jh_j$ $e''(T_{j+1})=V_{j+1}H_{j+1}$	36
Eq. 4.16	$L_{j-1}-V_j-L_j+V_{j+1}=0$	37
Eq. 4.21	$l_{j,c}=\left(\dfrac{l_j}{v_1}\right)_{ca}v_{1,c}$	39
Eq. 4.22	$v_{j,c}=\left(\dfrac{v_j}{v_1}\right)_{ca}v_{1,c}$	39

ERRATA

Page 30 paragraph 5:

Thus making a set of 5N equations which are to be solved to determine the component flow rates (2N), total flow rates (2N), temperature profiles (N), thus 5N variables.

The degree of freedom for this system is zero (5N-5N=0), thus the system is completely defined. The column pressure is estimated from the tray hydraulics and other tray properties using empirical equations for calculation of pressure drop. The average pressure drop per stage is calculated based on the average properties of liquid and gas.

Page 39 Step-6 after equation 4.22 to be added:

If the convergence criterion for the component flow rates is not achieved then the corrected component flow rates calculated above are taken for further calculations and the calculations steps are restarted from step-3 till the required convergence criterion is achieved.

Page 40 paragraph 2:

If the required convergence is reached then the iterations are stopped here, but if the required convergence criteria are not achieved all steps from step-2 are repeated for the new set of temperatures throughout the column.