

DESIGN OF ETHANOLAMINE SWEETENING PROCESSES
USING A REACTION EQUILIBRIUM MODEL

By

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
December, 1980

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**Dedicated to my parents,
JERONIMO and CRISTALINA VAZ**

PREFACE

A correlation model based on chemical reaction equilibrium of an Ethanolamine-H₂S-CO₂-Water mixture is devised to predict the vapor liquid equilibrium behavior of this system. Only two equilibrium constants are required to be defined for each amine. The model performs better than any existing in the literature. Using this model algorithms were developed for the process design of major pieces of equipment in an ethanolamine sweetening unit. A computer program based on these algorithms was written and tested with operating data. Several sets of literature and design data were also examined. The agreement is satisfactory considering the several simplifying assumptions that were required to be made. The simulation model provides a powerful tool for studying ethanolamine sweetening systems.

I am deeply indebted to my thesis adviser, Prof. Robert N. Maddox, for his intelligent guidance, inspirational dedication to research, cooperation and great human understanding and for the excellent art of developing even the hidden talents of his graduate students. Without his encouragement this work may not be in the present form.

My sincere thanks are due to my Advisory Committee members Professors John H. Erbar, Kenneth J. Bell and Gilbert

J. Mains. Their assistance and advisement is appreciated. The help provided by all faculty and staff of the School of Chemical Engineering is also acknowledged.

Financial support from the School of Chemical Engineering and Fluid Properties Research Inc. (FPRI) is gratefully received.

Working with people like Dr. C. B. Panchal and Dr. Mushtaque Ahmed was a great experience. My special thanks are due to Mr. Suresh Balakrishnan for all his help. The companionship of my cousins Loretta, Mona, and Kipoli Furtado during the tiresome hours of writing this dissertation is highly appreciated.

Finally, I express my deepest gratitude to my brothers, sisters and all family members and friends for their constant support and sacrifices in making this achievement a reality. Mr. Avertano Furtado and Mr. Rosario Furtado were partly responsible for my higher education in this country and a special "thank you" is due to them. My parents deserve special thanks for without their encouragement and sacrifice this graduate study would not have been possible.

NOTE: This manuscript was prepared using a Computer Text Formatting Program called "SCRIPT" developed at the University of Waterloo, Waterloo, Canada in September 1978 and "OSUPUB", a special edition of the above developed at Oklahoma State University in April 1979. Thanks are due to Mr. John Sherblom of the University Computer Center for his assistance in formatting this dissertation.

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NOMENCLATURE

H, H'	Henry's Law constant
H''	inverse Henry's Law constant
$K1.....K7$	pseudo-equilibrium constants in present model
$K1'.....K7'$	pseudo-equilibrium constants in Kent and Eisenberg model
$K1''.....K7''$	equilibrium constants in Klyamer et al. model
m, M	molality of ethanolamine
$pCO_2, ppCO_2$	partial pressure of CO_2 , mm Hg
pH_2S, ppH_2S	partial pressure of H_2S , mm Hg
P	total pressure, mm Hg
z	carbamate ion concentration, (RR^+NCOC^-)
γ_w	activity coefficient of water
α	CO_2 loading in amine, (mol CO_2 /mol amine)
β	H_2S loading in amine, (mol H_2S /mol amine)
γ	activity coefficient of an ion
a	ratio between the activity of un-ionized ethanolamine and the activity of water
T_A	temperature of amine (absorber)
T_g	temperature of gas (absorber)
T_n	temperature of stage 'n' in regenerator

L	moles CO ₂ in liquid phase/mole amine entering regenerator
V	moles CO ₂ in vapor phase/mole amine entering regenerator
L	moles H ₂ S in liquid phase/mole amine entering regenerator
V	moles H ₂ S in vapor phase/mole amine entering regenerator
S	moles steam/mole amine entering regenerator
A _w	moles water entering/mole amine entering regenerator
W	moles water returned from condenser/ mole amine entering regenerator
C _p	heat capacity
ΔH _r	total heat of absorption
C _r	amine circulation rate (moles amine/total moles gas in)
MEA	monoethanolamine
DEA	diethanolamine
DIPA	diisopropanolamine
DGA	diglycolamine
APM	Amine Process Model
Y _{CO2}	mole fraction CO ₂ (absorber)
Y _{H2S}	mole fraction H ₂ S (absorber)
x _{H2O}	liquid phase mole fraction of water
p [*] H _{2O}	vapor pressure of water (stripper)

Y_A mole fraction acid gas (absorber)

Subscripts

i represents stream entering the
stage (in absorber)

i_n represents stream entering the absorber

o represents stream leaving the
stage (in absorber)

out represents stream leaving the absorber

n refers to stream leaving stage 'n'
in stripper

n-1 refers to stream entering stage 'n'
in stripper

w.v. refers to water vapor

A_m refers to an ethanolamine

w refers to water

CHAPTER I

INTRODUCTION

The alkanolamines are the most generally accepted and widely used of the many available solvents for the removal of hydrogen sulfide and carbon dioxide from natural and manufactured gas streams. Their introduction into the gas sweetening industry is credited to Bottoms (1) who obtained a patent in 1930 covering their use for sweetening natural gas. The main reason for the popularity of these solvents, especially monoethanolamine (MEA) and diethanolamine (DEA), is their reactivity. Also, these solvents are available at a comparatively low cost.

Several amine sweetening processes have been described in detail (11,29) but for improved equipment design, better knowledge of the equilibrium between the acid gases and ethanolamine solutions is required.

Several investigators have measured hydrogen sulfide and carbon dioxide solubility in ethanolamine solutions. Much of this experimental work, however, has limited utility for design because the concentration and temperature ranges of the data are too narrow, the data are not consistent with other independent work and/or the data are for only hydrogen

sulfide or only carbon dioxide, but not for mixtures of the two acid gases. The engineer is often at a loss as to a way to proceed in estimating Ethanolamine-acid gas equilibrium and required amine feed solution to be circulated to treat a given feed gas. Stringent limits on allowable emissions of hydrogen sulfide are now commonly enforced. The pollution abatement equipment designer finds only severely limited information at the very low loadings encountered at the top of a contactor.

The traditional approach of using mass transfer coefficients to design H₂S-CO₂-Ethanolamine absorption systems met with limited success. This is not surprising since amines are known to react chemically with H₂S and CO₂. The equilibrium solubility of either acid gas is a function of temperature, hydrogen sulfide and carbon dioxide partial pressures in the vapor phase, amine type, and amine concentration in the liquid phase. The interactive relationships between these variables would be very difficult to describe through a simple mass transfer coefficient.

In an effort to describe the vapor-liquid equilibrium of an Ethanolamine-H₂S-CO₂-water system some models have been proposed in the last five years (13,14,16). One of the objectives of this work is to examine some of the models which use chemical reaction equilibrium as a means of predicting vapor-liquid equilibrium data for ethanolamine solutions. An alternate model was developed and tested for

selected amines viz. monoethanolamine(MEA), diethanolamine (DEA), di-isopropanolamine(DIPA), and diglycolamine(DGA). The range of applicability of the Kent-Eisenberg model (16) was increased to cover other amines and concentration ranges than those covered by the original authors.

The design of most amine sweetening systems in use today is based on "rules of thumb" and the experience of the designer, often resulting in gross over design. The present day price of energy and the associated operating expenses have put pressure on designers to improve the economics of acid-gas treatment plants. Improved design procedures are seen as a big step toward alleviating these needs. To provide a step in this direction the reaction equilibrium correlation models were used to develop a process design scheme for conventional gas sweetening units shown in Figures 1 and 2. A versatile computer program was developed to make the necessary heat and material balances. The program provides a quick method to evaluate the design and operation of a gas sweetening unit. The computer program uses a rigorous calculation technique and converges all trial and error calculation to within 0.05 percent or less.

Obviously, the objective here was also to provide an adequate tool for studying other problems related to the gas sweetening area. Predicting steam consumption in regenerators, hydrogen sulfide selectivity of various ethanolamines and acid gas retention in lean amines are some of the typical problems that can be solved.

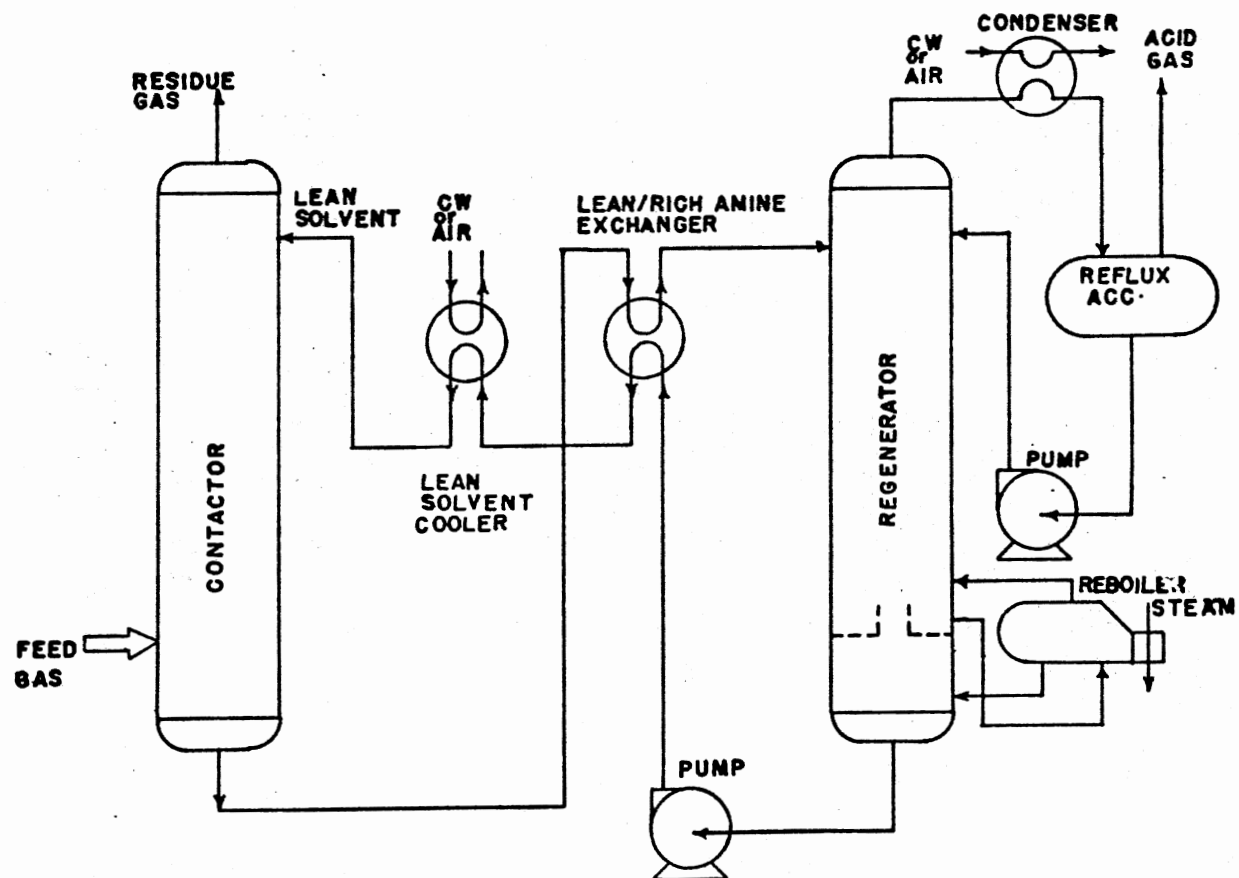


Figure 1. Flow Diagram of Basic Amine Process

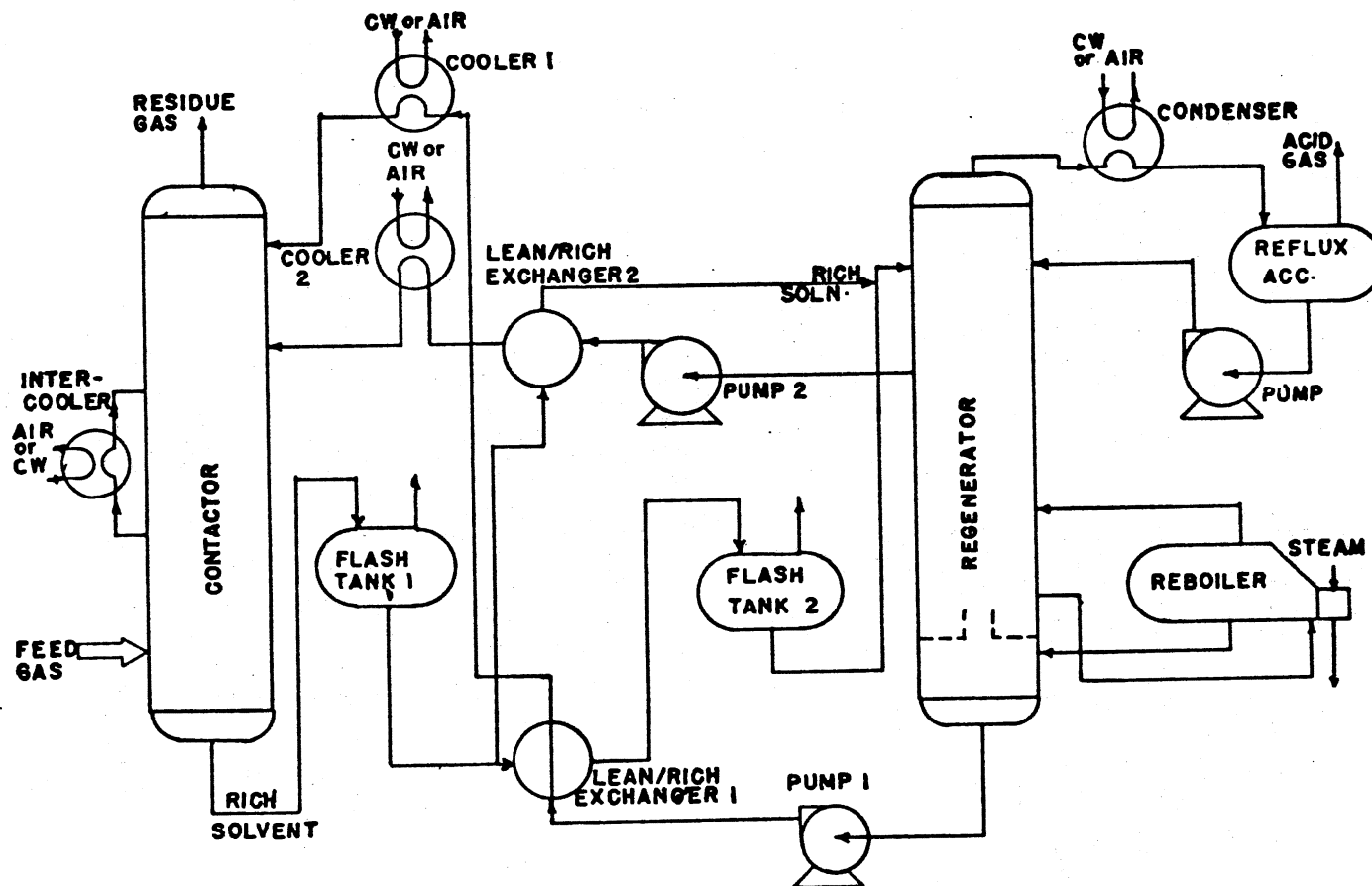


Figure 2. Split Stream Amine Process

CHAPTER II

LITERATURE REVIEW

Determination of the solubility of carbon dioxide and hydrogen sulfide have been made by several investigators (2,4,5,7,12,33). However these do not cover the wide range of temperatures and amine concentrations encountered in industrial process units. The data for low acid gas loadings (less than 0.1 mole H₂S/mole amine) and low acid gas partial pressures (less than 1 mm Hg, H₂S) are meager. In order to extrapolate outside the range of existing data, a number of workers have attempted to correlate and predict the partial pressures of the acid gases above ethanolamine solutions.

Most of these attempts postulate that certain reactions occur in solution and propose a thermodynamic model for the reaction equilibrium. Atwood et al. (6) attempted to model the H₂S-H₂O-ethanolamine system while Danckwerts and McNeill (9) considered the equilibrium of the CO₂-H₂S-ethanolamine solutions. Danckwerts and McNeill (9) show that the vapor pressure of the acid gas species is related to the free acid gas concentration in the liquid phase by a Henry's Law relationship, and the free acid gas concentration, in turn, is determined by liquid phase ionic equilibrium. However, there

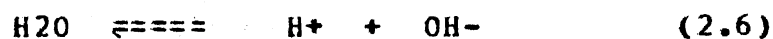
is substantial lack of agreement between the predicted vapor pressures and the experimental data. A possible reason may be the nonidealities introduced by the many ionic species in solution. This approach was modified by Klyamer (13) and Klyamer and Koleshnikova (14) for the H₂S-ethanolamine solution and the CO₂-ethanolamine solutions respectively.

Recently, Klyamer et al. (15) extended their model to the CO₂-H₂S-H₂O-ethanolamine system. They obtained equations relating the partial pressures of the acid gases to the composition of the solutions and the temperature. In modifying the Danckwerts-McNeill approach, Kent and Eisenberg (16) forced the amine equilibrium constants to fit published partial pressure data for the H₂S/Amine and CO₂/Amine system. They used these constants to predict the equilibrium for the H₂S-CO₂-Amine-H₂O systems. Both these models are relatively inaccessible. Also, they represent a new area to many process engineers because they involve several equilibrium equations, usually non-linear, which are to be solved simultaneously by algebraic reduction or some other numerical technique. These last two models will be briefly discussed.

Klyamer et al. Model

Klyamer et al. (13,14) postulated that the following reactions occur in solution:





Here $RR'NH$ represents an amine. The following charge and mass balances can be written for the reacting species:

Charge balance:

$$[RR'NH_2^+] + [H^+] = [HCO_3^-] + [RR'NCOO^-] + 2[CO_3^{2-}] + [OH^-] + [HS^-] + 2[S^{2-}] \quad (2.8)$$

Mass balances are written for each of the constituents involved in the reacting system. Mass balances for the ethanolamine, hydrogen sulfide and carbon dioxide are as follows:

$$[RR'NH] + [RR'NCOO^-] + [RR'NH_2^+] = M \quad (2.9)$$

$$[H_2S] + [HS^-] + [S^{2-}] = \beta M \quad (2.10)$$

$$[CO_2] + [RR^{\circ}NCOO^-] + [HCO_3^-] + [CO_3^{=}] = \alpha M \quad (2.11)$$

The partial pressure of CO_2 and H_2S in the gas phase can be related to the liquid phase composition through Henry's Law:

$$H^{CO_2} = [CO_2]/p_{CO_2} \quad (2.12)$$

$$H^{H_2S} = [H_2S]/p_{H_2S} \quad (2.13)$$

In concentration units, the following thermodynamic equilibrium constants can be defined.

$$K1'' = (\gamma^2/a\gamma_w^2)([RR^{\circ}NH_2+][OH^-]/[RR^{\circ}NH]) \quad (2.14)$$

$$K2'' = (\gamma^2/a^2\gamma_w^2)([RR^{\circ}NH_2+][RR^{\circ}NCOO^-]/[RR^{\circ}NH]^2 p_{CO_2}) \quad (2.15)$$

$$K3'' = (\gamma^2/\gamma_w)[H+][HCO_3^-]/[CO_2] \quad (2.16)$$

$$K4'' = \gamma[H+][CO_3^{=}]/[HCO_3^-] \quad (2.17)$$

$$K5'' = \gamma^2[H+][HS^-]/[H_2S] \quad (2.18)$$

$$K6'' = \gamma^2[H+][OH^-]/\gamma_w \quad (2.19)$$

$$K7'' = \gamma[H+][S^{=}]/[HS^-] \quad (2.20)$$

The equilibrium constants of the reactions, the inverse Henry's law constants and the average ion activity coefficient, which is dependent upon the ion concentration, must be known in order to determine the concentration of the thirteen species in solution.

The final expressions used for prediction of the partial pressures of the acid gases above ethanolamine solutions are given by

$$p_{CO_2} = (1/K_2'') \left(\gamma^2 / (a^2 \gamma_{\omega}^2) \right) \left(z(A'' + B'') / (m - z - A'' - B'')^2 \right) \quad (2.21)$$

$$p_{H_2S} = (K_6'' / (K_1'' K_5'' H'' H_2S)) \left(\gamma^2 / (a \gamma_{\omega}) \right) \left(A''(A'' + B'') / (m - z - A'' - B'') \right) \quad (2.22)$$

and,

$$A'' = m - z - B'' - (K_1'' K_3'' H'' CO_2 / (K_2'' K_6'')) \left(z / (a(B'' - z)) \right) \left(z / (a(B'' - z)) \right) \quad (2.23)$$

where,

$$B'' = m \alpha - H'' CO_2 p_{CO_2}$$

$$A'' = m \beta - H'' H_2S p_{H_2S}$$

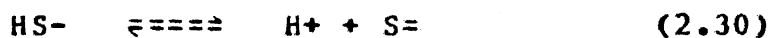
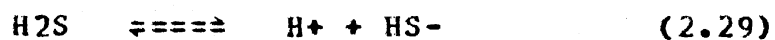
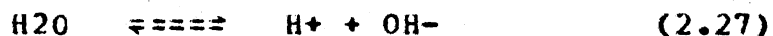
and,

$$z = [RR^+ NCOO^-]$$

Equations (2.21) to (2.23), which contain three unknowns, p_{H_2S} , p_{CO_2} , and z were solved by a numerical procedure like the Newton Raphson method.

Kent and Eisenberg Model

Kent and Eisenberg (16,17) described the H₂S-CO₂-Amine System equilibrium with the following equations:



Again, the equilibrium partial pressures of CO₂ and H₂S were related to the free concentrations of CO₂ and H₂S in solution by the Henry's Law relationship as follows:

$$p_{CO_2} = H^{CO_2}[CO_2] \quad (2.31)$$

$$p_{H_2S} = H^{H_2S}[H_2S] \quad (2.32)$$

The mass and charge balance equations are identical to those used by Kiyamer et al. (13). Instead of using ionic characterization factors as recommended by Danckwerts, Kent and Eisenberg used the following expressions for pseudo-equilibrium constants:

$$K1^{\circ} = [H^{+}][RR^{\circ}NH]/[RR^{\circ}NH_2^{+}] \quad (2.33)$$

$$K2^{\circ} = [HCO_3^{-}][RR^{\circ}NH]/[RR^{\circ}NCOO^{-}] \quad (2.34)$$

$$K3^{\circ} = [H^{+}][HCO_3^{-}]/[CO_2] \quad (2.35)$$

$$K4^{\circ} = [H^{+}][OH^{-}] \quad (2.36)$$

$$K5^{\circ} = [H^{+}][CO_2]/[HCO_3^{-}] \quad (2.37)$$

$$K6^{\circ} = [H^{+}][HS^{-}]/[H_2S] \quad (2.38)$$

$$K7^{\circ} = [H^{+}][S^{2-}]/[HS^{-}] \quad (2.39)$$

The thirteen equations, including the four balance equations are solved to obtain the partial pressures of H_2S and CO_2 over solutions at a given composition and a particular temperature. Any standard computational technique may be used to solve the resulting set of non-linear equations. A simpler method is to reduce the equations through suitable

algebraic manipulation. The set of three expressions which result are as follows:

$$pH_2S = \{H \cdot H_2S / (K_6 \cdot K_7)\} \{A[H+]^2 / (1 + [H+] / K_7)\} \quad (2.40)$$

$$pCO_2 = \{H \cdot CO_2 / (K_3 \cdot K_5)\} \{B[H+]^2 / (1 + [H+] / K_5 + M[H+] / (K_2 \cdot K_5 \cdot C))\} \quad (2.41)$$

and,

$$\begin{aligned} [H+] = & A \{1 + K_7 / (K_7 + [H+])\} / \{1 + M / (K_1 \cdot C)\} \\ & + B \{1 + K_2 \cdot K_5 / (K_2 \cdot K_5 + K_2 \cdot [H+] + M[H+] / C)\} / \\ & \{1 + M / (K_1 \cdot C)\} + K_4 / ([H+](1 + M / (K_1 \cdot C))) \end{aligned} \quad (2.42)$$

where,

$$A = M\beta - pH_2S / H \cdot H_2S$$

$$B = M\alpha - pCO_2 / H \cdot CO_2$$

and,

$$C = 1 + [H+] / K_1 + pCO_2 K_3 / (K_2 \cdot H \cdot CO_2 [H+])$$

Equations (2.40) to (2.42) are easier to solve because they contain only 3 unknowns.

Kent and Eisenberg (17) report that they tested the model by using published constants. They failed to get a good match of the published data.

Consequently, they decided to accept all the published constants (other than K_1 and K_2) and determined K_1 and K_2 by

forcing a fit with the experimental data. The values of K_1 and K_2 were obtained for the simple systems $\text{CO}_2\text{-H}_2\text{O-Ethanolamine}$ and $\text{H}_2\text{S-H}_2\text{O-ethanolamine}$ and were used to predict the partial pressures for the mixed system $\text{H}_2\text{S-CO}_2\text{-H}_2\text{O-Ethanolamine}$. As reported by Moshfeghian et al. (18) and Kent and Eisenberg (16) the data comparisons were satisfactory. However, both Moshfeghian (18) and the original authors tested the performance of the model for only the basic amines (MEA and DEA). The range of carbon dioxide and hydrogen sulfide loadings for which the comparisons were made were limited (0.1 to 0.9 moles CO_2 or H_2S /mole amine). Also, Kent and Eisenberg discovered that the fitted pseudo-equilibrium constants showed an Arrhenius dependence on temperature.

Subsequent sections of this thesis give details of a new acid gas-ethanolamine correlation model which is based on the correct set of equilibrium reactions and includes comparisons for new low pressure data.

CHAPTER III

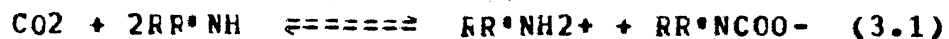
THE ACID GAS-AMINE EQUILIBRIUM MODEL

Although aqueous ethanolamine solutions have been extensively used for many years for removing H_2S and CO_2 from natural and manufactured gas streams, the relevant chemistry is poorly understood. The models proposed by Klyamer et al. (13) and Kent-Eisenberg (16) as described in the preceding sections postulate several chemical equilibrium equations. These reactions between amine and hydrogen sulfide and carbon dioxide were first presented by Danckwerts and McNeil (9). Conclusive laboratory evidence that the reactions occur as indicated in the foregoing models is not available. Most authors seem to implicitly assume that water is necessary for the removal process. Vidaurre and Kahre (50) suggested recently that the quantity of CO_2 that is absorbed is primarily due to, and limited by, physical absorption into the water that is present.

Ascertaining whether or not water is involved in the chemistry of an aqueous system would be extremely difficult. Recently, Batt et al. (19) realizing the aforesaid shortcomings conducted several experiments to determine the dominant processes in the MEA- CO_2 and MEA- H_2S systems. Their investi-

gations are based on studying the Proton Nuclear Magnetic resonance (NMR) spectra and C13 NMR spectra of the reacting systems. Their laboratory studies indicate that water is not necessary for the reactions of H₂S and CO₂ with ethanolamines. A brief literature survey indicates that several other investigators concur with their findings. Hikita et al. (27) determined the kinetic rate constants and based on these studies proposed identical reaction mechanisms for the CO₂-ethanolamine system. Further support to these conclusions is provided by Alberty and Daniels (61) who report that only a small fraction of the CO₂ dissolved is hydrated.

Sada, Kumazawa et al. (60) used the same overall reactions to obtain film theory solutions of gas absorption with instantaneous and non-instantaneous parallel reactions. Their predicted absorption rates compared satisfactorily with the measured absorption rates of carbon dioxide and hydrogen sulfide into aqueous monoethanolamine solutions in a continuous stirred tank absorber. As confirmed by Batt et al. (19), when carbon dioxide and hydrogen sulfide react with ethanolamine solutions, the following overall reactions occur.



where RR^*NH represents the amine (MEA, DEA etc). The rate controlling step of reaction (3.1) above is (19)



Reaction (3.2) is a simple protonation reaction (19).

To date the reactions as proposed above have not been used to predict partial pressures of acid gases over alkanolamine via an equilibrium model. Since these reactions represent the dominating process in the CO_2 - H_2S - H_2O -Amine system an equilibrium model based on these reactions should be more tractable and is expected to be at least comparable to any presently available model.

The model for the equilibrium in the alkanolamine solutions presented here, uses the ideas of Kent and Eisenberg for calculation of the pseudo-equilibrium constants. This model avoids the major deficiency of the previous models. Based on pure thermodynamic considerations of chemical equilibrium, that is the principle of minimum Gibbs free energy,

$$(dG_t)_{T,P} = 0$$

one would expect the new model to give the same results as the Kent-Eisenberg model since both systems of reactions have the same set of key components⁽¹⁾ However, depending upon the method used to generate solutions of the thermody-

namic equations and the manner in which the equations are written, the possibility exists that the solutions might not be unique. That is, such solutions could be either global minima or else they might merely be local minima of the Gibbs free energy. Thermodynamically the local minima correspond to the so called metastable states while global minima correspond to true equilibrium states. Such a question, while important, cannot be given a general answer because the answer depends upon the shape of the Gibbs free energy surface for the system under consideration(66). Only the salient features of the model will be presented here. The main reactions occurring in a CO₂-H₂S-H₂O-Amine system are as follows:

Protonation of the amine



Formation of carbamate ion



Dissociation of carbon dioxide



Ionization of water

¹The chemical species involved in these reactions are usually called key components in order to distinguish them from other species which are present in the system, but neglected.



Dissociation of bicarbonate ion



Dissociation of hydrogen sulphide



Dissociation of bisulfide ion



In these equations RR^+NH is the chemical formula of the ethanolamine.

A rigorous thermodynamic approach to the problem of calculating chemical equilibrium in electrolyte solutions involves the use of activity coefficients for each species in solution requiring interaction parameters between each species. The activity coefficients are then used to calculate the effect of composition and ionic strength on the chemical equilibrium constants. Such a method has been proposed by Edwards, Newman and Prausnitz (32) for aqueous solutions of volatile weak electrolytes. However because of assumptions in their model, their correlation is not suitable for concentrated solutions of these compounds. Also the ionic entropies or salting out parameters required for the estimation have not been determined for ethanolammonium or

carbamate ions. To avoid this problem and to minimize computer time required for calculating the activity coefficients of each individual species a more empirical method is used to develop the model. The equilibrium relations are written in terms of pseudo-equilibrium constants.

$$K1 = \frac{[RR \cdot NCOO^-][RR \cdot NH_2^+]}{[RR \cdot NH]_2^2 [CO_2]} \quad (3.11)$$

$$K2 = \frac{[RR \cdot NH_2^+][HS^-]}{[RR \cdot NH][H_2S]} \quad (3.12)$$

$$K3 = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (3.13)$$

$$K4 = [H^+][OH^-] \quad (3.14)$$

$$K5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (3.15)$$

$$K6 = \frac{[H^+][HS^-]}{[H_2S]} \quad (3.16)$$

$$K7 = \frac{[H^+][S^{2-}]}{[HS^-]} \quad (3.17)$$

The equilibrium partial pressures of CO_2 and H_2S are related to the free concentrations of CO_2 and H_2S in solution through Henry's Law as follows:

$$HC02 = pCO_2/[CO_2] \quad (3.18)$$

$$HH2S = pH2S/[H2S] \quad (3.19)$$

The balance equations for the reacting species are:

Electroneutrality

$$[H+] + [RR^+NH_2^+] = [RR^+NCOO^-] + [HCO_3^-] + 2[CO_3^{=}] + [OH^-] + [HS^-] + 2[S=] \quad (3.20)$$

Mass Balance

$$[RR^+NH] + [RR^+NH_2^+] + [RR^+NCOO^-] = M \quad (3.21)$$

$$[H_2S] + [HS^-] + [S=] = \beta M \quad (3.22)$$

$$[CO_2] + [RR^+NCOO^-] + [HCO_3^-] + [CO_3^{=}] = \alpha M \quad (3.23)$$

Here α and β are the mole ratios in the liquid phase (Carbon to nitrogen and sulfur to nitrogen respectively) and are the experimentally measured concentrations. A solution could be attempted for equations (1) to (13) using suitable mathematical techniques since we have thirteen independent equations and the thirteen unknowns, $[H+]$, pH_2S , pCO_2 , $[RR^+NH_2^+]$, $[RR^+NCOO^-]$, $[HCO_3^-]$, $[CO_3^{=}]$, $[OH^-]$, $[S=]$, $[HS^-]$, $[RR^+NH]$, $[H_2S]$ and $[CO_2]$

The problem however, is one of solving a system of non-linear algebraic equations. Most algorithms presently available for the purpose take a considerable amount of computer time and require good initial guesses. These problems are not uncommon to non-linear methods. However, these were further compounded by the fact that some of the species in solutions have very low concentrations (10^{-15} gmole/liter) as compared to some other species (2.0 gmole/liter).

To avoid such problems and especially that of convergence, the system of equations was algebraically reduced to the following, more tractable set of three equations containing three unknowns.

$$pH_2S = \frac{HH_2S \cdot A \cdot [H^+]^2}{K_6 K_7 (1 + [H^+]/K_7)} \quad (3.24)$$

$$pCO_2 = \frac{HCO_2 \cdot B \cdot [H^+]}{(K_3 \cdot K_5 \cdot (1 + [H^+]/K_5) + K_2 \cdot K_6 \cdot M \cdot [H^+]/(K_1 \cdot C))} \quad (3.25)$$

and,

$$[H^+] = \frac{(A(1 + K_7/(K_7 + [H^+])) + B(1 + 1/(1 + [H^+]/K_5 + K_2 \cdot K_6 \cdot M / (K_1 \cdot K_3 \cdot C))) + K_4/[H^+])}{(1 + K_1 \cdot M / (K_6 \cdot C))} \quad (3.26)$$

where,

$$A = BM - [H_2S]$$

$$B = \alpha M - [CO_2]$$

and,

$$C = 1 + K_1[H+] / K_0 + K_6 K_2 [CO_2] / (K_1 [H+])$$

Equations 3.24 to 3.26 are easily solved by any iterative method. The "successive substitution" method described by Carnahan (20) was successfully employed.

In developing the equilibrium model the values of all the dissociation constants (K_3 through K_7) and Henry's Law constants (H_{CO_2} and H_{H_2S}), except K_1 and K_2 , were retained as obtained from the literature. The value of K_1 was obtained by fitting the model represented by equations (2,4,6,7, and 9) to pure H_2S -amine data at various temperatures. The value of K_1 obtained as a function of temperature was then used to fit the model represented by the group of equations (1,3,4,5, and 8) to pure CO_2 -amine data. The fitted pseudo-equilibrium constants show an Arrhenius type dependence on temperature. A non-linear fitting program based on the Marquardt algorithm was suitably modified for use. The constants obtained from the pure H_2S -Amine and CO_2 -Amine data can be used to predict the partial pressures of mixtures of H_2S and CO_2 over aqueous alkanolamine solutions. Comparisons between measured and calculated data are given in a subsequent chapter.

CHAPTER IV

THE AMINE PROCESS MODEL

Although a variety of alkanolamine acid-gas absorption process systems has been in use for the past half-century, no detailed or rigorous calculational schemes are available. All available methods are either empirical or are based on gross approximations and "rules of thumb" (11). Sufficient data and operating experience with several ethanalamines is required to permit a judicious selection of a treating solution for a wide range of conditions and process types. Again, the choice of amine concentration may be quite arbitrary and is usually made on the basis of operating experience. Regenerator and absorber heights are often the result of designer recommendation or suggestion. The main cause for this lack of rigor in alkanolamine acid-gas absorption-process system design has been the non-availability of a reliable method for prediction of the vapor liquid equilibrium in the concentration and temperature ranges encountered in commercial units.

The need for a rigorous calculational technique for designing acid-gas removal plants has always existed but is felt even more today. Some of the relevant factors responsible for this are:

1. With the advent of the digital computer, simulation (or mathematical modelling) of entire chemical processing plants and of portions of these plants is becoming extremely popular. Computer simulations enable the engineer to examine the behavior of a plant being designed under different operating conditions and with different equipment configurations. Simulations of existing plants are also useful, since the effects of changed operating conditions can be studied without disruption of the actual plant.
2. A digital computer simulation of the plant could be used to optimize the acid gas treatment plant without investing a large amount of engineering time. The effect of several variables can be studied in this manner. Several operational questions such as the effect of feed composition, feed rate, contactor and regenerator operating pressures and temperatures and steam requirements can be answered with a good degree of accuracy. From a plant design standpoint such basic decisions as process flow scheme variations and proposed operating conditions can be evaluated within a reasonable time.
3. The ever increasing price of energy and associated operating expenses has put pressure on designers to improve the economies of acid gas treatment plants. The steam for heating in the regeneration of the amine is the single most important factor contributing to the cost of energy. A change in acid gas treatment chemical could reduce circulation rate by increased acid gas loading, reduce "stripping rate" in the regenerator and improve the removal of other contaminants.
4. Ambient criteria and emission standards for H_2S and other noxious gases are becoming more stringent. Predicting conditions at the top of the contactor has become increasingly necessary.
5. In spite of the common usage of amine treating processes, there are plants (49) which do not operate as designed, nor as predicted by published data. In fact, certain amine plants with a very high ratio of H_2S to

CO₂ in the feed gas are incapable of meeting rigid pipeline specifications with normal design criteria. The performance of some other installations considerably exceeds design expectations. In such cases, plant expenditure could probably have been reduced by more precise design premises.

The acid gas-amine equilibrium models presented in the previous chapters are adequate bases for designing a procedure for gas sweetening using ethanolamines. Using these models a computational scheme to provide the necessary heat and material balances for the process could be devised. Specifically, calculational procedures have been developed for the process design of the contactor, the regenerator and the flash drum. Preliminary design calculations have also been made for amine-amine heat exchangers, air or water coolers and pumps. These process units are put together to simulate several flow schemes of acid gas treating plants. A brief description of some of the more common flow schemes of acid gas treating plants follow.

Flow Systems for Gas Sweetening via Alkanolamines

The basic flow scheme for all alkanolamine acid-gas absorption-process systems is shown in Figure 1. The process flow scheme varies little, regardless of the aqueous amine solution used as the sweetening agent. The primary process equipment of concern includes the absorber column and stripper column, heat exchangers, pumps, the separation

equipment (flash drum) together with the associated piping. The sour gas containing H_2S and/or CO_2 enters the plant through a scrubber (not shown) to remove any free liquids and/or entrained solids. This gas is then passed upward through the absorber, countercurrent to a stream of the solution. Sweetened gas leaves the top of the absorber and flows to a dehydration unit before being considered ready for sale. The rich solution from the bottom of the absorber is heated by heat exchange with lean solution from the bottom of the stripping column and then fed to the stripping column at some point near the top. The amine-amine heat exchanger serves as a heat conservation device and lowers total heat requirements for the process. In units treating sour hydrocarbon gases at high pressure, the rich solution is customarily flashed, in a drum kept at an intermediate pressure to remove dissolved and entrained hydrocarbons before stripping. The lean amine solution from the bottom of the stripper, after being pumped through the amine-amine heat exchanger, is further cooled by exchange with air or water before being introduced to the top of the contactor to complete the cycle.

The lean amine solution is cooled to the 100 F temperature range because higher temperatures result in excessive amine losses through vaporization and also lower acid gas carrying capacity in the solution because of temperature effects.

The rich amine solution flows downward through the stripper in counter current contact with vapor generated in the reboiler. The reboiled vapor (consisting primarily of steam) strips the acid gases from the rich solution. The acid gases and the steam leave the top of the stripper and pass overhead through a condenser where the major portion of the steam is cooled and condensed and continually fed back to the system. Generally, this water is fed back at the top of the stripping column at a point above the rich solution feed and serves to force back amine vapors carried by the acid gas stream (29). Depending on the quantity of hydrogen sulfide available, the acid gases are either incinerated or further processed to marketable sulfur.

Figure 2 illustrates a more complex process for aqueous amine solutions. An energy-conservation measure is introduced with this process by way of additional heat recovery equipment. This modification uses two amine solutions fed at different points to the absorber, a semi-lean solution introduced at the midpoint and a lean solution introduced in the conventional manner at the top of the absorber. This process is particularly suited for treating sour gases with a high acid gas content__above approximately 30% (11). The liquid stream removed from the midpoint of the stripper is not completely stripped and serves to absorb the sour gas with higher acid gas concentrations at the bottom of the absorber. The lean solution introduced at the top of the

absorber contacts the gas with a lower acid gas concentration and reduces it to the specified level.

The obvious disadvantage of this process modification is the fact that it may increase the initial costs of the treating plant. The stripping column is taller and the system is more complex. In addition the two systems require separate piping systems with two sets of pumps, heat exchangers and coolers.

A modified form of the basic amine process, which is not shown in Figure 1, consists of dividing the lean solution before introduction into the absorber into two unequal streams. The larger stream is fed to the middle of the absorber while the smaller stream is circulated to the top of the column. In cases where gases of high acid gas concentration are treated, this scheme may be more economical than the basic scheme for two reasons (a) The diameter of the top section of the absorber will be appreciably smaller than that of the bottom section. (b) The lean solution stream fed to the middle of the absorber may not have to be cooled to as low a temperature as the stream flowing to the top of the column, resulting in reduction of heat exchange surface (29).

The Amine Process Model can simulate any of the processes outlined above. In order to facilitate adding or deleting of process units, the program was set up in a modular form. The design details of the major process units of

the Amine Process Model and the methods of computation are discussed below.

Absorption Column Calculations

The mathematical formulation of absorption with chemical reaction is exceedingly complex. The literature is replete with empirical correlations between absorption coefficients and tray efficiency data, for application to practical problems in plant design.

Probably the most comprehensive theoretical treatment of absorption of CO_2 , H_2S and carbonyl sulfide (COS) in solutions of alkalis and amines has been presented by Danckwerts and Sharma (51,52). Much data on the subject, available up to 1966 are reviewed and design procedures based on fundamental concepts are proposed. Although the design methods are considered to be sound in principle, Danckwerts and Sharma recognize that additional fundamental information will have to be obtained before rigorous design procedures can be developed.

Rosen (57), Love (58) and Fitzgerald and Richardson (49) have presented a series of charts which can be used to quickly and conveniently estimate equipment sizes and process conditions for many Amine sweetening operations. These are based on gross approximations and simplifying assumptions. Moreover, their range of usefulness is severely limited. The solubility of either CO_2 or H_2S in MEA solutions

is a strong function of the concentration of both solutes in the MEA solution. The absorption behavior of one solute cannot be defined without knowing the amount of the other solute absorbed at any particular stage under consideration. As a consequence the conventional graphical methods are not applicable, even though the gas phase is not highly concentrated in CO₂ and H₂S.

The major process variables to be considered in amine absorber design calculations are:

1. Amine solution rate
2. Column temperatures
3. Absorber column-diameter and,
4. Absorber height or number of trays.

In the approach of this thesis, the contactor is assumed to be filled with theoretical trays. This analysis of the separation process assumes that complete equilibrium is attained between the product streams from each stage. The computations may be corrected for the lack of equilibrium as a final step.

Estimation of Minimum Amine Circulation Rate

The condition for minimum solvent rate (or infinite stages) is established by postulating equilibrium between the phases at the bottom (or rich end) of the column. The

limiting "pinch" must occur at that end of the column since the inlet amine solute loadings are specified and since the equilibrium CO₂ and H₂S partial pressures rise rapidly with increasing solution concentrations ¹. These conditions are shown in Figure 4. Figure 4 (b) corresponds to a trivial case since the Y_{A,out}, X_{A,in} end of the absorber is totally specified and is also where the pinch occurs. Figure 4 (a) is the useful condition, since it corresponds to a pinch at the end of the cascade where one of the concentrations is not specified.

In order to compute the equilibrium conditions at the rich end of the tower we need to determine the effluent amine solution temperature. These equilibrium computations involve trial and error in temperature and amine loadings. The computational approach used is as follows.

1. Calculate total heat of absorption, ΔH_r
2. Calculate heat pickup by sweet gas in passing through the absorber, ΔH_{inert}
3. Assume an outlet temperature of Amine, T_{Am,out}
4. An overall enthalpy balance, provides the circulation rate:

$$C_{r,Am} = (\Delta H_r - \Delta H_{inert}) / [C_{p,Am} (T_{Am,out} - T_{Am,in})]$$

¹A preliminary calculation needs to check that the specification of gas effluent and amine inlet do not exceed equilibrium at the top of the column. That is, the partial pressures of CO₂ and H₂S of the lean amine to the top of the contactor should be less than the specified effluent gas partial pressures.

5. Use the overall material balance to obtain effluent amine solute loadings:

$$\alpha_{out} = \alpha_{in} + Y_{CO2}/Cr$$

$$\beta_{out} = \beta_{in} + Y_{H2S}/Cr$$

6. Use $T_{Am,out}$ and the effluent amine concentrations of CO_2 and H_2S to predict the partial pressures of CO_2 and H_2S .
7. Check to see if the calculated partial pressures in step 6 are equal to the actual partial pressures of CO_2 and H_2S in the inlet gas. Repeat from step 3 till convergence. (A recursive relation outlined in Appendix C was used to estimate the new guess of outlet temperature of amine)

An alternate approach, which gives slightly different results but is computationally much easier to implement is as outlined below:

1. Calculate the total heat of absorption, ΔH_r
2. Assume an outlet temperature of amine $T_{Am,out}$.
3. The assumed rich amine temperature and the partial pressures of the acid gas components in the entering gas stream are used to calculate the rich amine loadings via the Acid-Gas Amine Equilibrium Model.
4. An acid gas component balance around the absorption tower,

$$\alpha_{out} = \alpha_{in} + Y_{CO2}/Cr$$

$$\beta_{out} = \beta_{in} + Y_{H2S}/Cr$$

provides the circulation rate.

5. An overall enthalpy balance is used to check the assumed temperatures of rich amine.

$$H_r = Cr(T_{Am,out} - T_{Am,in}) C_{p,Am} + \Delta H_{inert}$$

6. Steps 1 through 5 above are repeated until the assumed and calculated temperatures are within an acceptably small tolerance.

Estimation of the Equilibrium Stage

Requirements

The composition, temperatures and relative flows of the inlet streams to the contactor are generally fixed, as is the column pressure. The Gibbs phase rule criterion of describing thermodynamic equilibrium allows one other variable to be set by construction or manipulation, namely the number of equilibrium stages. This variable is replaced by a separation variable, the concentration of one of the solutes in the effluent gas. The effluent gas concentration of the other solute must be estimated in order to start the calculation. Usually the stage to stage calculation is facilitated by the fact that the recovery fractions of both solutes in the effluent amine are quite high. Hence the size of the estimated solute concentration in the effluent gas will have little percentage wise effect on the concentration of that solute in the effluent amine.

Investigation of the degree of approach to equilibrium at the tower top is critical. The maximum allowable effluent gas partial pressures of CO_2 and H_2S should be substantially above the equilibrium pressures over the inlet amine. When not clear whether the H_2S concentration of the gas will fall below the maximum allowable effluent gas contamination

before the CO₂ level does or vice versa, a logical procedure is to set both solute mole fractions or partial pressures in the effluent gas at the maximum allowable values and run cases until the solute which reaches the maximum allowable mole fraction last, is known. The estimated overhead mole fraction of the nonlimiting solute can then be adjusted. The method of Crynes and Maddox (31) is used for estimating the heat of solution/dissolution of acid gases in the amines. The systematic stepwise procedure is outlined below (Refer Figure 3) :

1. Estimate the overhead (top tray) mole fraction of the solute that has not been specified.
2. Estimate the loadings of the rich amine leaving the contactor. (A rough calculation based on overall material balances provides good initial guesses.)
3. Estimate the rich amine temperature (A rough calculation based on overall energy balance provides initial guess.)
4. Compute the equilibrium partial pressures of CO₂ and H₂S over the effluent amine by using the Amine Equilibrium Model.
5. A component material balance for CO₂ and H₂S fixes the inlet amine loadings of CO₂ and H₂S to the stage.
6. Estimate the heat liberated by absorption of gases using the method outlined in Appendix A, to calculate heats of dissolution.
7. An enthalpy balance on this stage provides inlet amine temperature.
8. The calculations are repeated, until
 - a. the required number of stages has been obtained

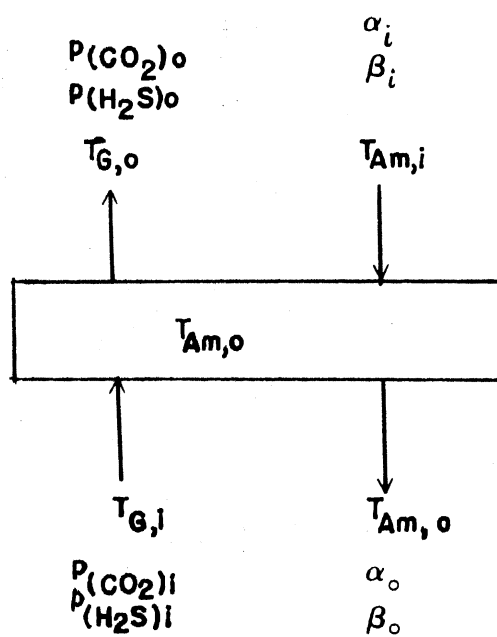


Figure 3. Nomenclature for an Absorber Stage

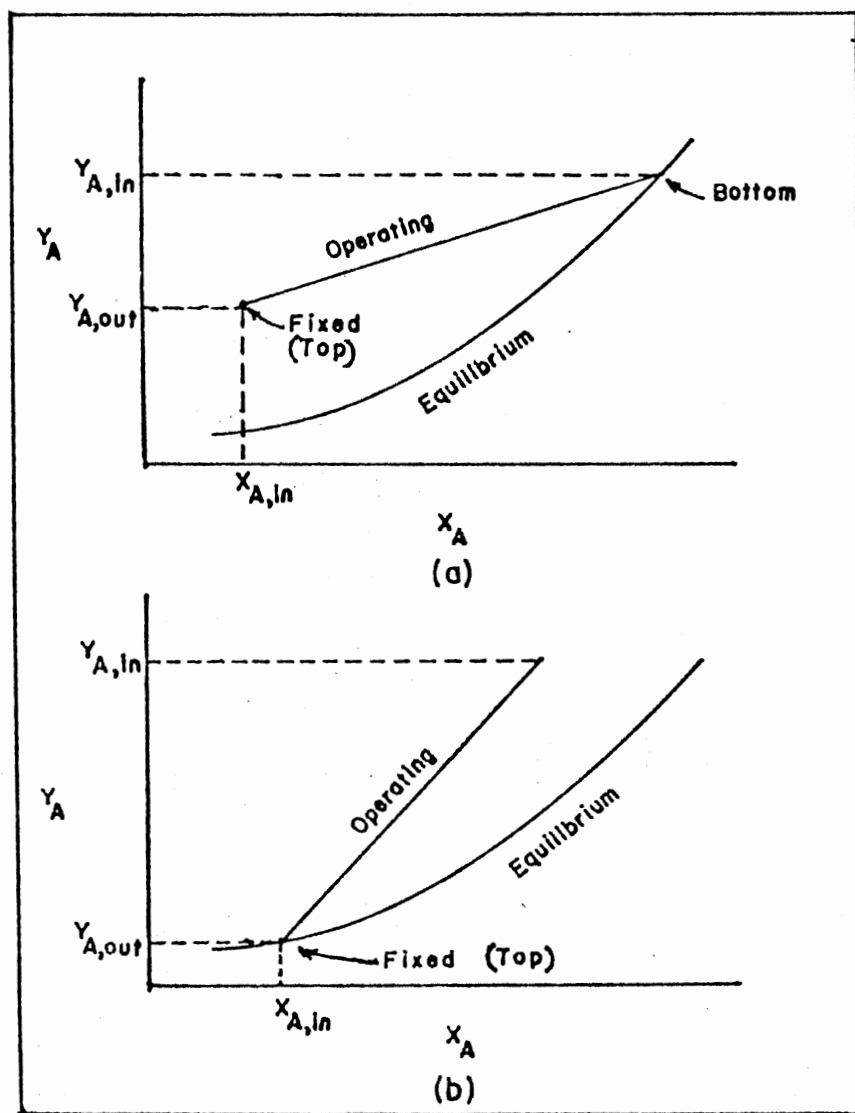


Figure 4. Minimum Flows with Equilibrium and Operating Lines (a) Useful Case (b) Trivial Case.

- b. or CO₂ or H₂S concentration (whichever one is specified) is under the maximum allowable concentration. (This step provides a good value for adjusting the estimated overhead mole fraction of the nonlimiting solute in step 1).

Check if the temperature of the entering lean amine is within some acceptably small tolerance. If not return to step 2a and repeat (A method of generating improved guesses for quick convergence is desirable. The method used in this thesis is explained in Appendix C.)

9. Check the over all material balance. If in error, repeat all steps from step 1.

This procedure was primarily designed for easy adaptation to a quick computer solution. Where available, existing equations were used for properties such as vapor pressure, heat capacity and density. These, and other correlated physical and thermal property data are also included in Appendix A.

Stripper Column Calculations

As in the case of absorbers stripping columns are designed to use either trays or packing. Principal design problems for the stripping column include estimating the heat load for the reboiler, calculating the column diameter and estimating the height or number of trays which is required.

At the present time a reliable rigorous technical approach to the prediction of lean solution acid gas loadings has not been published and this necessarily has spawned a rule-of-thumb approach to the selection of design stripping requirements. One of the main factors which hindered development of a proper theoretical approach to the problem of stripping was the non-availability of partial pressure data at low solute loadings or a reliable predictive method.

Estimation of Heat Duty on Reboiler

In most amine stripping operations heat is supplied to the column by steam or by a heat medium in the reboiler. The heat load includes (a) sensible heat to raise the temperature of the feed solution to that of the lean solution leaving the reboiler, (b) heat of reaction required for dissolution of the acid gases from the amine, and (c) the stripper column condenser duty which is essentially the heat required to evaporate water which leaves the stripping section of the column as vapor with the acid-gas stream and is condensed and returned to the stripper as reflux.

The quantity of stripping vapor required depends on the solution purity needed to produce the required product gas, the stripping column height and the type of solution. The ratio, moles water in the acid gas on the top tray of the stripping column to moles acid gas on that tray, referred here as the "reflux rate," is used in design as a convenient measure of the quantity of stripping vapor provided. The heat requirement for amine solution stripping is expressed in terms of pounds of steam per gallon of regenerated solution.

Fitzgerald and Richardson (49,59) report that operating regenerators clearly demonstrate a trend towards decreased stripping of H_2S from lean amine solutions with increase in the ratio of H_2S to CO_2 . Their data also illustrate an apparent asymptotic limit to residual H_2S stripping from MEA with increased regenerator heat input. This limit is not predictable using conventional stripping calculation methods.

Stripping-Column Stage Requirement

The column calculations were made based on the following assumptions:

1. The regenerator is assumed to be filled with theoretical (equilibrium) trays.
2. Vapor pressures and the laws of ideal solutions are used to estimate temperature on each stage. In the stripper the partial pressure of water in the vapor phase can be calculated from Raoult's Law where the moles

of each species in solution is considered in calculating the mole fraction of water. This is possible since water generally exists as the principal component even in concentrated solutions of electrolytes so that liquid phase nonideality effects on the partial pressure of water are negligible (65). The partial pressure of water is calculated from it's vapor pressure according to the following equation

$$p_{H_2O} = p^*_{H_2O} x_{H_2O}$$

where,

$p^*_{H_2O}$ is vapor pressure of water

and,

x_{H_2O} is liquid phase mole fraction of water.

3. No attempt has been made in the Amine Process model to correct for non-ideal behavior in the vapor phase. At low pressures, errors from assuming ideality are probably less than $\pm 5\%$ (65) but at pressures of 50 psia or higher, the errors will be greater than this and serious consideration should be made to correct for non-ideal behavior in vapor phase.
4. The method of Crynes and Maddox (31) is used for estimating the heat of dissolution of acid gases in the amines. The method uses acid gas partial pressures to calculate heats of reaction.
5. The normality of the lean amine leaving the stripper remains essentially the same as the feed amine.
6. The development of the following set of equations is purported to describe stripper performance:

For the n th theoretical tray in the regenerator the component material balances are written (Refer to Figure 5 for nomenclature) as:

$$CO_2: \quad L_{\alpha,n-1} + V_{\alpha,n+1} = L_{\alpha,n} + V_{\alpha,n}$$

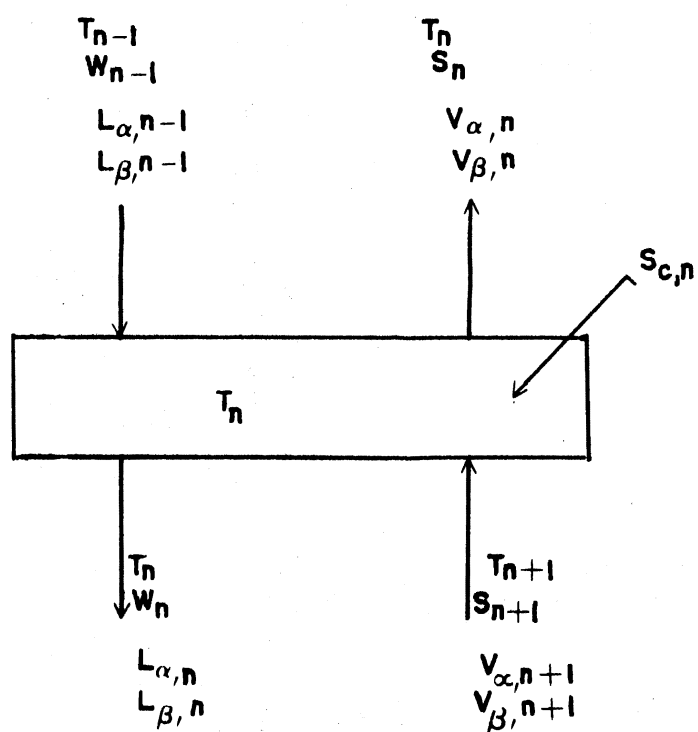


Figure 5. Nomenclature for Streams Leaving and Entering any Stripper Stage

$$\text{H}_2\text{S: } L_{\beta,n-1} + V_{\beta,n+1} = L_{\beta,n} + V_{\beta,n}$$

$$\text{H}_2\text{O: } W_n - 1 + S_{n+1} + A_{w,n-1} = A_{w,n} + W_n + S_n$$

The water associated with amine remains unchanged by our assumption (5) above, therefore,

$$A_{w,n-1} = A_{w,n}$$

The last equation reduces to,

$$W_n - W_{n-1} = S_{n+1} - S_n$$

If $S_{c,n}$ is steam condensed then,

$$S_{c,n} = S_{n+1} - S_n$$

Since there is no accumulation of water on the stage at steady state,

$$W_n = S_{n+1}$$

and,

$$W_{n-1} = S_n$$

Making an enthalpy balance on the stage:

$$\begin{aligned} \lambda_c S_{c,n} + S_{n+1} C_{p,w} (T_{n+1} - T_n) \\ = C_{p,A} (T_n - T_{n-1}) - \Delta H_r \end{aligned}$$

Finally, the Acid Gas-Amine Equilibrium Model is available to predict the partial pressures of H_2S and CO_2 .

For the stripper column, we can either determine or assign the number of theoretical plates to be contained in the stripper. To start these calculations, initial assumptions of the liquid and vapor rate profiles and the temperature profile must be made. There are many excellent estimating procedures available for simple absorbers and strippers (63). The possibility of having interstage coolers or reboilers, sidestreams, etc., make these estimating procedures unsuitable for most cases. Experience has shown that for the general purpose program, the specified feed solution rate and specified steam rate are good initial estimates of the liquid and vapor rates respectively for all trays in the column. The initial temperature profile can be estimated by linear interpolation between the two terminal temperatures. The first pass through the stripper yields the change in temperature for each tray that would be required to bring the energy balance for each tray into balance. The latest calculated temperature and concentration profiles are used to solve the material and energy balance equations. The entire process is repeated until the error in the material and energy balance on each tray and the overall energy balance around the entire column is reduced to some acceptably small tolerance.

Flash Drum Calculations

In absorber operations, when acid gas removal is carried out at high pressure, appreciable amounts of nonacidic gases are carried by the solution from the contactor to the regeneration section of the plant. These nonacidic gases constitute a nuisance if the acid gases are intended to be used further for the production of dry ice or elemental sulfur. Provisions, therefore must be made to separate these gases from the solution after it leaves the contactor and before it enters the regenerating section. To provide a maximum of vapor disengaging area, horizontal disengaging drums are frequently used. The acid gas can be recovered from the flashed vapor stream by contacting this stream with a small stream of lean amine solution in a small column usually installed at the top of the disengaging vessel.

The flash drum is calculated using a standard form of the equilibrium flash equations. Enthalpy balances are incorporated to ensure correct temperatures at the lower pressure. For the sake of brevity there is no detailed discussion of the flash calculation technique.

The major units, absorber, regenerator and stripper are calculated based on the foregoing principles. A computer program to simulate these units and the entire plant assembly shown in Figure 1 and 2 is written in Fortran IV. A modular approach was adopted to develop this program and hence it can be easily reorganised and converted to simulate other

plant configurations. Flow sheeting is flexible so far as arrangement of individual units is concerned. The program can be readily adapted as a subroutine for equilibrium stage calculations for other stage separation processes. Most of the process variables can either be specified or calculated. A block diagram for the overall program is included in Appendix B. The detailed description of the program, including internal documentation, flow diagrams and the mode of entering data for the various options is also in Appendix B. A sample output is also included.

CHAPTER V

COMPARISONS AND EVALUATIONS BETWEEN
MEASURED AND CALCULATED
DATA

In the preceding chapters, a new method for prediction of vapor-liquid equilibria in Ethanolamine- H_2S - CO_2 - H_2O systems, and the Amine Process Model were developed. These models will be separately evaluated by comparison with experimental data.

The Acid Gas Amine Equilibrium Model

The Acid Gas Amine Equilibrium Model developed here, is based on the dominating reactions of the CO_2 - H_2S -Ethanolamine- H_2O system and is expected to perform better than other presently available prediction models. The best and the most popular of these other models is the Kent-Eisenberg Model. In all the comparisons with experimental data, a parallel comparison is always made with the Kent-Eisenberg Model. Not all literature data were examined in this comparison because of the limited scope of this work. However, an attempt was made to examine as much data as possible, especially the data published in recent years.

As mentioned before in developing the present model two constants (K_1 and K_2) were derived for each amine type (MEA, DEA, DGA, and DIPA) by fitting the model with H_2S -Amine- H_2O and CO_2 -Amine- H_2O system partial pressure data. Kent and Eisenberg report values of K_1 and K_2 only for MEA and DEA. Also their data are based on data published before 1975. Their values were refitted for improved accuracy, with recent literature data for MEA and DEA. Constants were also derived for DGA and DIPA. These latter amines did not form part of Kent and Eisenberg's study. Thus their model was extended to include these amines, which are becoming increasingly popular in gas sweetening.

In developing the models no individual experimental points from any one source were ignored, even when there was wide scatter in the data. The same kind of differences exist between different sources obtained from literature. Literature data from all available sources could not be procured and therefore was not used. A different fit of the data and consequently a different set of coefficients would certainly have been obtained if individual experimental points in a given set of measurements had been ignored in developing the correlation model especially when deviation errors from these points appeared to be radically different from the main set of data. The choice of using smoothed, rather than raw data also exists. Clearly different sets of the fitted constants (K_1 and K_2) will be obtained depending

on the ternary system (either H₂S-Amine-H₂O or CO₂-Amine-H₂O) data used to derive them.

The evaluations of the model are categorized based on the amine type.

Monoethanolamine

Aqueous monoethanolamine solutions were once used almost exclusively for acid gas treatment, particularly in high pressure operations but are slowly being replaced by other systems. However, this is still a preferred solvent. It's low molecular weight, resulting in a greater carrying capacity at moderate concentrations (on a weight basis), high alkalinity and the ease with which it can be separated from the acid gas constituents are some of the advantages which in many cases more than counterbalance inherent disadvantages. These factors have contributed to making MEA the most researched Amine. There is relatively a large amount of data on the solubility of H₂S, CO₂ and their mixtures in aqueous solutions of MEA. Leibush and Schneerson (2) measured the solubilities in a 2.5N MEA solution at 25 deg C. Partial pressures of the acid gases did not exceed 75 mm Hg. Muhlbauer and Monaghan (7) determined the solubility of mixtures of CO₂ and H₂S in a 2.5N MEA solution at 25 and 100 deg C for partial pressures of the acid gases below 1000 mm Hg. Jones et al.(8) measured the solubility of mixtures of CO₂ and H₂S in a 2.5 N MEA solution at four temperatures

between 40 and 120 deg C at partial pressures of CO₂ and H₂S upto 3000 and 1000 mm Hg. respectively. Lee et al (33) measured the solubility of mixtures of CO₂ and H₂S in a 5.0 N MEA solution at 40 and 100 C. Partial pressures of CO₂ ranged from 0.1 to 810 psia and partial pressures of H₂S ranged from 0.1 to 510 psia. The same authors (34) have reported data for mixtures of acid gases at high partial pressures over 2.5N MEA solution and compared their results with two methods of prediction. Incidentally, Otto and Mather have reported extensive and sometimes exclusive data on all the amines (MEA, DEA, DIPA, DGA) under consideration in this work. The author believes most of their data are reliable and accurate. Oftentimes, therefore, their data were preferentially used along with data from other sources, to fit the model to obtain K₁ and K₂. Figure 6 shows a comparison of hydrogen sulfide partial pressures predicted by the present model and the Kent-Eisenberg model with data from Lee et al. (34). There is good agreement between the experimental values reported in the literature and the curves calculated by use of the reaction equilibrium models. Figure 7 shows the same comparison for CO₂ in MEA solution. In reality the information presented in Figure 6 and Figure 7 is nothing but a comparison of how well the reaction equilibrium constants K₁ and K₂ describe the system. The new model presented here fits the data better than the Kent-Eisenberg model. However, for the H₂S data the difference in

the prediction performance is marginal, although the present model gives an excellent fit. Figures 8 and 9 show comparisons for mixtures of H₂S and CO₂ at 40 and 100 deg C respectively, cases for which the data were not used in developing the equilibrium constants K₁ and K₂. The agreement is excellent. The same points were used by Kent-Eisenberg (16) to generate similar plots. These have not been reproduced here. The sensitivity of the model to values of K₁ and K₂ and indirectly, the data used to obtain them is illustrated by Figure 10 which shows the predictions for the same raw data as was used for Figure 8. The predicted values of partial pressures have changed considerably but are still within reasonable agreement.

Further proof of improved performance of the present model as compared to the Kent-Eisenberg model is evident in Figure 11 which shows partial pressures of H₂S over 2.5N MEA solution as a function of H₂S loading in the liquid phase with parameters of CO₂ loading. The experimental data used as a basis for comparison are fundamentally the Jones et al. (8) data though some were taken from Maddox (47) for ease of reading the curves. The data comparison is favorable though at high CO₂ loading there appears to be some deviation at low H₂S loading. Figure 12 shows the same comparison for CO₂ partial pressure as a function of CO₂ liquid with parameters of H₂S liquid loading. Again the reaction equilibrium models do an excellent job of predicting CO₂ partial pressure as a function of CO₂ and H₂S loading in the liquid phase.

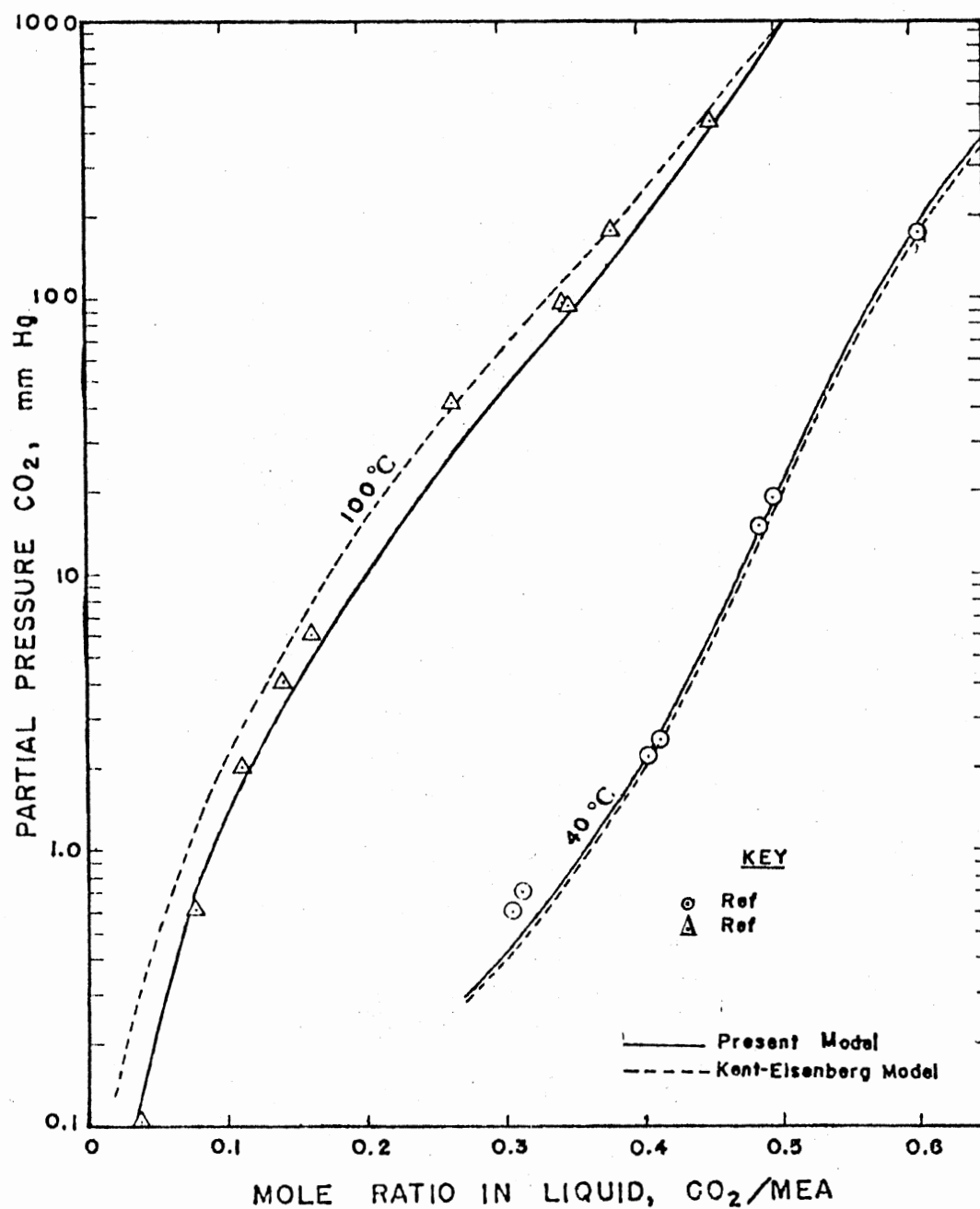


Figure 6. Comparison of Experimental and Calculated Values of Partial Pressures of CO₂ at 40 and 100 C Over 2.5N MEA Solution

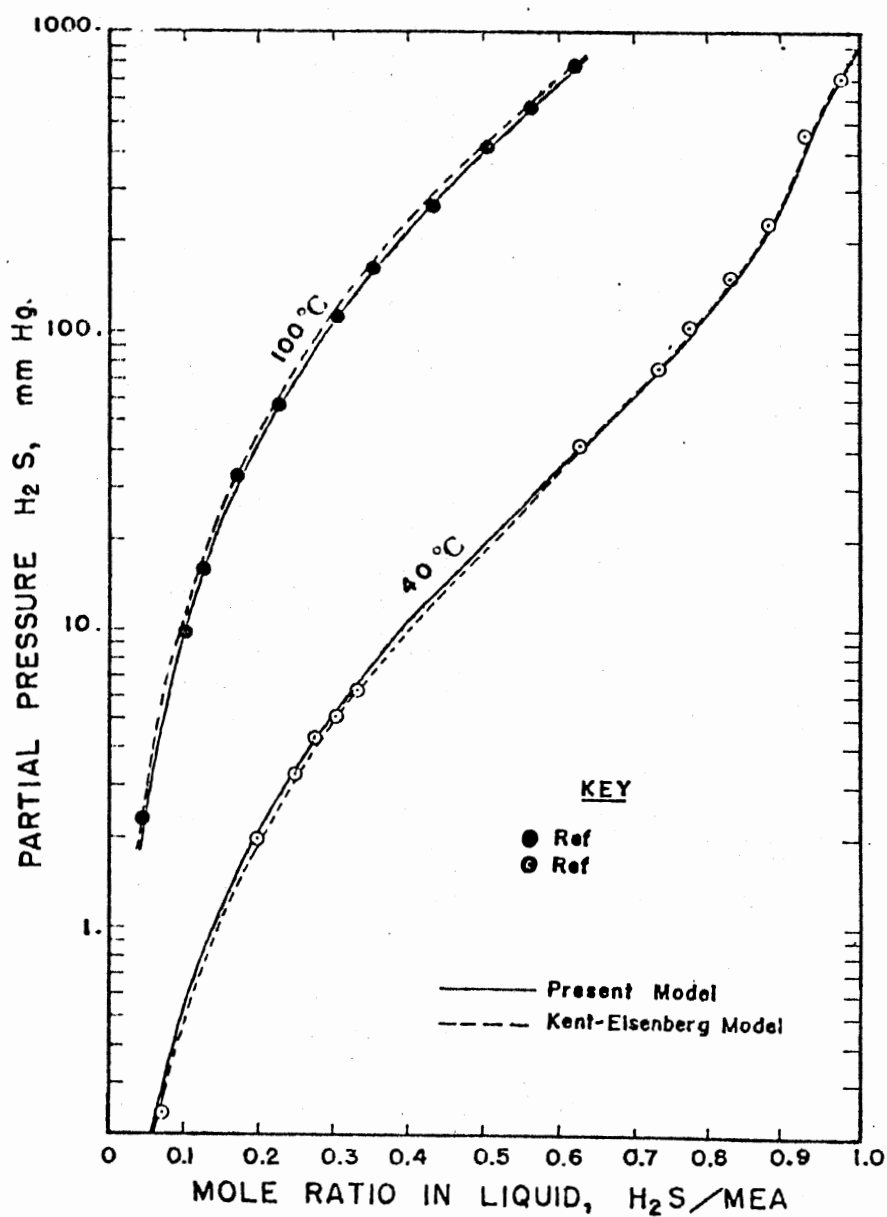


Figure 7. Comparison of Experimental and Calculated Values of Partial Pressures of H_2S at 40 and 100 C Over 2.5N MEA Solution

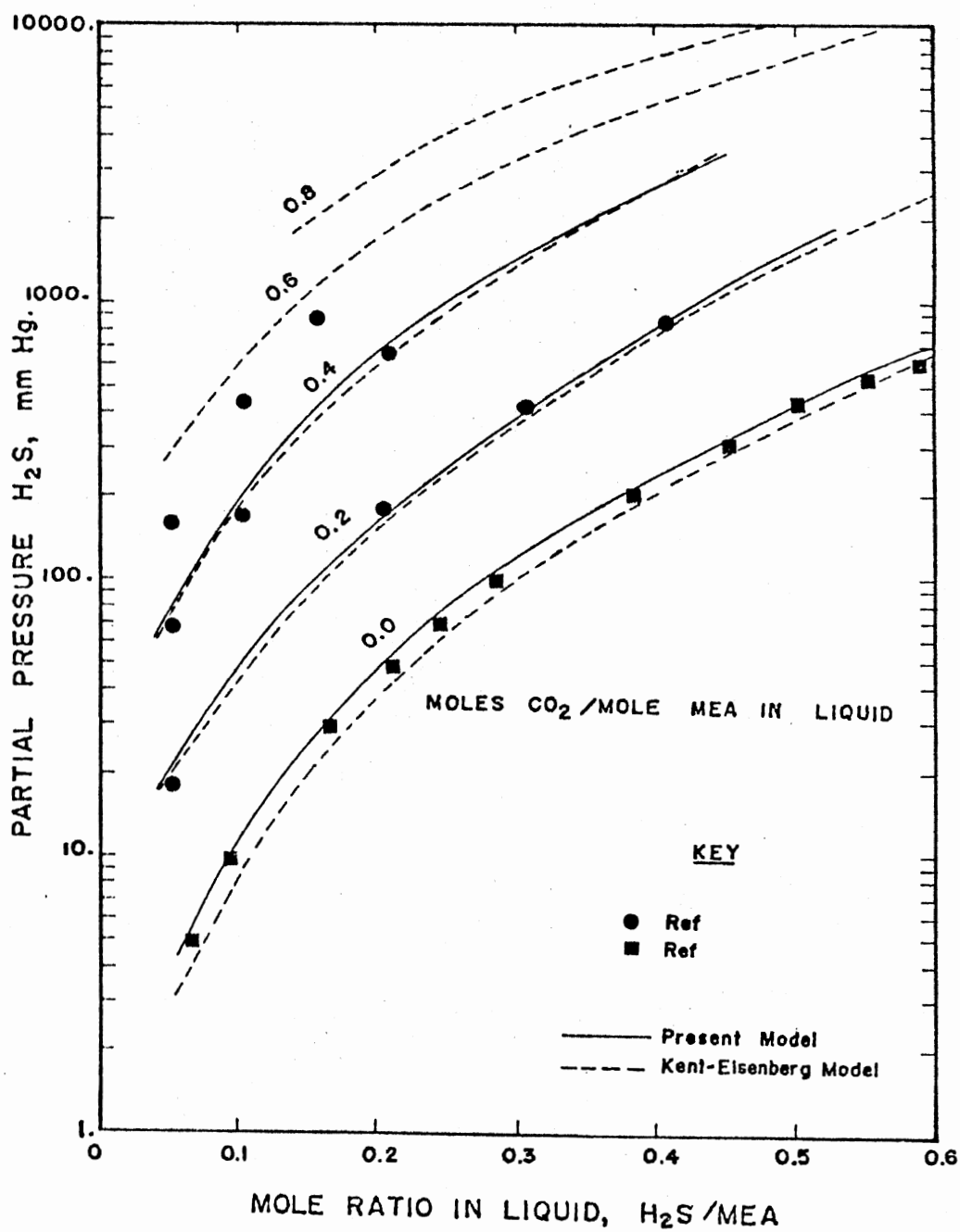


Figure 8. Comparison of Predicted and Measured Values for H_2S and CO_2 Partial Pressures Over 2.5N MEA Solution at 40 C

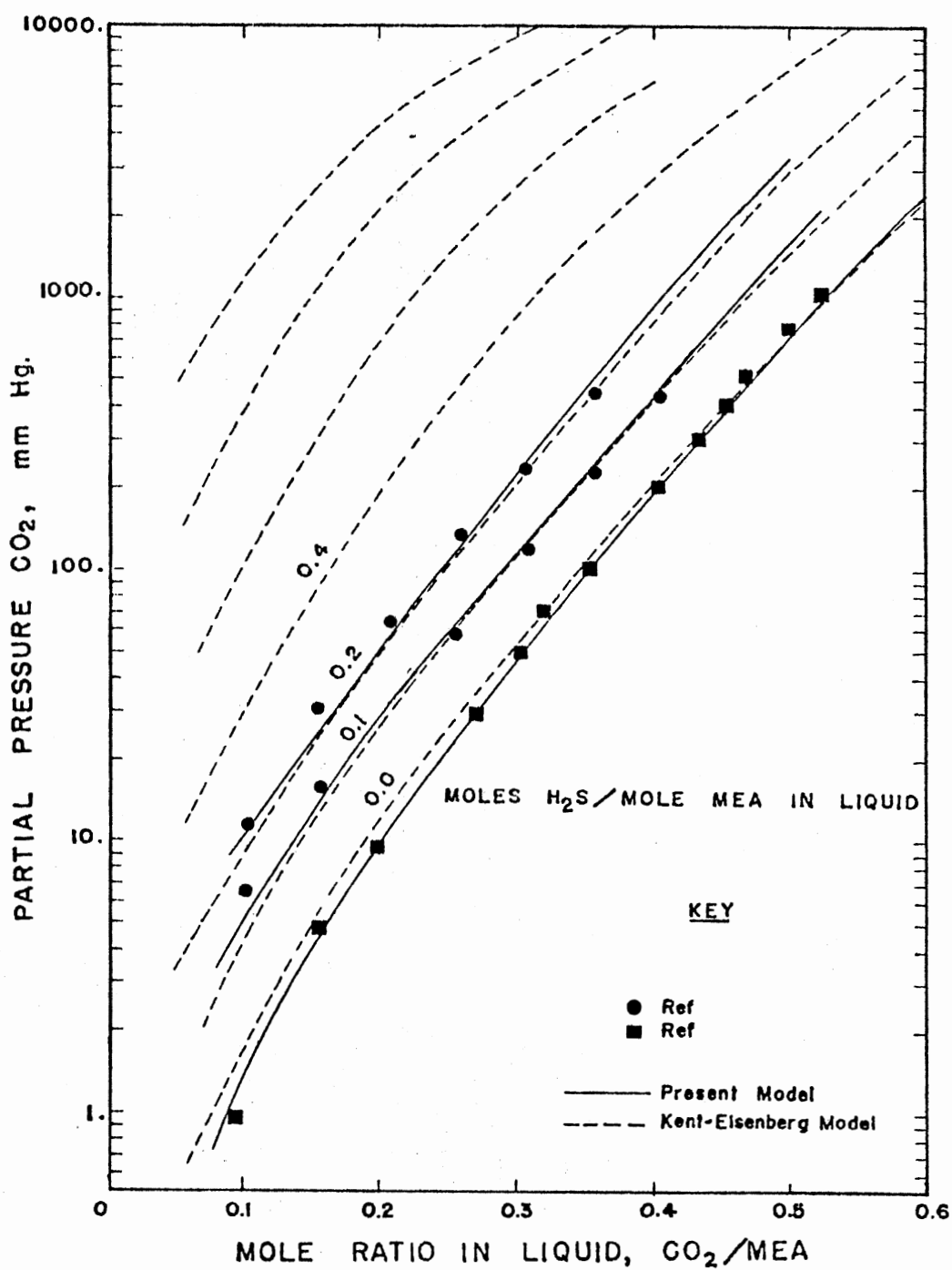


Figure 9. Comparison of Predicted and Measured Values for H_2S and CO_2 Partial Pressures Over 2.5N MEA Solution at 100 C

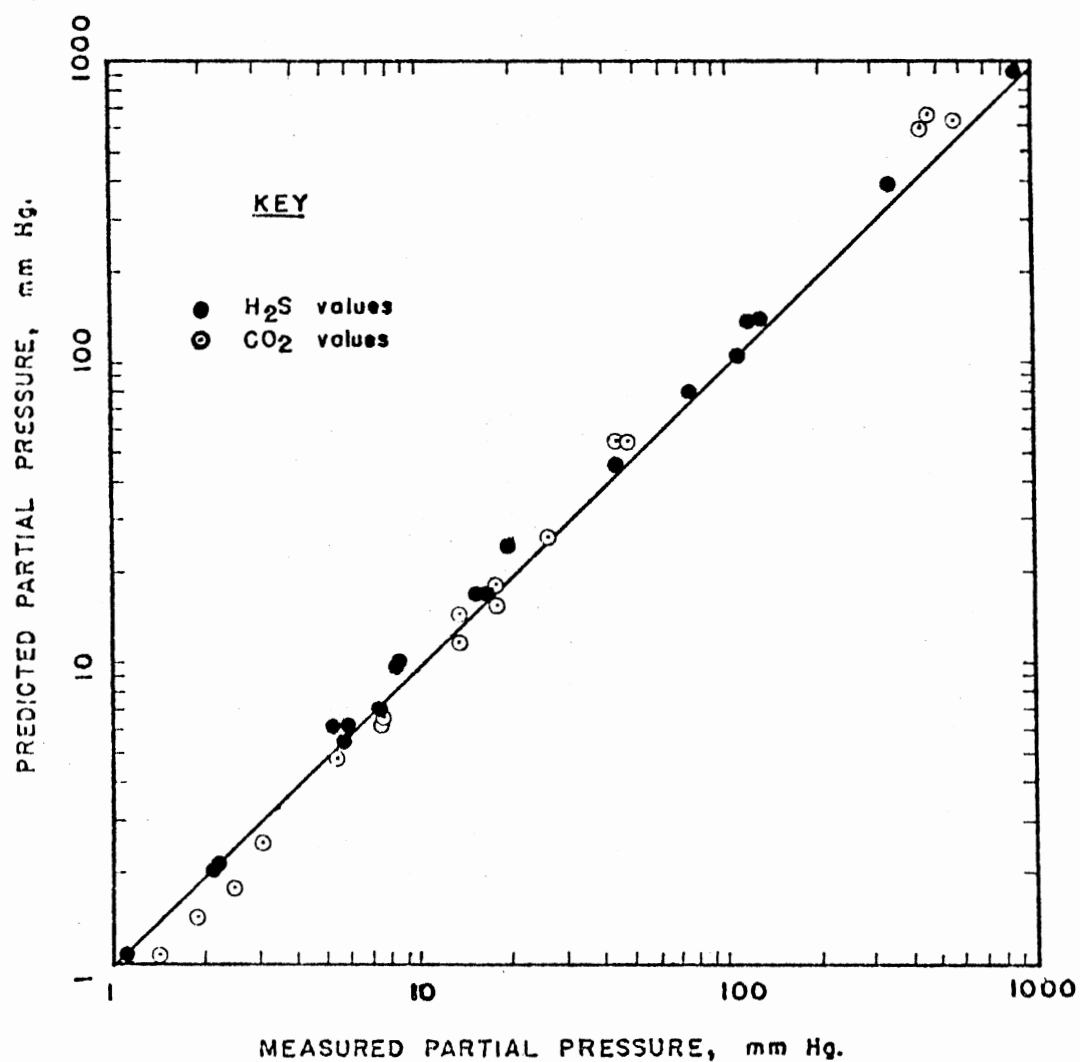


Figure 10. Comparison of Predicted and Measured Values for H_2S and CO_2 Partial Pressures Over 2.5N MEA Solution at 40 C

Figures 13 and 14 show the same comparison with the experimental data of Lee et al. (12). Here there are some discrepancies in the data and the calculated results. However, essentially these same discrepancies exist between the experimental data of Lee et al. and the data of Jones et al. For this reason, the deviations shown in Figures 13 and 14 appear to be caused by differences in reported experimental values rather than a weakness in the reaction equilibrium models. This trend is in agreement with that experienced by Moshfeghian et al. (18) in their studies. The superiority of the present model, especially in predicting H_2S partial pressures, is evident from Figure 13. However, the prediction capability for CO_2 partial pressures is nearly the same (Figure 14).

The data comparisons made above are for the equilibrium solubility of the acid gases in MEA solutions in the range of partial pressures from 1 to 5000 KPa (or 7.5 to 37,000 mm Hg.). There is a need for data at conditions typical of the operation of amine regenerators and at the top of amine contactors. Recently, some data were published by Isaacs et al. (35,36). Figures 15, 16 and 17 show comparisons for the low pressure data at 80 and 100 C. The results for the solubility of H_2S - CO_2 mixtures in 2.5 kmol/cu. meter solution are presented in Table I. While neither method can be said to predict the experimental values with absolute accuracy both the models are in reasonable agreement. This is espe-

cially so if we consider the probable experimental uncertainties involved in measuring such low pressures and loadings.

The authors (35,36) claim that a comparison of the new data with a previous extrapolation of the data obtained at higher pressures by them in a different apparatus, shows a disagreement of up to 15%. Besides there is wide scatter in the experimental data reported by these authors for low acid gas loadings. Again, mixture data comparisons at these low loadings, as shown in Table I, indicate that the present model is at least as good as the Kent-Eisenberg model. Table II gives summaries of deviation errors between calculated and measured CO₂ and H₂S partial pressures for the monoethanolamine solutions under consideration. These tables also compare the Kent and Eisenberg model with the present model. As a general policy some individual experimental points especially at low partial pressures, which produce large deviation errors have not been ignored while computing the absolute average percent deviation (AAPD). This measure tends to distort the AAPD values somewhat. However, when the AAPD computed is radically influenced by such points, a reference has been made in the table.

In general, both the models under consideration reproduce the experimental results of the simple systems (i.e. systems containing only CO₂ or H₂S) very well. This is to be expected from the manner in which these models have been

TABLE I
COMPARISON OF THE PRESENT WORK WITH OTHER METHODS
OF PREDICTION AND EXPERIMENTAL LOW
PRESSURE DATA FOR 2.5N MEA
SOLUTION AT 100 C

pH ₂ S, mm Hg						pCO ₂ , mm Hg		
H ₂ S	This Work	K & E*	Measured		This Work	K & E*	Measured	
CO ₂ =0.0	0.02	0.4	0.4	0.3		-	-	-
	0.06	3.9	3.9	5.3		-	-	-
	0.10	11.4	11.4	13.5		-	-	-
CO ₂ =0.02	0.02	0.9	0.9	0.5		0.1	0.1	0.1
	0.06	5.5	5.5	6.2		0.2	0.2	0.4
	0.10	14.3	14.2	16.5		0.2	0.3	0.7
CO ₂ =0.06	0.00	0.0	0.0	0.0		0.4	0.4	0.3
	0.02	1.9	1.9	1.5		0.5	0.5	0.8
	0.06	9.1	9.0	8.3		0.8	0.8	1.9
	0.10	21.1	20.8	21.0		1.2	1.2	2.6
CO ₂ =0.10	0.00	0.0	0.0	0.0		1.2	1.2	1.4
	0.02	3.2	3.1	2.3		1.5	1.5	2.5
	0.06	13.4	13.2	12.8		2.2	2.3	4.4
	0.10	29.2	28.8	27.8		3.1	3.1	5.7
AAPD# =		21.5	20.7			33.0	32.9	

#AAPD is Absolute Average Percent Deviation

* K & E -- Kent and Eisenberg Model

developed. For mixtures, the prediction of the partial pressures by both models worsens with increasing loadings of CO₂ and H₂S and with decreasing temperature. However, overall the new model performs better than the Kent-Eisenberg model.

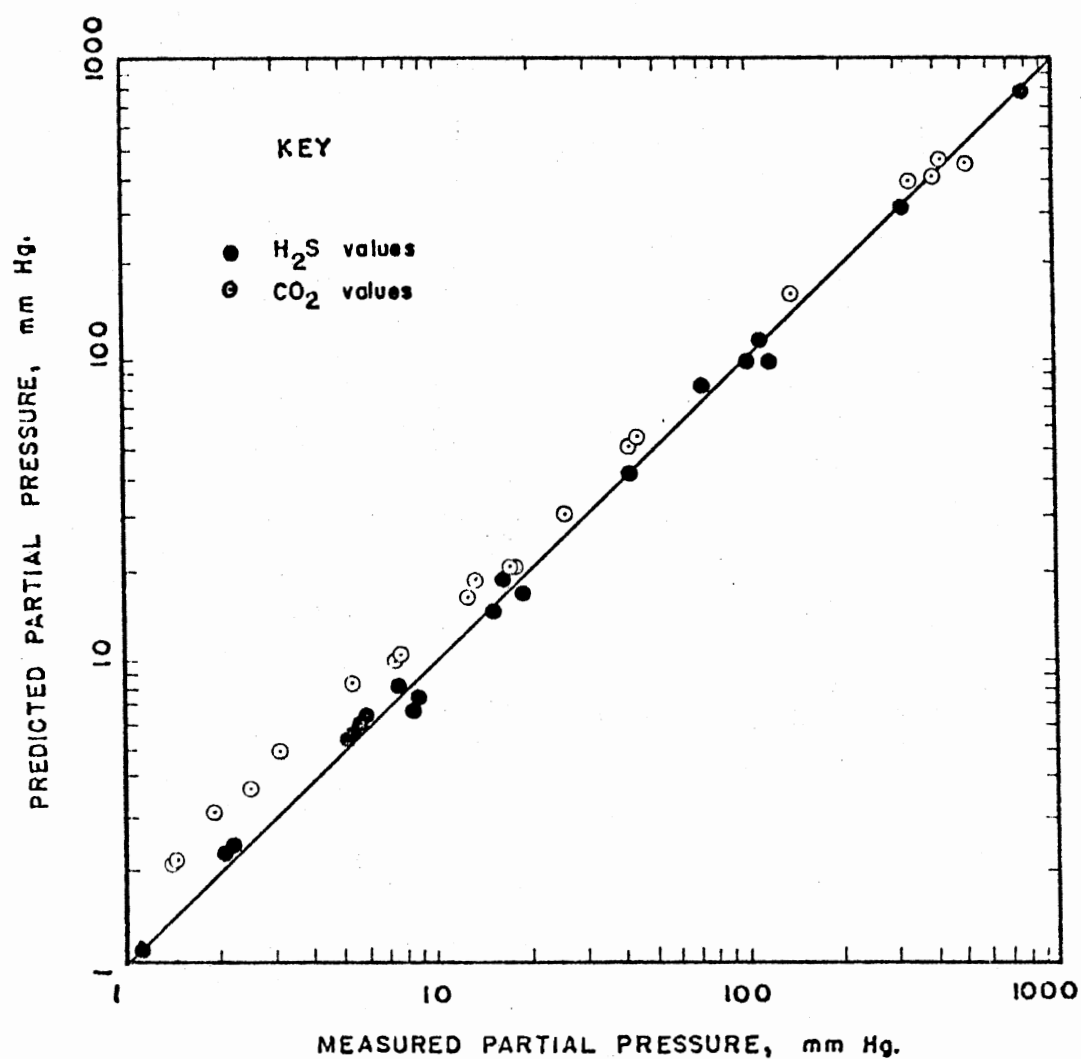


Figure 11. Comparison of Predicted and Measured Values for H_2S and CO_2 Partial Pressures Over 2.5N MEA Solution at 40 C

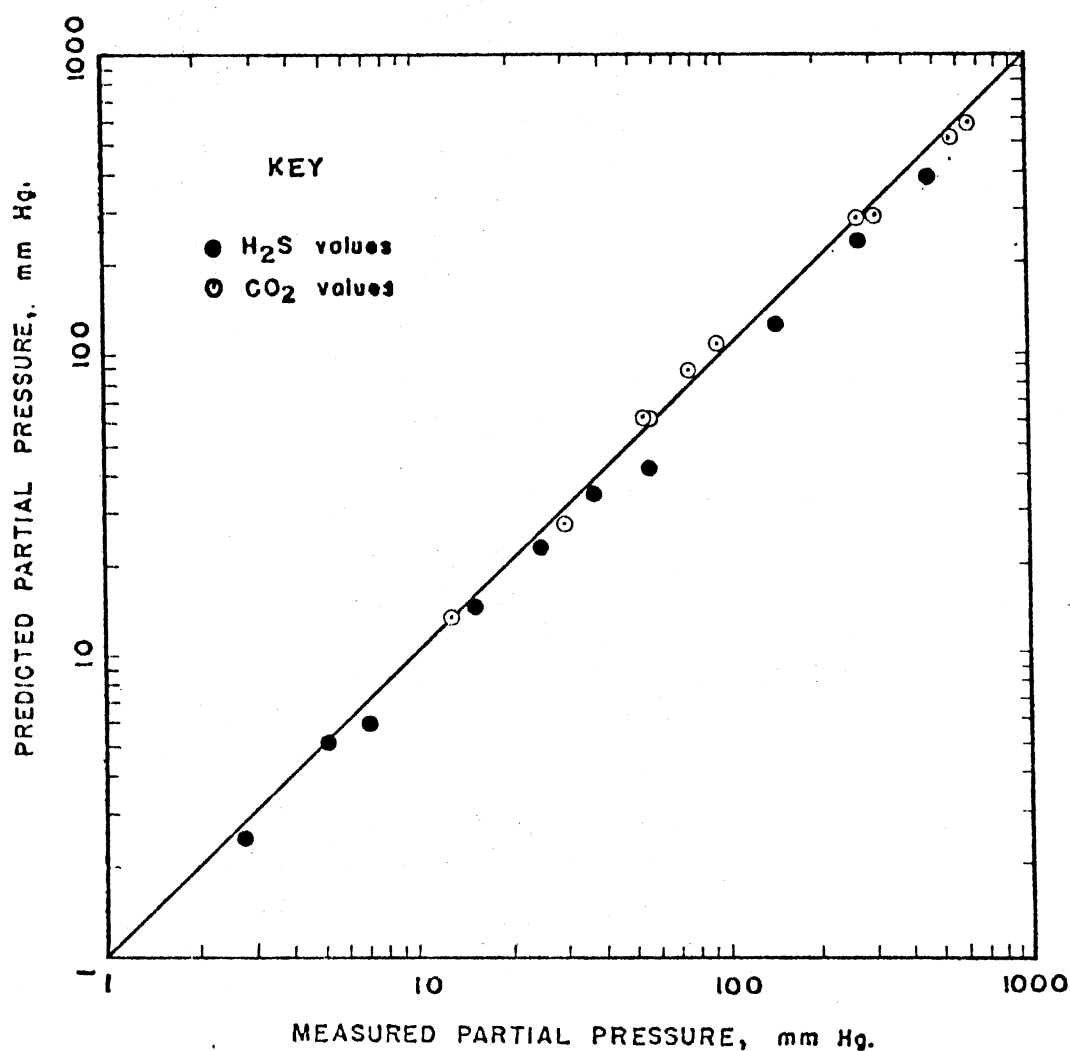


Figure 12. Comparison of Predicted and Measured Values for H₂S and CO₂ Partial Pressures Over 2.5N MEA Solution at 100 C

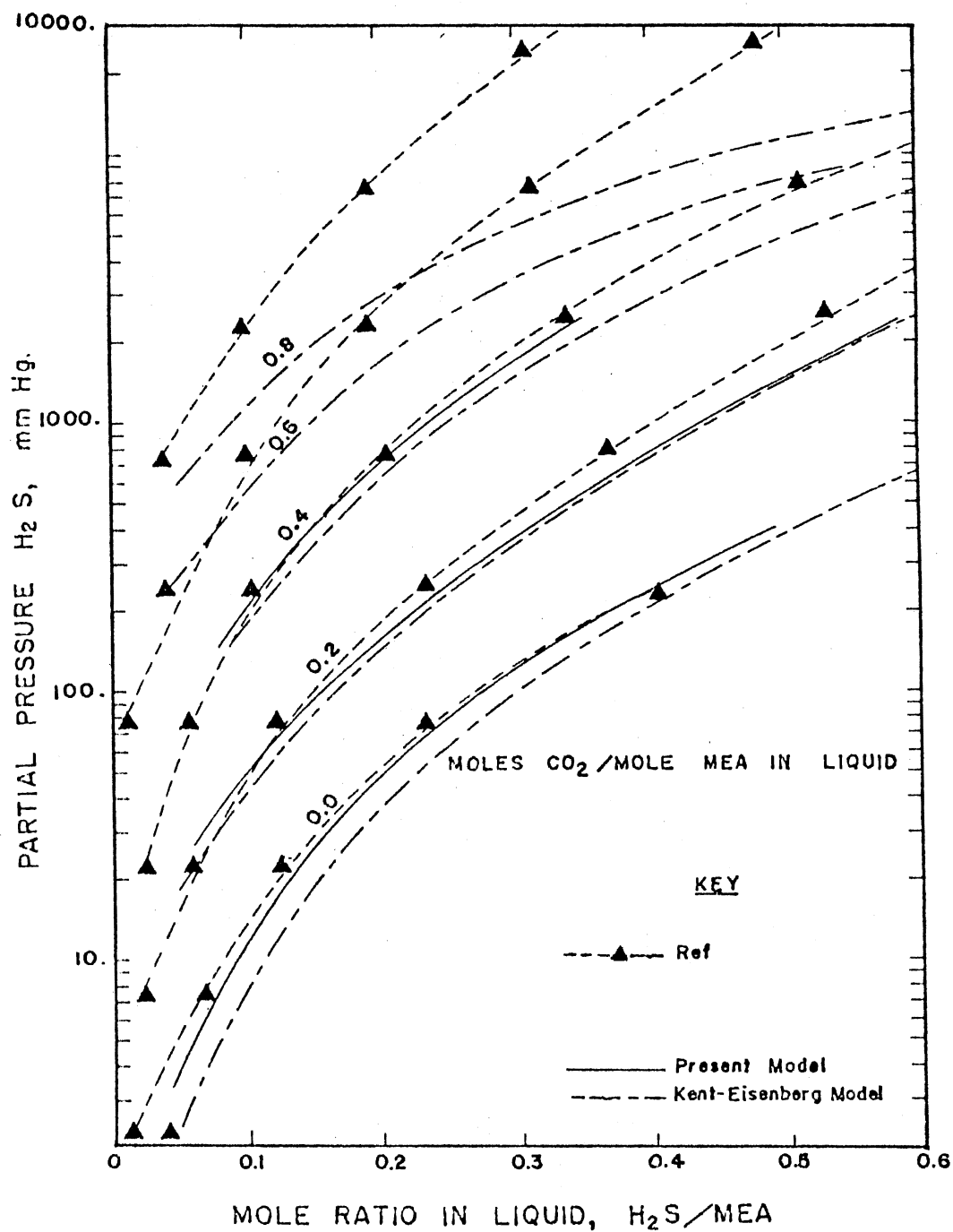


Figure 13. Comparison of Predicted and Measured Values for H_2S Partial Pressures Over 2.5N MEA Solution at 100 C

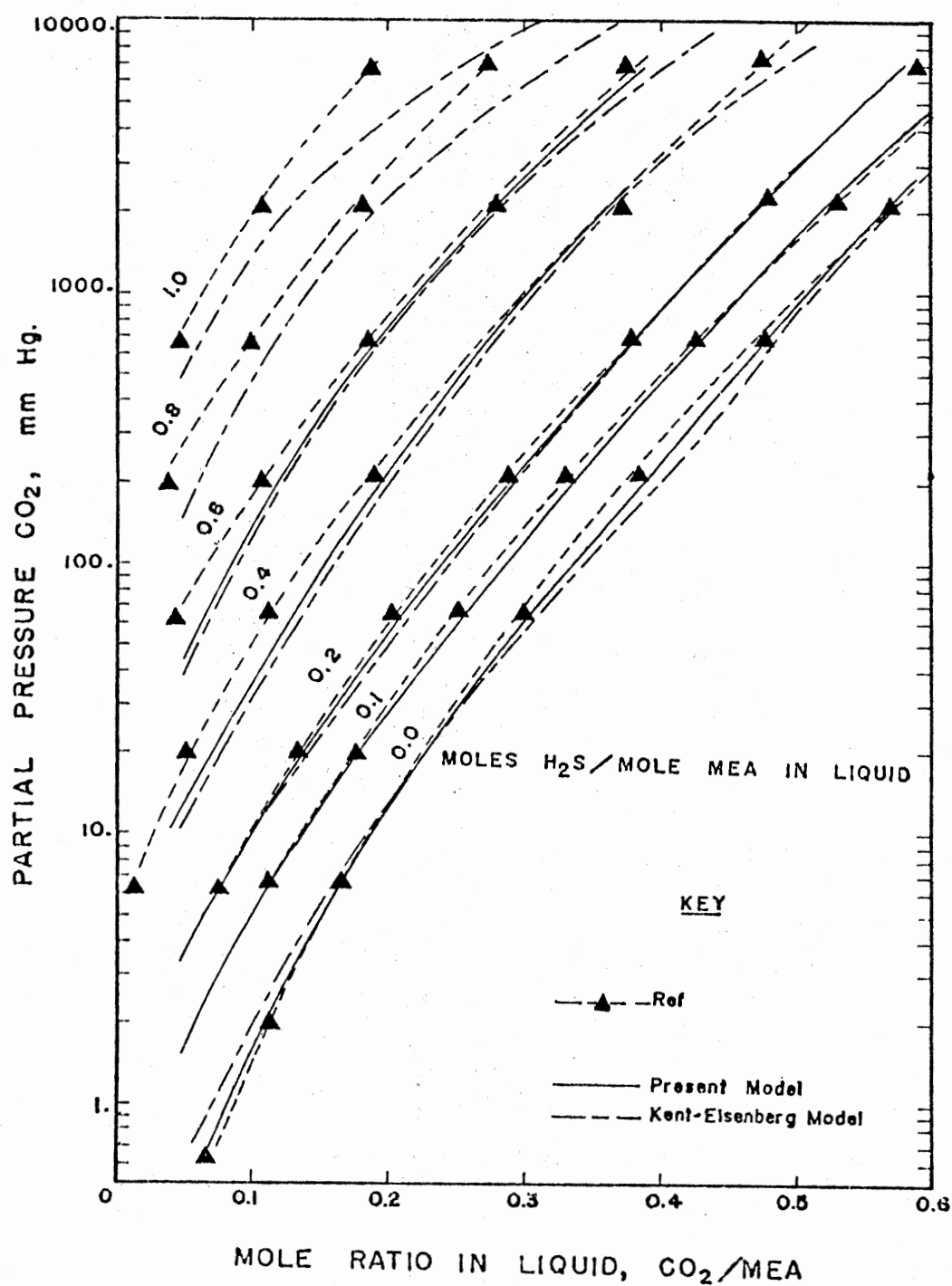


Figure 14. Comparison of Predicted and Measured Values for CO₂ Partial Pressures Over 2.5N MEA Solution at 100 C

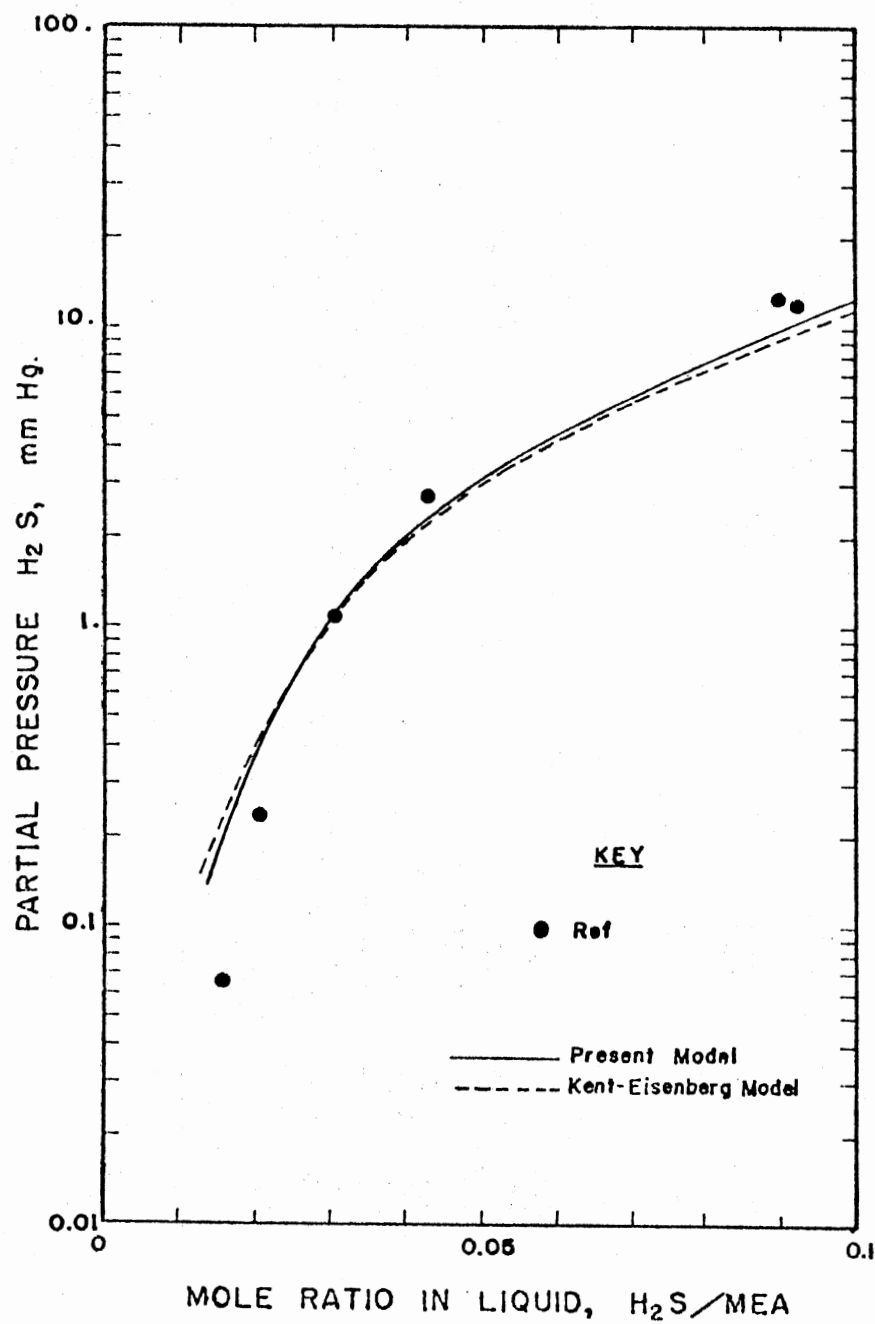


Figure 15. Comparison of Predicted and Measured Values for H₂S Partial Pressures Over 2.5N MEA Solution at 100 C (Low Pressure Data)

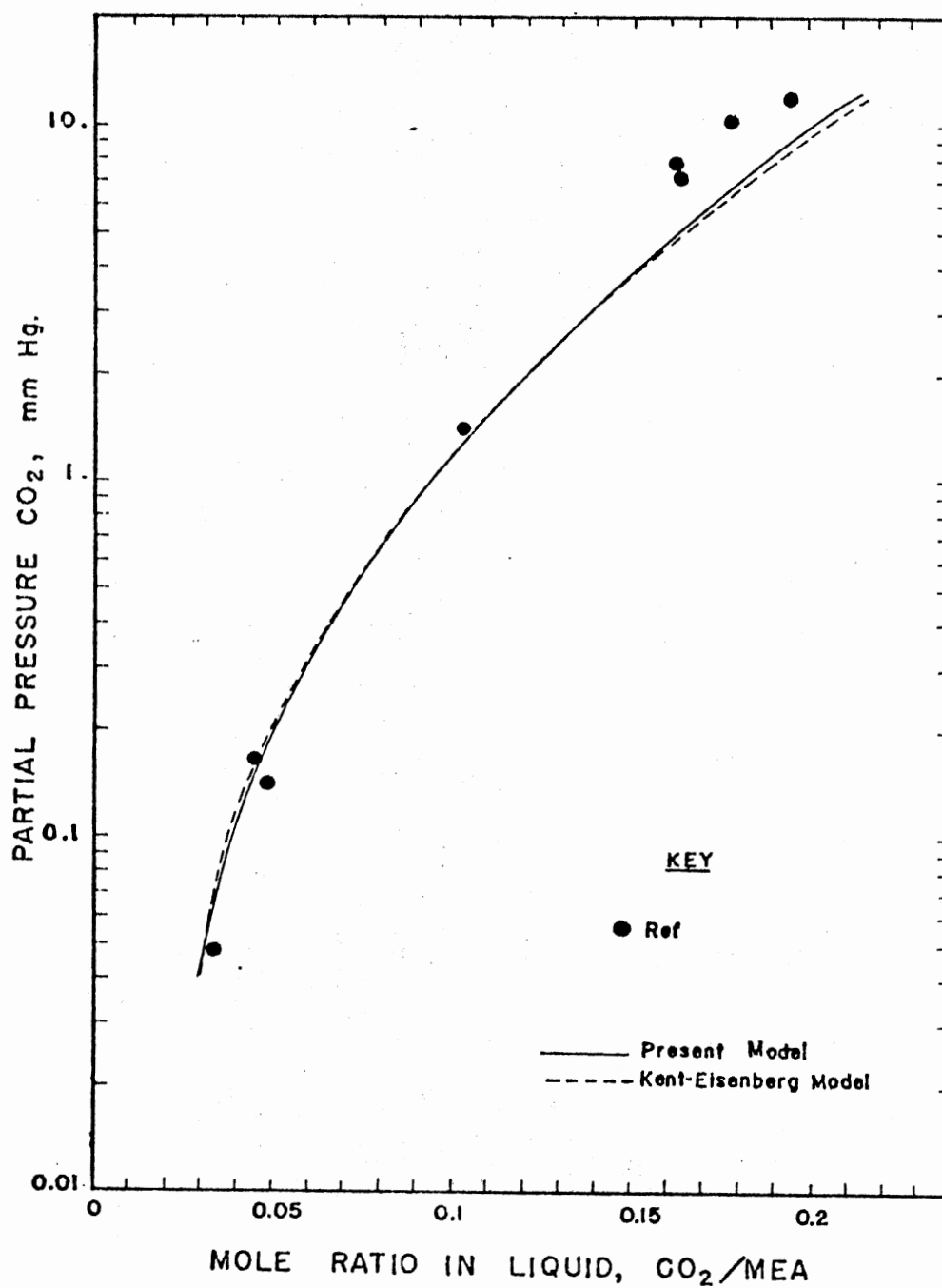


Figure 16. Comparison of Predicted and Measured Values for CO₂ Partial Pressures Over 2.5N MEA Solution at 100 C (Low Pressure Data)

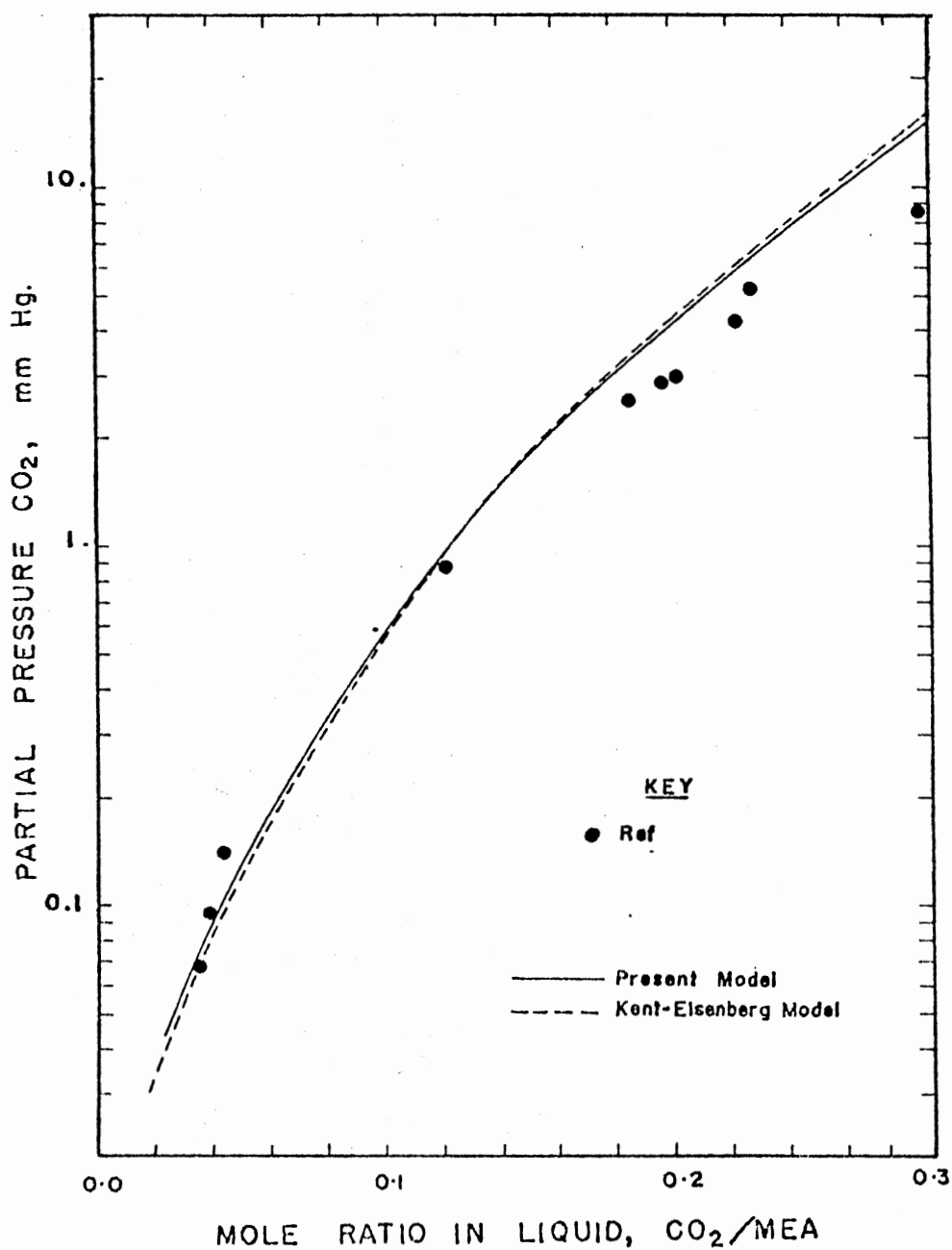


Figure 17. Comparison of Predicted and Measured Values for H₂S Partial Pressures Over 2.5N MEA Solution at 80 C (Low Pressure Data)

TABLE II
SUMMARY OF DEVIATION ERRORS BETWEEN CALCULATED AND
MEASURED H₂S AND CO₂
PARTIAL PRESSURES FOR MEA
SOLUTIONS

System	No. of pts	ABS. AVG. PCT. DEVIATION				Remark
		H2S		CO2		
		part. press.		part. press.		
		K & E	This Model	K & E	This Model	
MEA-H2S-H2O at 40 and 100 C	32	2.8	1.5	-	-	
MEA-CO2-H2O at 40 and 100 C	26	-	-	19.8	18.1	
MEA-CO2-H2S-H2O at 40 and 100 C	31	26.9	25.9	44.7	39.5	3
MEA-CO2-H2S-H2O at 100 C	10	18.7	13.7	8.5	9.2	
MEA-CO2-H2S-H2O at 40 C	20	15.9	10.8	27.7	31.6	
MEA-CO2-H2S-H2O at 100 C	14	20.7	21.5	32.3	32.7	1
MEA-CO2-H2S-H2O at 100 C	50	39.9	41.4	52.1	52.5	2
MEA-H2S-H2O at 40 and 100 C	7	19.7	19.6	-	-	
MEA-CO2-H2O at 40 and 100 C	19	-	-	46.2	45.7	1 and 2

- 1 - low pressure (< 30 mm. Hg) data.
 2 - low pressure (< 30 mm. Hg) raw data, include several points with very high percent deviations.
 3 - includes a few points with very high percent deviation.
 K & E - Kent and Eisenberg model.

Diethanolamine

Aqueous solutions of DEA have been used for many years for treatment of refinery gases containing appreciable amounts of COS and CS₂, besides H₂S and CO₂. The low vapour pressure of diethanolamine makes it suitable for low pressure operations as vaporization losses are quite negligible. The S.N.P.A-DEA (29) process is responsible for the growing popularity of DEA. The S.N.P.A.-DEA process has been widely accepted and is at present the preferred choice for the treatment of high pressure natural gases with high concentrations of acidic components especially if COS and CS₂ are also present in appreciable amounts. Younger (41) reports that in the last ten years nearly all the new sour gas processing plants in Canada have either used DEA or Sulfinol. Compared to MEA, the solubility data for DEA are few. The most usable collections are those of Lee et al. (37, 38, 42), Atwood (6), Leibush and Schneerson (2), and Mason and Dodge (5). Recently some mixture data have been presented by Lawson and Garst (39).

Over the range of temperatures and solution concentrations considered in the comparisons (up to 1 mole CO₂ or H₂S/mole Amine, and 120 °C) the predictions of both the models are in good agreement with the data from various literature sources. The major discrepancy is at the lower temperatures especially at 0 °C. However the deviation of the predicted values of the partial pressure from the experimen-

tal values shown in Figures 18 and 19 are smaller in the case of the present model than the Kent-Eisenberg Model. These figures further support the competitiveness of the new model. Table III provides a summary of deviation errors between measured and calculated partial pressures of acid gases for DEA solutions at various temperatures.

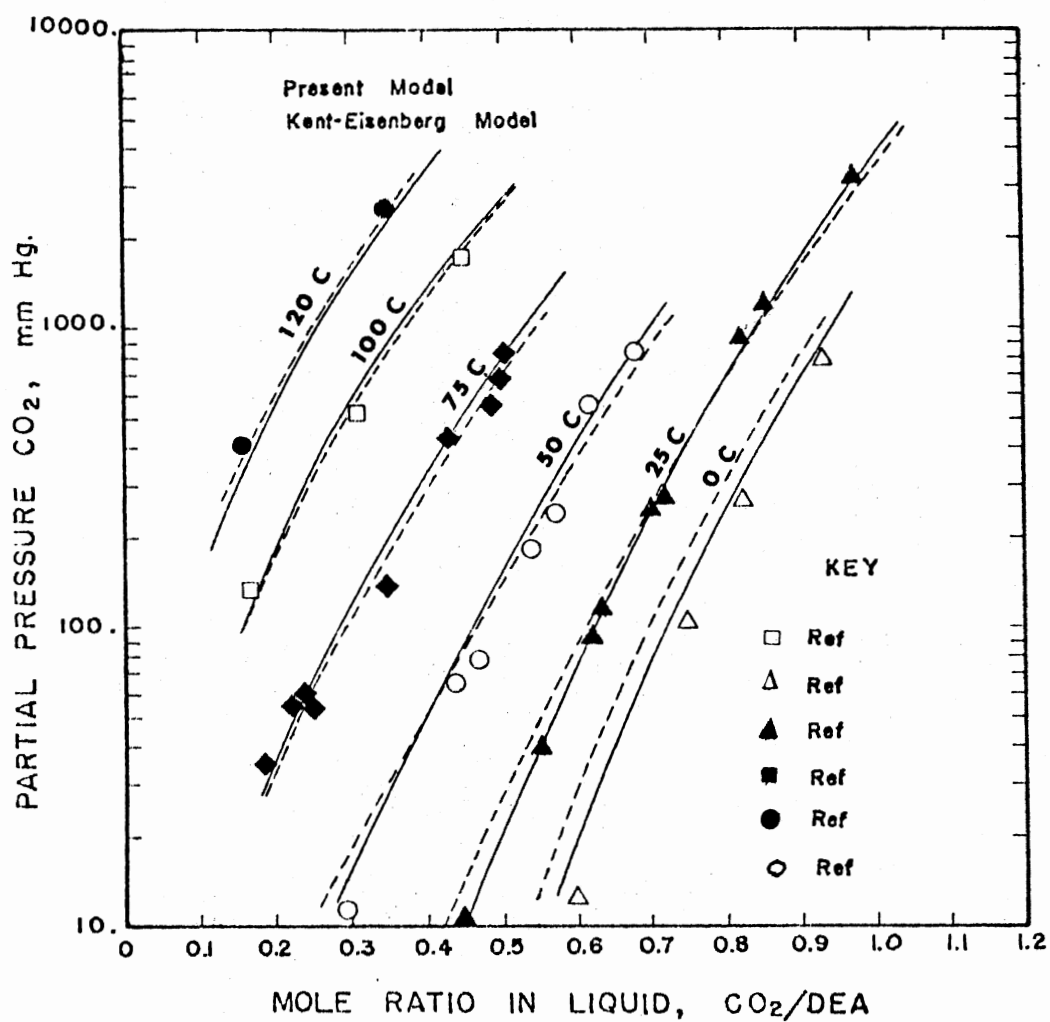


Figure 18. Comparison of Predicted and Measured Values of CO₂ at Various Temperatures in 2.0N DEA Solution

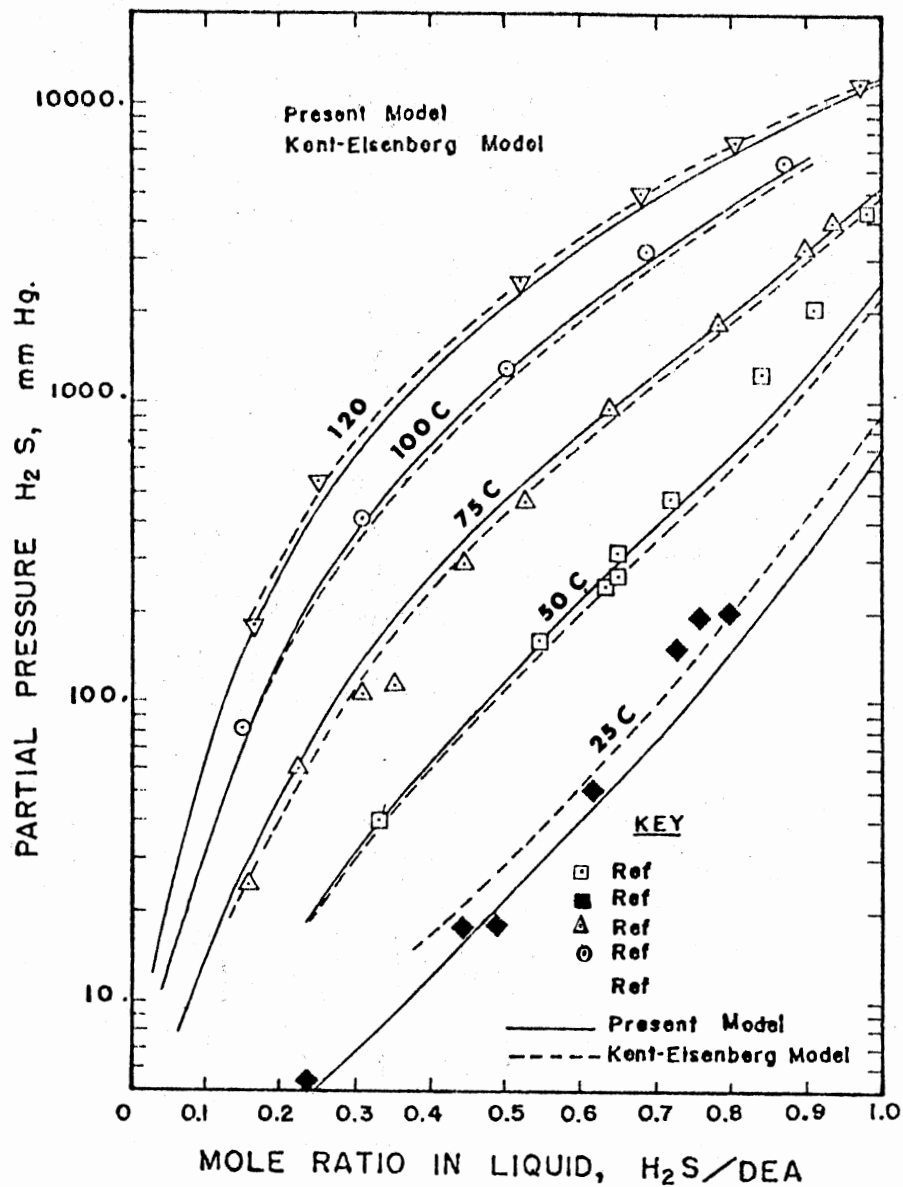


Figure 19. Comparison of Predicted and Measured Values of H_2S at Various Temperatures in 2.0N DEA Solution

TABLE III
SUMMARY OF DEVIATION ERRORS BETWEEN CALCULATED AND
MEASURED H₂S AND CO₂
PARTIAL PRESSURES FOR DEA
SOLUTIONS

System	No. of pts	ABS. AVG. PCT. DEVIATION				Remark
		H2S		CO2		
		part. press.		part. press.		
		K & E	This Model	K & E	This Model	
DEA-H2S-H2O (0 to 120 C)	38	20.5	24.6	-	-	
DEA-CO2-H2O (0 to 120 C)	34	-	-	26.2	20.8	
DEA-H2S-H2O (0 to 120 C)	29	32.4	2.3	-	-	1

1 - represents data at high loadings
(>1 mol H₂S or CO₂/mol amine)
K & E - Kent and Eisenberg model.

Diisopropanolamine

Diisopropanolamine (DIPA) has been widely used in Europe for removal of acid gases from synthesis gas and from refinery gases and liquids. It is used in the ADIF process, the Sulfinol process and the SCOT process, all licensed by Shell. DIPA solutions are reported to be less corrosive than MEA or DEA solutions, have a greater selectivity for H_2S over CO_2 than MEA or DEA and can remove COS without excessive degradation of the solution. It is also reported to have low regeneration steam requirements.

Few solubility data for the acid gases in DIPA solutions have been published until recently. The only data provided are by Isaacs et al. (43, 44). As before the partial pressure data for the ternary systems, H_2S -DIPA- H_2O and CO_2 -DIPA- H_2O were used to obtain K_1 and K_2 . Figures 20 and 21 are the results of fitting the equilibrium models. Surprisingly there is very little difference between the predictions of the two models. Their prediction capability is worst at higher acid gas loadings. There is some scatter in the data at the lower temperature at loadings between 0.5 to 0.7 moles CO_2 or H_2S /mole Amine. However, further justification from other data is required before these data can be rejected.

Figures 22, 23, 24 and 25 show data comparisons for the solubility of mixtures of acid gases at 40 and 100 deg C over 2.5N DIPA solutions. The predictions are satisfactory

over most of temperature and concentration ranges over which data has been reported. The present model is seen to be at least comparable to the Kent-Eisenberg model, as can be seen from Table IV, which gives summaries of deviation errors for different sets of data for this system.

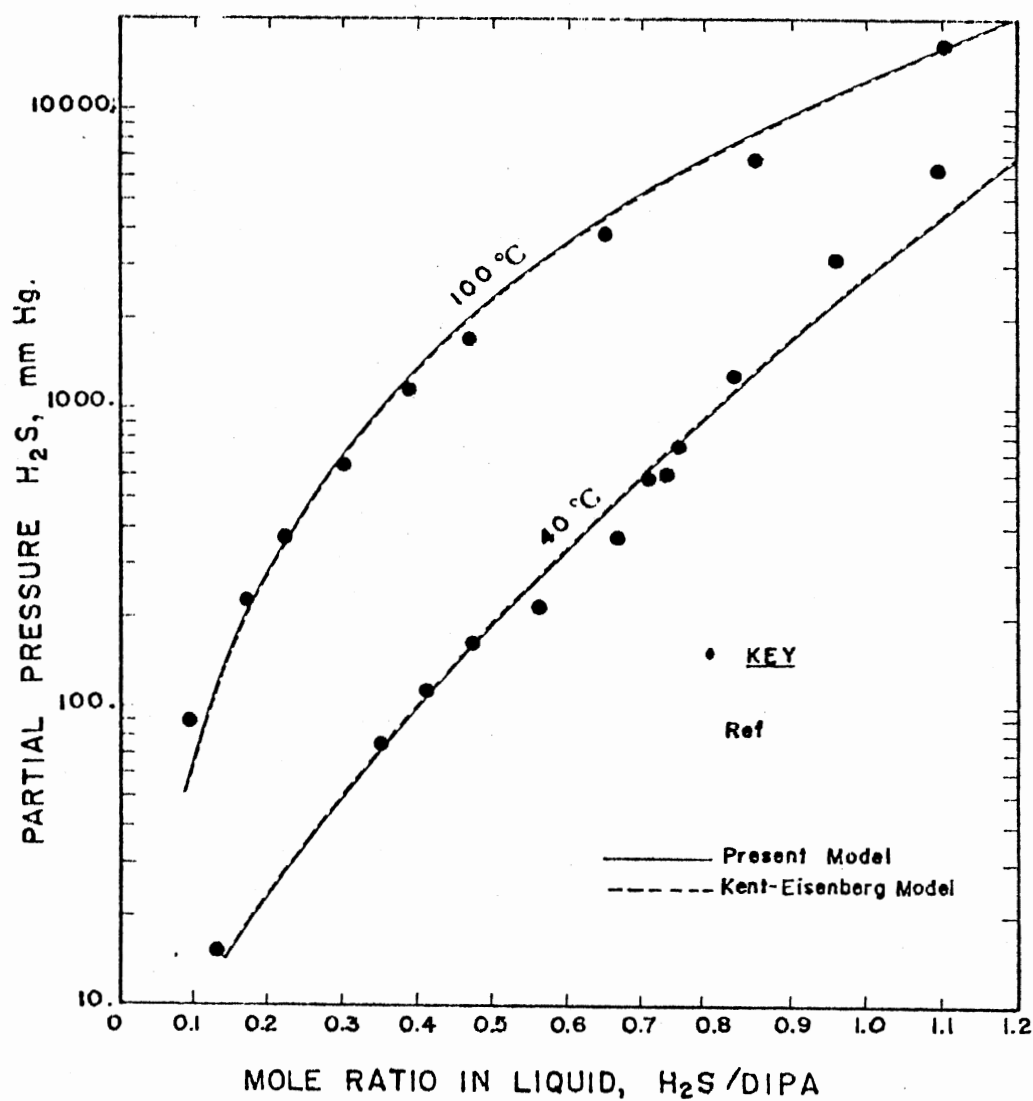


Figure 20. Comparison of Predicted and Measured Values of H_2S Partial Pressures Over 2.5N DIPA Solution at 40 and 100 C

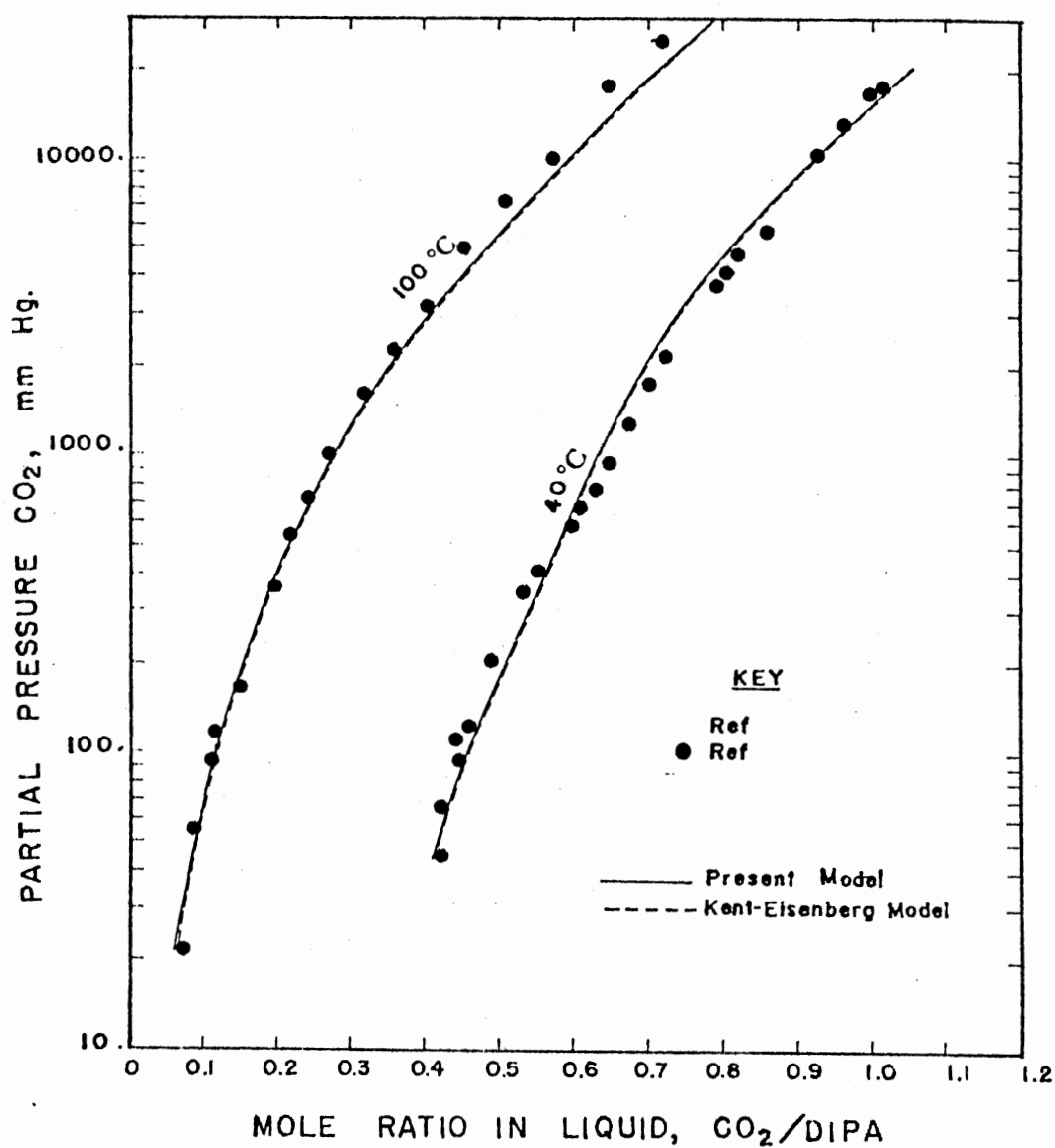


Figure 21. Comparison of Predicted and Measured Values of CO₂ Partial Pressures Over 2.5N DIPA Solution at 40 and 100 C

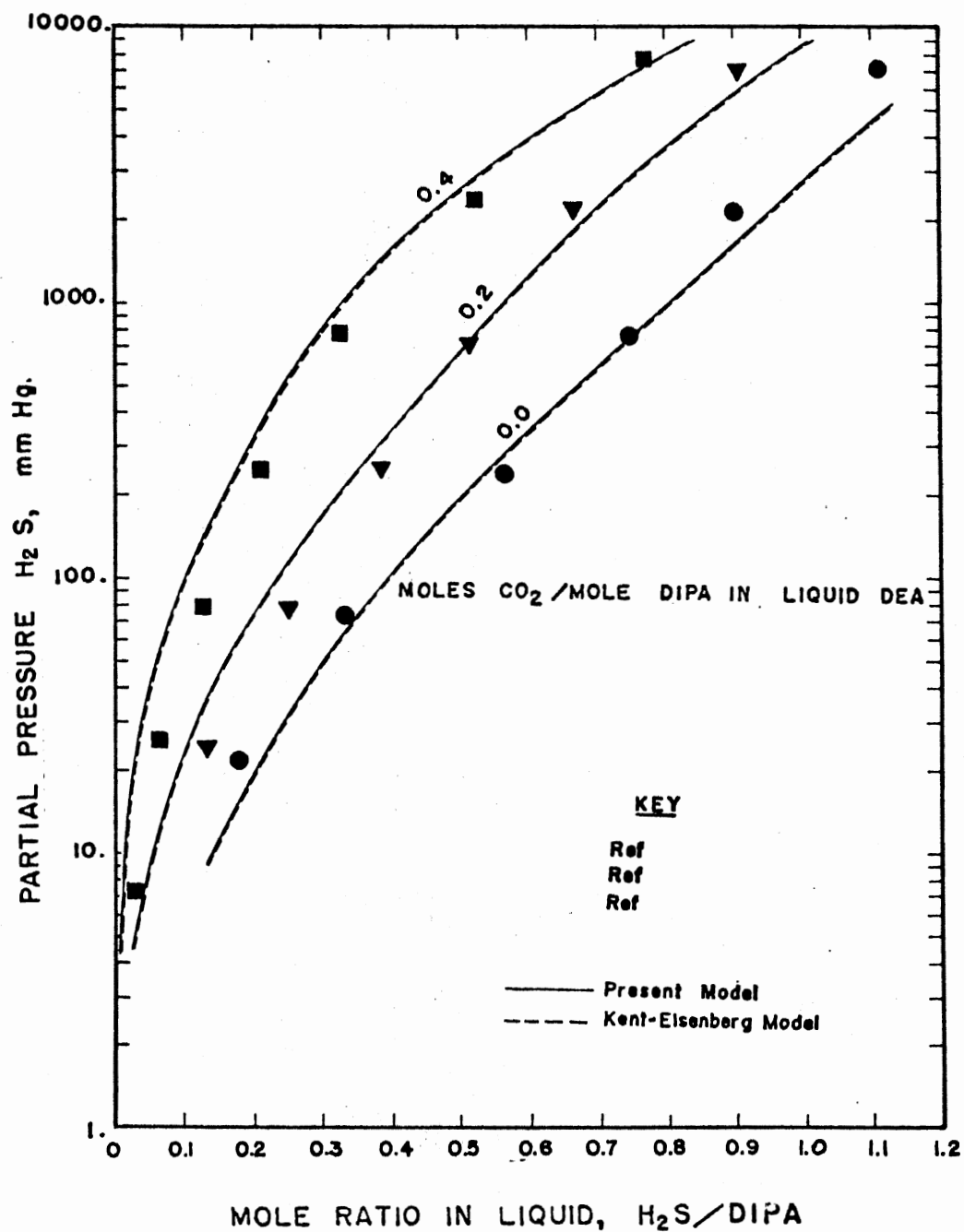


Figure 22. Comparison of Predicted and Measured Values of H_2S Partial Pressures Over 2.5N DIPA Solution at 40 C

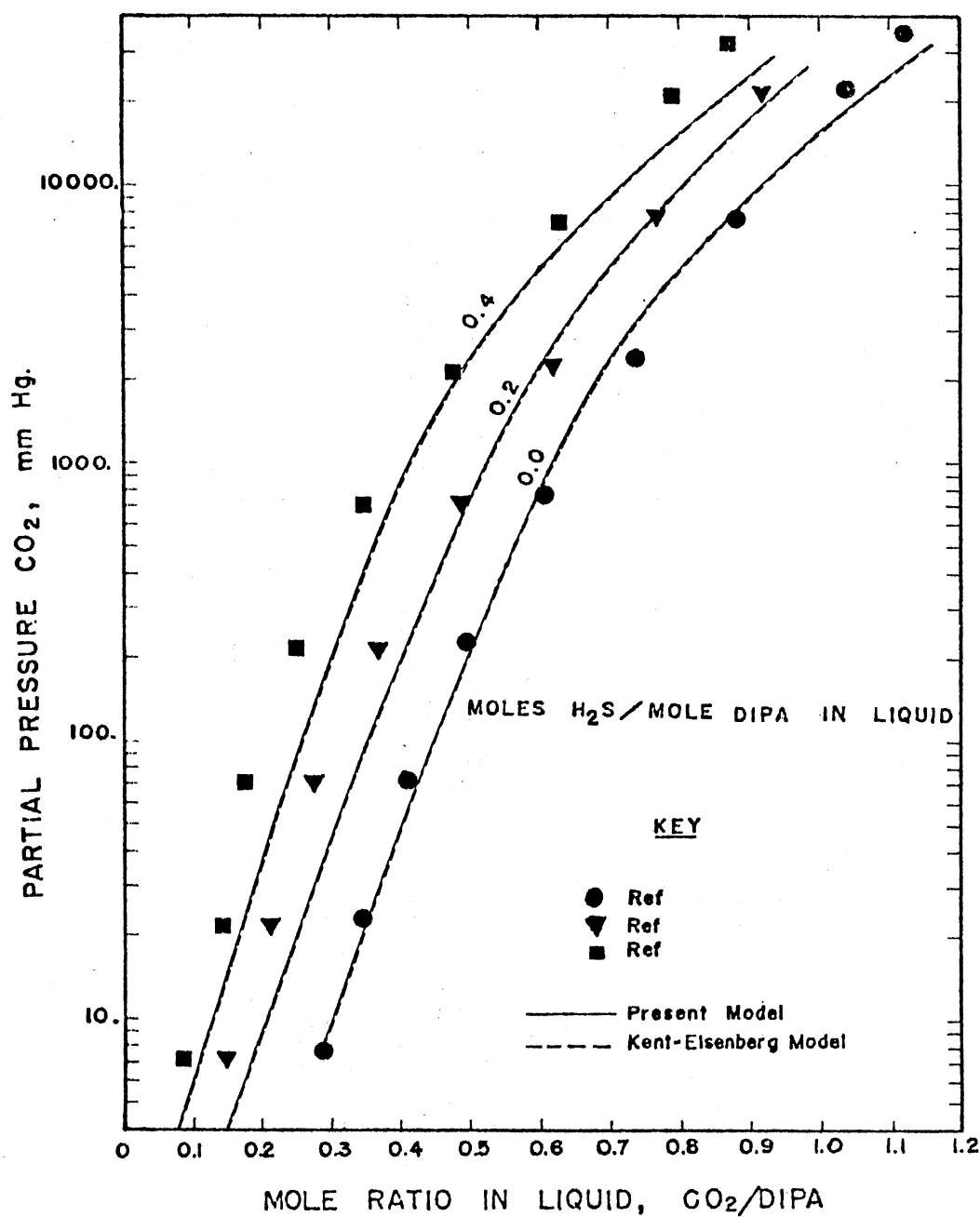


Figure 23. Comparison of Predicted and Measured Values of CO₂ Partial Pressures Over 2.5N DIPA Solution at 40 C

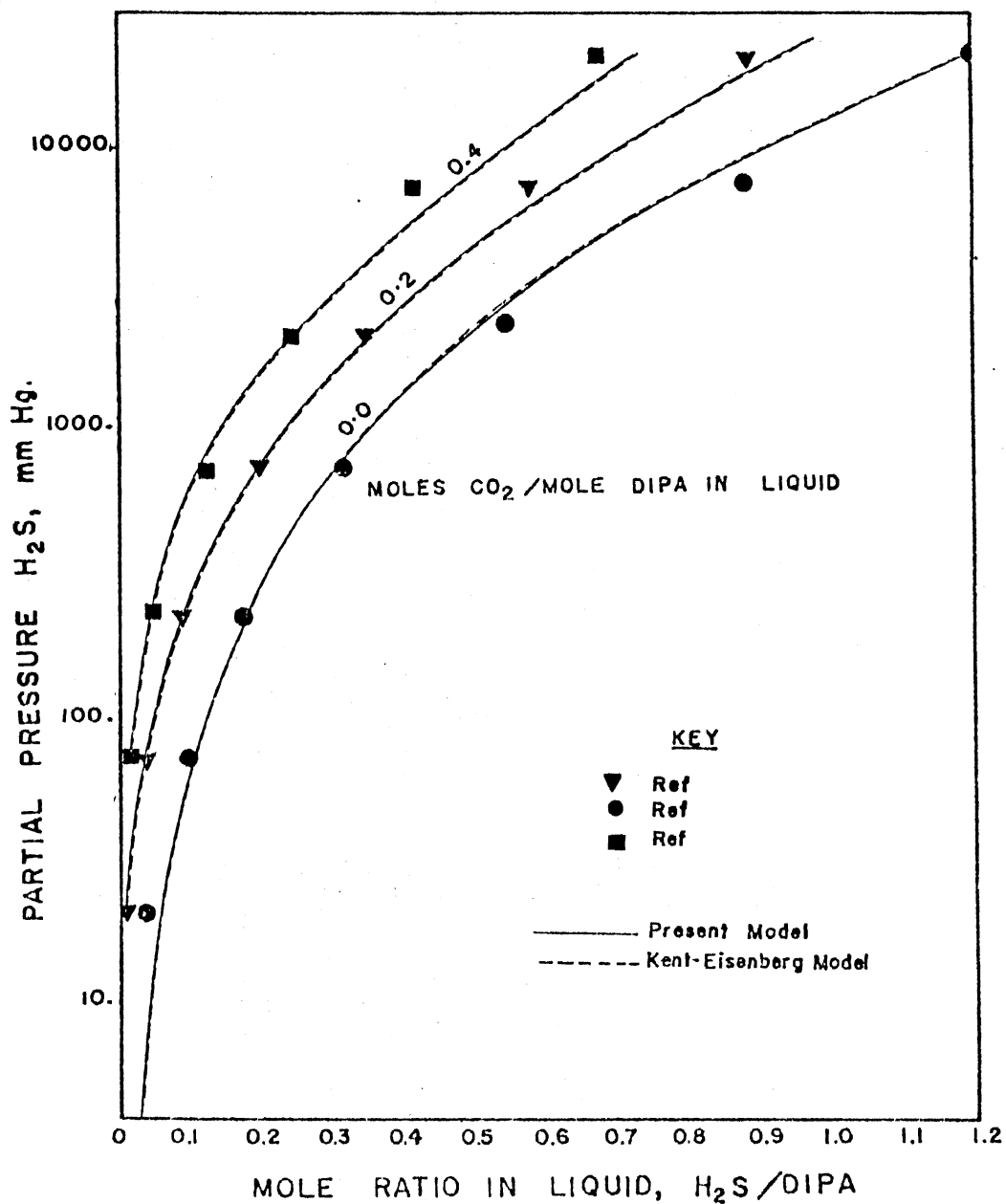


Figure 24. Comparison of Predicted and Measured Values of H_2S Partial Pressures Over 2.5N DIPA Solution at 100 C

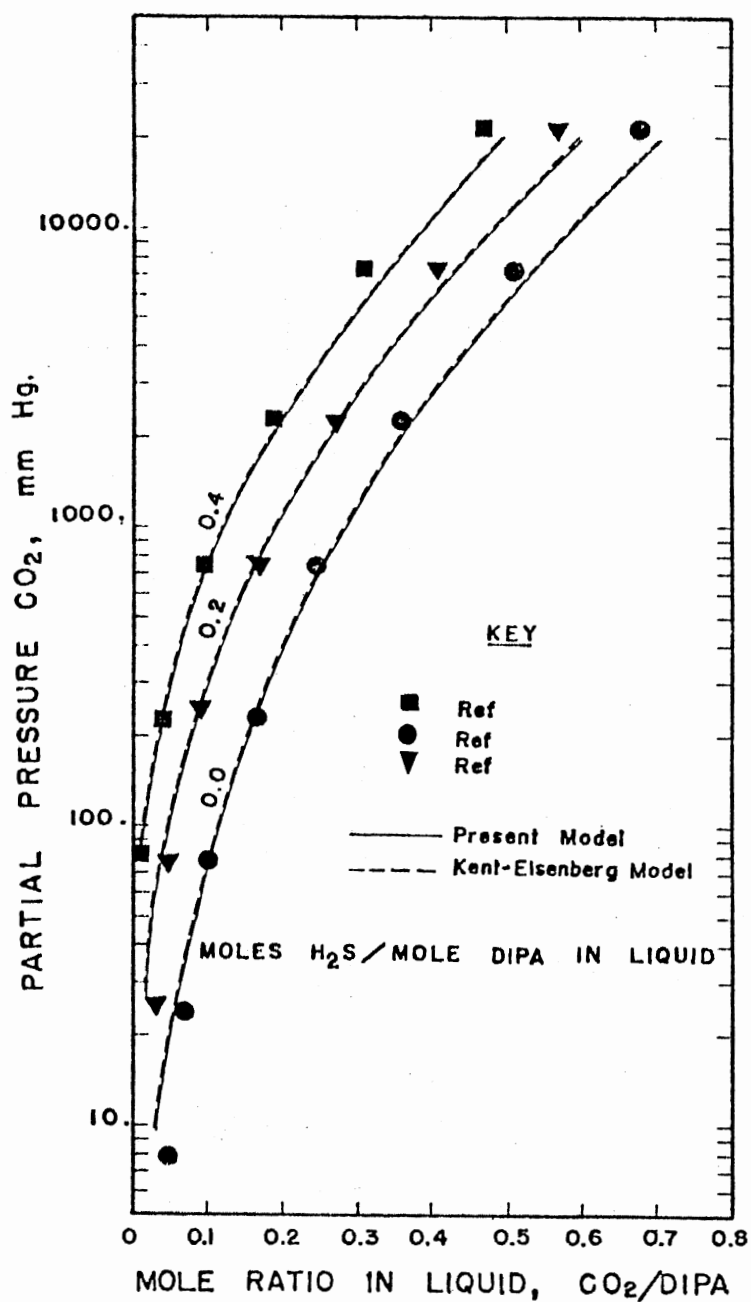


Figure 25. Comparison of Predicted and Measured Values of CO₂ Partial Pressures Over 2.5N DIPA Solution at 100 C

Diglycolamine

The process employing this solvent is the Fluor Econamine process. The use of Diglycolamine (DGA) was patented by Blohm and Riesenfeld (45). DGA is $\beta\beta'$ -hydroxyaminoethyl ether and has the same molecular weight as diethanolamine. However, it has the reactivity of primary amines with a much lower vapor pressure than MEA. The only source of solubility data for this system in the literature is one by Martin et al. (46). Solubility data for mixtures of acid gases in DGA solutions are not available.

Figures 26 and 27 show the comparisons of predicted and experimental solubility for the single acid gas (H₂S or CO₂) systems at 100 and 50 deg C. The summary of deviation errors for this amine is tabulated in Table IV. The agreement between the measured and calculated partial pressures is reasonable considering the scatter in the data. The predictions of both models are almost identical. More accurate data are needed before any definite conclusions can be drawn.

The present model and the Kent-Eisenberg model are adequate for predicting the vapor liquid equilibrium of CO₂-H₂S-Ethanolamine-H₂O systems especially for the temperature and concentration ranges commonly encountered in operating plants. The superiority of the new model has been established in the case of the basic amines (MEA and DEA). In the case of the other amines the performance of the model is at least comparable to the Kent-Eisenberg model.

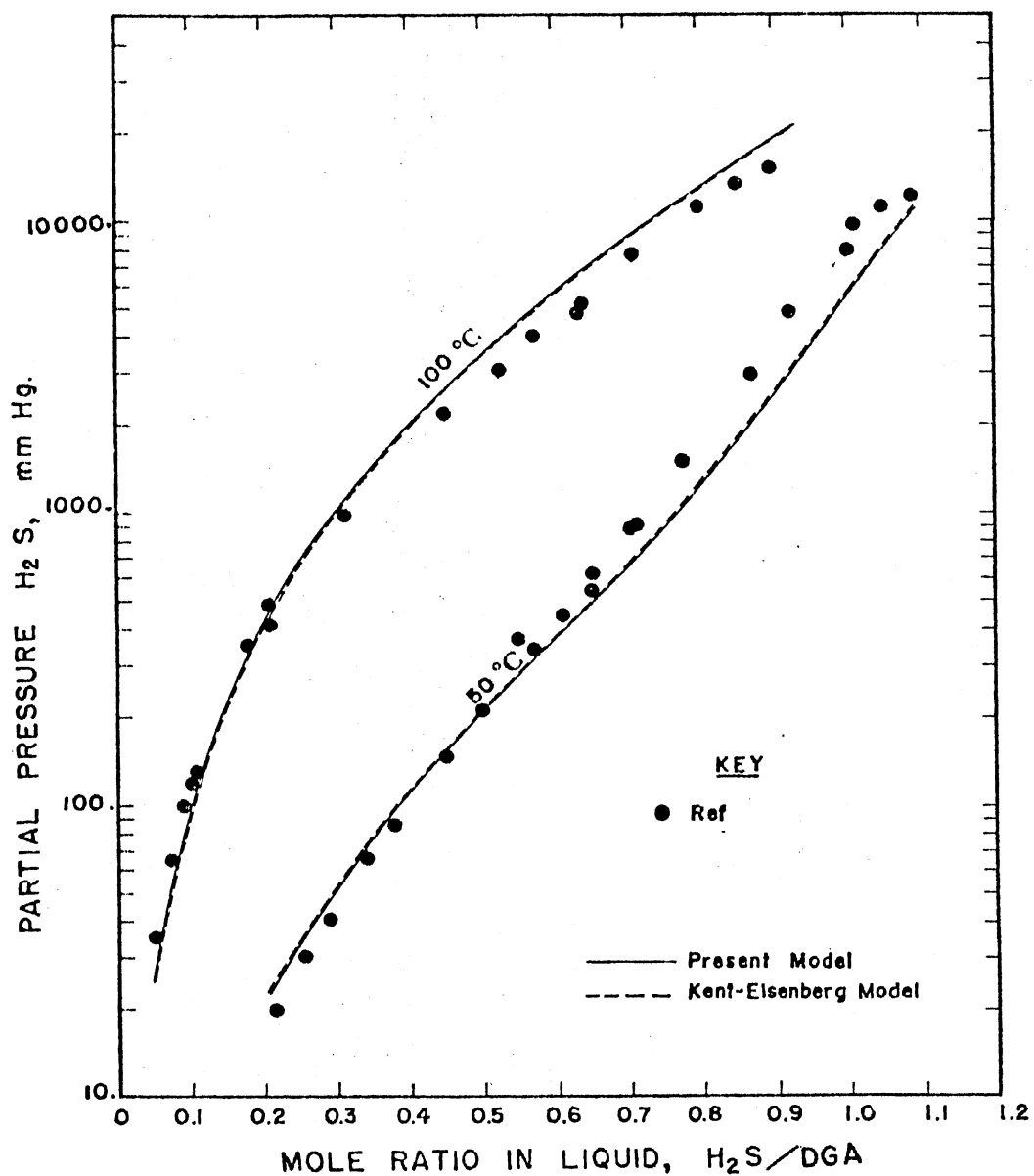


Figure 26. Comparison of Experimental and Predicted Solubility of H_2S in 60% by Weight DGA Solution at 50 and 100 C

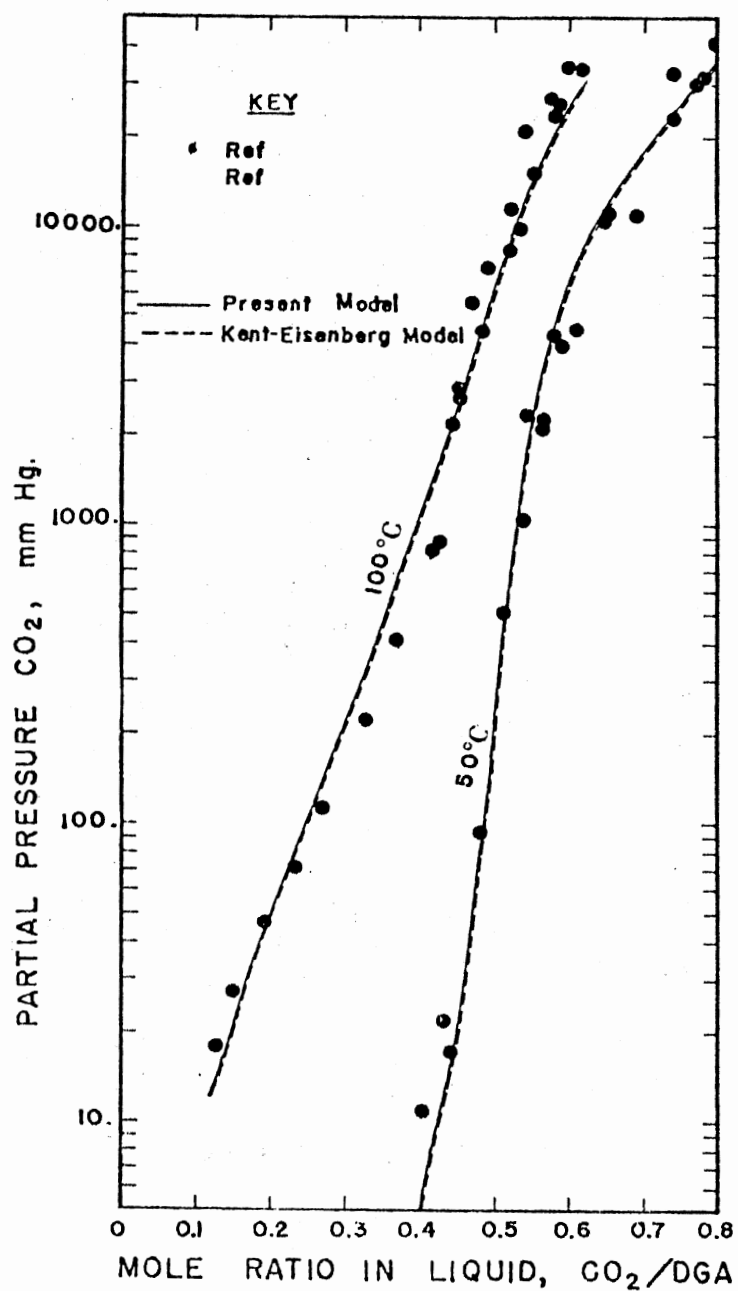


Figure 27. Comparison of Experimental and Predicted Solubility of CO₂ in 60% by Weight DGA Solution at 50 and 100 C

TABLE IV
SUMMARY OF DEVIATION ERRORS BETWEEN CALCULATED AND
MEASURED H₂S AND CO₂
PARTIAL PRESSURES FOR DGA
AND DIPA

System	No. of pts	ABS. AVG. PCT. DEVIATION				Remark
		H2S		CO2		
		part. press.		part. press.		
		K & E	This Model	K & E	This Model	
DGA-H2S-H2O at 50 and 100 C	39	23.2	23.1	-	-	
DGA-CO2-H2O at 50 and 100 C	46	-	-	28.5	28.8	
DIPA-H2S-H2O at 40 and 100 C	24	17.2	17.2	-	-	
DIPA-CO2-H2O at 40 and 100 C	45	-	-	26.3	25.1	
DIPA-CO2-H2S-H2O at 40 C	21	40.1	40.7	-	-	1 and 2
DIPA-CO2-H2S-H2O at 40 C	26	-	-	37.1	36.9	2 and 3
DIPA-CO2-H2S-H2O at 100 C	20	22.2	22.2	-	-	1
DIPA-CO2-H2S-H2O at 100 C	25	-	-	51.4	51.3	2 and 3

1 - The CO₂ partial pressure was not tabulated
in literature source

2 - The H₂S partial pressure was not tabulated
in literature source

3 - includes a few points with very high
percent deviation.

K & E - Kent and Eisenberg model.

The Amine Process Model

The Amine Process Model was developed in the preceding chapters. The model is based on rigorous mathematical calculations of the heat and material balances. In order to check the calculations of the model a comparison with operating data in commercial installations treating natural gas is desirable. However such data are not readily available. Moreover, information on the concentration of regenerated amine or the sweet gas composition at the top of the contactor is seldom available at the accuracy level required. Plant test data are often incomplete and are always difficult to obtain. However operating data from a large commercial natural gas treating plant (53) was obtained. Also design data for a gas treating plant using DEA was procured from an established consulting firm (53). These sample problems along with several other commercial data obtained from literature will be briefly discussed. The temperature and concentration profiles are also discussed for two different cases.

Sample Problems

Gas Plant Data. Operating data for a DGA absorber unit processing 216 MMSCFD with an average acid gas content of 5.93% CO₂ and 4.78% H₂S was obtained (53). The raw data obtained over a period of time shows substantial variation and therefore only average values are quoted here. These

TABLE V
DGA ABSORBER COMPARISON WITH OPERATING
PLANT DATA

Absorber specifications :

Gas in at 90 deg F, 134 psia , 6.23% CO₂, 7.10% H₂S
6.2N DGA in at 136 deg F with loadings of
0.0180 mol CO₂/mol DGA, 0.0009 mol H₂S/mol DGA

Sweet Gas specification = 0.25 grains/100 SCF (0.0004%)

Solution Circulation Rate = 0.4437 mol DGA/mol Sour Gas.

Sweet Gas		Rich amine		Rich Amine Temp.	Theoretical Plates	Source
pp, mm. Hg		mol/mol				
CO ₂	H ₂ S	CO ₂	H ₂ S	deg F		
NA#	NA#	0.1537	0.1614	190 ~		Ref (53)
11.00	182.00	0.1552	0.1081	186.4	1	APM*
0.08	31.15	0.1584	0.1520	195.0	2	APM*
0.00	0.62	0.1584	0.1607	197.6	3	APM*
0.00	0.02	0.1584	0.1609	197.8	4	APM*

* APM ---Amine Process Model

~ reported as tray-2 temperature

NA - not available

TABLE VI
DGA ABSORBER COMPARISON WITH OPERATING
PLANT DATA

Absorber specifications :

Gas in at 90 deg F, 134 psia , 5.95% CO₂, 4.78% H₂S
6.2N DGA in at 136 deg F with loadings of
0.0180 mol CO₂/mol DGA, 0.0009 mol H₂S/mol DGA

Solution Circulation Rate = 0.4437 mol DGA/mol Sour Gas.

Sweet Gas		Rich amine		Rich Amine	Theo.	Source
pp, mm. Hg		mol/mol		Temp.	Plates	
CO ₂	H ₂ S	CO ₂	H ₂ S	deg F		
5.80	94.01	0.1504	0.081	180.5	1	APM*
0.01	4.37	0.1521	0.1074	186.98	2	APM*
0.00	0.04	0.1521	0.1086	187.88	3	APM*
0.00	0.01	0.1521	0.1086	188.06	4	APM*

* APM ---Amine Process Model

TABLE VII
DGA REGENERATOR CALCULATIONS FOR
DIFFERENT NUMBER OF
STAGES

Stripper pressure is 20 psia
(taken to be 22.5 psia at top, 27.5 psia in reboiler)

Condenser Temperature, 203 deg F

Steam rate, 1.4 lb. steam/gal DGA

Rich DGA in at 195 deg F with loadings of
0.1584 mol CO₂/mol DGA and 0.1609 mol H₂S/mol DGA

Theo. Stages	Lean Amine mol/mol		Reflux Rate	Lean Amine Temp. deg F	Source
	CO ₂	H ₂ S			
2	0.08186	0.00841	2.93	256.1	APM*
3	0.08304	0.00252	1.49	256.9	APM*
4	0.08323	0.00065	1.01	257.2	APM*

* APM --- Amine Process Model

values are listed in Table V and VI where the absorber comparisons are shown. The rich amine loadings compare reasonably with the plant data. The amine temperature profile resulting from the computer solution indicates a bottom plate temperature of 197.8 deg F. This value cannot be directly compared to the plant data since temperature of only the second tray has been reported (190 F). Nevertheless, the value obtained by calculation seems satisfactory. An intercooler was used, but no operating data was reported. To give an idea of how the rich amine concentrations and temperatures change, the computed values for 1,2 and 3 stages are also tabulated. No residual (sweet) gas concentrations are reported, these were assumed to be reduced to pipeline specifications (0.25 grains per 100 cu. ft. or 0.0004 Mole% H_2S). The operating amine circulation rate (0.4437) corresponds to nearly twice the minimum circulation rate (0.24 lb moles DGA/lb moles gas in.) that was computed.

Table V shows computed results for 1,2,3, and 4 stages for a different acid gas composition in the gas feed. These compositions represent yearly values and therefore no direct comparisons are possible. However, the calculated results are as expected and show a definite trend of increasing rich amine concentration and temperature with an increase in the number of stages.

No stripper data were made available for this plant. For illustration, stripper runs were made with amine feed

concentration the same as that obtained leaving the contactor. The regenerated lean amine loadings and temperatures are shown for 3, 4 and 5 stages in Table VII.

Plant Design Data. Tables VIII and IX summarize the comparisons of the design (53) specifications with the results obtained from typical runs of the Amine Process Model. The data supplied by the designer are not complete and require the assumption of some data. The comparison therefore need to be taken only as an indicator of expected behavior or performance.

The comparison of the two absorber designs indicates some deviations. The rich amine loadings estimated by the designers compare well with the model calculations. The absolute error in the leaving amine temperature calculated by our procedure is 3.8 F. Also, the sweet gas compositions are of the same order of magnitude; however they are closest for 4 theoretical stages. Moreover the degree of absorption of CO₂ is considerably higher in our calculations. A possible reason for this is that our calculations are based on purely equilibrium considerations and the number of stages indicated are theoretical stages. The value of sweet gas temperature is about 0.4 deg F lower than obtained by our calculations. From the absorber computations presented one might be tempted to conclude (i) that the separation is relatively simple and does not require large towers and (ii) that H₂S is more difficult to remove to a given level than

TABLE VIII
DEA ABSORBER COMPARISON WITH DESIGN DATA

Absorber specifications :

Gas in at 90 deg F, 72 psia ,0.8% CO₂, 2.03% H₂S
2.0N (20 wt %) DEA in at 37.8 deg F with loadings of
0.1000 mol CO₂/mol DEA, 0.0100 mol H₂S/mol DEA

Solution Circulation Rate = 0.1075 mol DEA/mol total gas.

Sweet Gas pp, mm. Hg		Rich amine mol/mol		Rich Amine Temp. deg F	Theo. Plates	Source
CO ₂	H ₂ S	CO ₂	H ₂ S			
0.0148	0.303	0.173	0.199	115		Ref 11
3.45	14.88	0.166	0.1626	108.8	1	APM*
0.53	1.85	0.1731	0.1943	110.7	2	APM*
0.23	0.59	0.173	0.1973	111.1	3	APM*
0.23	0.17	0.1739	0.1984	111.1	4	APM*

* APM ---Amine Process Model

TABLE IX
DEA REGENERATOR COMPARISON WITH DESIGN
DATA

Stripper pressure is 28 psia
(taken to be 26 psia at top, 30 psia in reboiler)

Steam rate, 1.1 lb. steam/gal DEA

Rich DEA (2.0N, 20 wt %) in at 203 deg F with loadings
of 0.1652 mol CO₂/mol DEA and 0.2199 mol H₂S/mol DEA

THEO. Stages	Lean Amine mol/mol		Reflux Rate	Lean Amine Temp. deg F	Source
	CO ₂	H ₂ S			
	0.1	0.01	6.98	252.0	REF 53
4	0.01306	0.01878	6.66	252.8	APM*
5	0.0107	0.01542	6.41	252.9	APM*
6	0.00927	0.01337	6.28	252.9	APM*
7	0.00837	0.01204	6.18	252.9	APM*

* APM --- Amine Process Model

CO₂. Both of these deductions are erroneous and need to be revised based on stage efficiencies. This phenomenon is explained further in the footnote ¹ below.

The overall comparison of the "stripper" design with the plant design data is good except for the lean amine loadings predicted by the designer, which are considerably different. The lean amine CO₂ loadings leaving the stripper predicted by our design method are an order of magnitude less than the design data value. One possible reason for the discrepancy may be the steam rate used in our calculations. The designers specify a steam rate of 1.1 lb steam/gal solution, to the reboiler, whereas in our calculations this value was assumed inside the stripper. However the most probable reason for the discrepancy is that the designer "guesstimated" the acid gas loadings. An higher CO₂ loading was apparently picked for a conservative calculation of the

¹Our calculations assume equilibrium stages (100% efficiency), whereas the possibility of using stage efficiencies (eg. Murphree) which are considerably different for CO₂ and H₂S, exists. Such data are generally not available and their use is not practical. This option is included in the program but its use is left entirely to the discretion of the user. On the basis of information presented by Kohl and Riesenfeld (29) Murphree vapor efficiencies of 15% for CO₂ and 45% for H₂S are typical. Also efficiencies in such absorbers can vary markedly with stage location by as much as a factor of 10 or more. However, these efficiencies are determined to a major extent by the rates of reactions of the solutes with the ethanolamine in the liquid phase. Since the reaction rate is much faster in the case of H₂S, the Murphree vapor efficiency for H₂S is expected to be considerably higher. This however, may or may not be true when both H₂S and CO₂ are present. The rate phenomenon affecting the efficiencies is distinct from the equilibrium phenomenon

amine circulation rate. The temperature of overhead vapor from regenerator is overestimated by 4 deg F by our calculations whereas the reboiler temperature (or lean amine temperature) is underestimated by 3 deg F. The calculational run with five theoretical stages (including reboiler and condenser) is closest in comparison to the design. The reflux ratio (lb moles steam/lb mole acid gas) calculated at the top of the regenerator indicates a deviation of 10% from the design value.

Maddox Example. Maddox (11,47,48) has discussed the preliminary design of an amine sweetening plant in the form of sample problems. Design information (59) that allows estimation of the unregenerated portion of the amine stream leaving the regenerator is used to work out an illustrative problem in detail. Table X compares the example problem results with those calculated using the Amine Process Model. As reported in an earlier paper (19) the agreement between the two sets of calculations is excellent. The only area of significant disagreement is the temperature of the amine leaving the contactor. This difference is undoubtedly due to the fact that infinite dilution heats of reaction were used in the book example while the computer program generates heats of reaction for each stage of the contactor using the amine loading and the gas partial pressures that exist on that stage.

governing the solubilities (29).

Table XI shows a comparison of the regenerated amine residual acid gas composition from the example and the computer program. Two different numbers of theoretical stages are shown for the regenerator in order to provide a comparison. With six theoretical stages (plus reboiler) in the regenerator there is good agreement between the two calculations for the loading in the regenerated amine.

Typical Stripper Run. Maddox (11) discusses the principal problems in the design of a stripper in the form of a sample problem. The temperatures in the stripper are governed by the operating pressure. This source states the recommended ranges of temperature in the stripper. The ranges of other parameters as used in industry are also quoted. An Amine Process Model run calculates values that compare well with the indicated range of temperatures and amine loadings of the sample problem. Table XII compares the results of the simulation model with the sample problem. The reflux ratio calculated by the model is in error by only 6%. The resultant error in condenser heat duty is approximately 12%. The temperature is overpredicted by less than 1 deg F. The program calculates the volumetric vapor flow rate at both the top and bottom of the stripper. As may be expected and as shown in Table XII the critical point for estimating the stripper diameter will be the bottom.

TABLE X
COMPARISON OF AMINE PROCESS MODEL DESIGN
CALCULATIONS FOR A CONTACTOR
WITH A LITERATURE
SOLUTION

Absorber specifications :

Gas in at 90 deg F, 900 psig , 2.5% CO₂, 0.5% H₂S
2.5N MEA in at 122 deg F with loadings of
0.1275 mol CO₂/mol MEA, 0.0025 mol H₂S/mol MEA

Solution Circulation Rate = 0.0817 mol MEA/mol Sour Gas.

Sweet Gas pp, mm. Hg		Rich amine mol/mol		Rich Amine Temp. deg F	Theoretical Plates	Source
CO ₂	H ₂ S	CO ₂	H ₂ S			
-	0.189	0.396	0.067	135-140		Ref 11
6.08	8.93	0.371	0.061	127	1	APM*
0.03	0.05	0.372	0.064	130	2	APM*
0.03	0.02	0.372	0.064	130	3	APM*

* APM ---Amine Process Model

TABLE XI
COMPARISON OF AMINE PROCESS MODEL DESIGN
CALCULATIONS FOR A REGENERATOR
WITH A LITERATURE
SOLUTION

Stripper pressure is 20 psia
(taken to be 18 psia at top, 22 psia in reboiler)

Steam rate, 1 lb. steam/gal MEA

Rich MEA in at 190 deg F with loadings of
0.384 mol CO₂/mol MEA and 0.064 mol H₂S/mol MEA

Theo. Stages	Lean Amine mol/mol		Lean Amine Temperature deg F	Source
	CO ₂	H ₂ S		
	0.1274	0.0025	240.0	Ref 11
4	0.1532	0.0056	235.0	APM*
7	0.132	0.0022	235.8	APM*

* APM --- Amine Process Model

TABLE XII
COMPARISON OF AMINE PROCESS MODEL RESULTS WITH
TYPICAL MEA STRIPPER DESIGN FROM A
LITERATURE SOURCE (53)

Process Variable	Data From Ref(53)	APM+
Solution Used:		
15.3 wt. % (2.5N) MEA		
Rich Solution:		
CO ₂ loading, moles /mole Amine	0.4607	0.4607*
H ₂ S loading, moles /mole Amine	0.0611	0.0611*
Feed Temperature, deg. F	190.	190.*
Lean Solution:		
CO ₂ loading, moles /mole Amine	0.15	0.129
H ₂ S loading, moles /mole Amine	negligible	0.00168
No. of trays	12-20	6*
Stripper Pressure(avg.), psia	22	22*
Top Tray Pressure, psia	20	20
Bottom Tray Pressure, psia	24	24
Top tray Temperature, deg F	200	218
Condenser Temperature, deg F	150	150*
Reboiler Temperature, deg F	240.	240.7
R. R.#		
(moles H ₂ O in A.G./mol A.G. stripped)	3.0	3.2
Steam to Reboiler, lb. steam/gal. sol	1.17	1.17*
Overhead Acid Gas composition:		
mole CO ₂ /mole Amine entering	0.3107	0.3323
mole H ₂ S/mole Amine entering	0.06107	0.595
moles H ₂ O/mole amine entering	1.1152	1.288
Bottom Vapor Composition:		
mole CO ₂ /mole Amine entering	-	0.0377
mole H ₂ S/mole Amine entering	-	0.0014
moles H ₂ O/mole Amine entering	3.035	3.127

* indicates specified values, remaining
are calculated by model.

R. R. is Reflux Rate.

+ APM is Amine Process Model

Plant A. Operating data for an aqueous diethanolamine plant in high pressure natural gas service have been presented by Berthier (56). These data along with the design calculations are presented in Table XIII. These data were obtained in the early phases of development of the SNPA-DEA process. Substantially lower amine circulation rates are currently being used (29). The lean amine loadings used are those obtained after regeneration, since no operating data for these has been provided. The comparison is excellent. The operating circulation rate is about 1.5 times the minimum circulation rate (not shown) calculated by the program. As expected, two theoretical absorber trays are sufficient to bring the acid gas level to the specified concentration in the sweetened gas. Five stripper equilibrium trays are required to strip the rich amine to the low concentrations required. In the case of the stripper, a pressure drop of 4 psia was assumed. This established the reboiler temperature at 273.1 deg F, in excellent agreement with the operating result of 272 deg F. These results suggest that the Amine Process Model adequately describes the design of an amine sweetening unit. Complete tray by tray details of the results for the absorber and stripper of this plant are included in Appendix B.

Plant B. When large quantities of CO₂ are absorbed together with H₂S, lower H₂S levels are (29) obtainable in the product gas. Pertinent operating data on an absorber

TABLE XIII

DESIGN AND OPERATING RESULTS FOR AN AQUEOUS
DIETHANOLAMINE PLANT IN HIGH
PRESSURE NATURAL GAS
SERVICE

Process Variable	Operating Data	Calculated by APM#
Gas Feed, MMSCFD	35.5	35.5
Feed Gas analysis :		
H ₂ S, %	15.0	15.0
CO ₂ , %	10.0	10.0
Outlet Gas Analysis :		
H ₂ S, %	4.420E-4	<1.E-3 *
CO ₂ , %	1.974E-4	<1.E-3 *
Steam, lb. /gal. sol	0.995	0.995
ABSORBER :		
Lean Amine loadings,		
H ₂ S, mol/mol Amine	-	0.0219
CO ₂ , mol/mol amine	-	0.0063
Rich Amine loadings,		
H ₂ S, mol/mol amine	-	0.4231 *
CO ₂ , mol/mol amine	-	0.2737 *
No. of Trays	30	2
Pressure, psig	1000.0	1000.0
Rich Amine Temp., deg F	-	124.5
STRIPPER :		
Rich Amine loadings,		
H ₂ S, mol/mol amine	-	0.423
CO ₂ , mol/mol amine	-	0.273
Lean Amine loadings,		
H ₂ S, mol/mol amine	-	0.022
CO ₂ , mol/mol amine	-	0.0062 *
No. of Trays	20	5
Pressure, psig	25.	25.
Reboiler Temp., deg F	272.0	273.1 *

* indicates the values are calculated,
remaining were specified.

APM - Amine Process Model

(tower packed with stoneware Raschig rings) utilizing an aqueous diethanolamine solution to absorb both CO_2 and H_2S have been presented by Kohl and Riesenfeld (29). The operating data have been compared with the predicted data of a 3-stage absorber. The results shown in Table XIV also include a stripper run for which data were not available. The predictions are close to the plant data for all the absorber variables specified.

Plant C. Typical design and performance data for plants employing the Fluor Econamine process (using a Diglycolamine solution), as presented by Kohl and Riesenfeld are reproduced in Table XV. The Amine Process Model simulation run results for this case are shown for comparison. The acid gas loadings of the lean amine entering the absorber are the same as those at the bottom of the stripper. These loadings have not been provided by the designer and therefore no comparisons can be made. However the comparison is satisfactory for the remaining variables. The solution circulation rate is approximately 1.5 times the minimum rate calculated by the program. The temperature of rich amine leaving the contactor predicted by the computer program is 8.5 deg F lower than that reported by Holder (64). Clearly this difference is a result of using partial pressure data to predict heats of absorption rather than using the value at infinite dilution. As shown in Table VI, three theoretical plates are necessary to bring the H_2S level in the treated gas to the

required (0.25 grains/100 SCF) level. Also, only three stripper stages are sufficient to bring the H₂S concentration in the regenerated amine to a level low enough to be effective in the contactor. The calculated stripper temperatures are very close to those obtained by Holder. Since absolutely no quaternary system data are available for DGA, the present simulation can be very useful.

Plant D. Operating and calculated data for 3 ADIP plants (using DIPPA) are shown in Table XVI. The 3 plants clean up the synthesis gas from an oil gasification unit, the gases from a catalytic cracking unit and off gases from gas oil hydrodesulfurizer respectively. The available data are incomplete and therefore the comparison can at best be looked upon as an indicator of expected performance.

Plant E. Typical design and operating data for this commercial installation was again obtained from Kohl and Riesenfeld (29). In this case the plant treats a low pressure natural gas with low acid gas content. The natural gas is to be purified to a very low H₂S level. A 17% (2.75N) MEA has been used under these conditions. The results of the plant simulation (Refer Table XVII) are compared with the operating data. Again, the comparison is satisfactory, indicating the plant model is capable of describing the process. The design calculations presented here are not optimized, since the operating variables are set somewhat arbitrarily.

The operating amine circulation rate is about 1.3 times the minimum required in the process. The model also predicts the reboiler temperature in the stripper within 1 C.

TABLE XIV
COMPARISON OF DATA FOR AQUEOUS DIETHANOLAMINE
PLANT ABSORBER USED TO REMOVE
H₂S AND

Process Variable	Run #1 Plant Data	Calc. Results for Run #1	Run #2 Plant Data	Calc. Results for Run #2
ABSORBER :				
Gas Feed, SCF/hr	87000	87000	71900	71900
Inlet Gas Temp, F	-	95.0	-	95.0
Pressure, psig	350	350	340	340
Feed Gas Analysis :				
CO ₂ , %	15.0	15.0	15.0	15.0
H ₂ S, %	0.2052	0.2052	0.1184	0.1184
Outlet Gas Analysis :				
CO ₂ , %	2.5	0.303*	4.2	0.002*
H ₂ S, %	0.0189	0.018*	0.00314	0.001*
Solution Rate,				
(mol DEA/mol gas in)	0.26	0.33#*	0.3583	0.504\$
Lean Sol. Temp, F	-	113	-	113
DEA, wt. %				
	35.00 (3.5N)	35.00 (3.5N)	41.00 (4.0N)	41.00 (4.0N)
Lean Sol. Analysis :				
CO ₂ , mol/mol amine	0.1241	0.1241	0.0407	0.0407
H ₂ S, mol/mol amine	0.0025	0.0025	0.00495	0.00495
Rich Sol. Analysis :				
CO ₂ , mol/mol amine	0.5920	0.5691	0.4238	0.4258
H ₂ S, mol/mol amine	0.0084	0.0082	0.0072	0.0073
Rich Sol. Temp, F				
	-	155*	-	164*
No. of Stages				
	-	2	-	2

* indicates calculated values.

minimum solvent rate.

\$ 1.1 times the calculated minimum solvent rate.

TABLE XV
COMPARISON OF DESIGN DATA FOR FLUOR ECONAMINE
PROCESS WITH THE RESULTS OF AMINE
PROCESS MODEL

Plant Variable	Plant Data	APM#
Gas Feed, MMSCFD	100	100
Feed Gas Analysis :		
CO ₂ , %	5	5
H ₂ S, %	5	5
Outlet Gas Analysis :		
CO ₂ , %	-	0.00002*
H ₂ S, %(0.25 grains/100 SCF)	0.0004	0.000085*
Solution Circulation Rate (60 wt. % or 6.2N DGA) mol Amine/mol gas treated	0.3633	0.3633
Stripping Steam, lb./gal.	1.5	1.5
Absorber :		
Number of trays	20	3
Temperature in, deg F	110	110
Temperature out, deg F	180	171.5*
Pressure, psig	900	900
Stripper :		
Number of Trays	18 + 4	3
Pressure, psig	8	8
Temperature Top, deg F	220	220.5*
Reboiler Temperature, deg F	250	252.1*
Lean Sol. Analysis:		
CO ₂ , mol/mol amine	-	0.091*
H ₂ S, mol/mol amine	-	0.0011*
Rich Sol. Analysis:		
CO ₂ , mol/mol amine	-	0.2299*
H ₂ S, mol/mol amine	-	0.1400*

* indicates value is calculated.

TABLE XVI
COMPARISON OF OPERATING DATA OF ADIP PLANTS WITH
THE RESULTS OF AMINE PROCESS MODEL

Plant Variable	Plant # 1	APM	Plant # 2	APM	Plant # 3	APM
Gas Feed, cu.ft/hr.	700000	700000	85000	85000	1200000	1200000
H ₂ S, %	0.5	0.5	10.4	10.4	15.6	15.6
CO ₂ , %	5.5	5.5	2.5	2.5	-	-
Absorber press, psia	364.7	364.7	294.7	294.7	373.7	373.7
Absorber Temp., F	104.0	-	95.0	-	104.0	-
No. of Trays in Absorber	25	2	20	4	15	2
Outlet Gas						
H ₂ S, %	0.0002	0.0*	0.001	0.001*	0.01	0.001*
CO ₂ , %	-	0.0	-	0.000	-	-
Rich Amine Temp., F	-	146*	-	143*	-	126*
Amine Circ. Rate	0.07	0.140#	0.173	0.197#	0.253	0.469#

- minimum amine circulation rate calculated by program.

* - represent calculated values, rest are specified.

APM - Amine Process Model results.

- - amine circulation rate,
in lb. moles amine/lb. moles gas in.

TABLE XVII

COMPARISON OF CALCULATED AND OPERATING RESULTS FOR
LOW PRESSURE NATURAL GAS TREATING
PROCESSES

Process Variable	Plant data	Calculated Results
Gas Feed, MMSCFD	50	50
H ₂ S content, %	0.25 - 0.284	0.268
CO ₂ content, %	0.30 - 0.40	0.350
Outlet Gas Composition :		
H ₂ S content, %	3.2E-5 - 4.8E-4	<4.0E-4 *
CO ₂ content, %	-	<5.0E-4 *
Solvent Solution :		
17% MEA (2.75N)		
Rate of Flow	0.0176 - 0.0264	0.022
(mol/mol of treated gas)		
ABSORBER :		
Number of Trays	23	3
Temp. of Rich Amine, deg C	-	39.6*
Pressure, psig	200	200
STRIPPER :		
Number of Trays	20	5
Pressure, psig	12	12
Feed Temp., deg C	93.3	93.0
Still Top Temperature, deg C	116.0	116.0*
Reboiler Temperature, deg C	121.0	122.0*
Steam Rate, lb. steam/gal. sol	1.2	1.08

* indicates values are calculated

Temperature and Concentration Profiles in the Contactor

The process design scheme presented here assumes that the gas and liquid streams leaving a plate have the same temperature (thermal efficiency = 100 percent). This is not necessarily true. The gas and liquid temperatures depend on how complete the heat transfer process is. However from basic mass and heat transfer theory one can deduce that thermal stage efficiencies generally are greater than mass-equilibration efficiencies. In any case, incomplete thermal equilibration on the plates would not change the plate requirement substantially, since the equilibrium partial pressures of CO₂ and H₂S are important on only the bottom plates.

Most amine process calculations assume that all of the heat of absorption is carried down with the liquid phase and that the sensible heat of the vapor is negligible. This assumption is close to reality because of the high liquid-to-gas ratios encountered in the amine absorbers and especially for the overall enthalpy balance through which the effluent liquid temperature is found. However, the temperature profile for intermediate plates in the column is influenced by the vapor heat capacity, in addition to the heats of reaction and heat capacity of the solution.

To study this effect and to further confirm the Amine Process Model some runs were made based on the data pre-

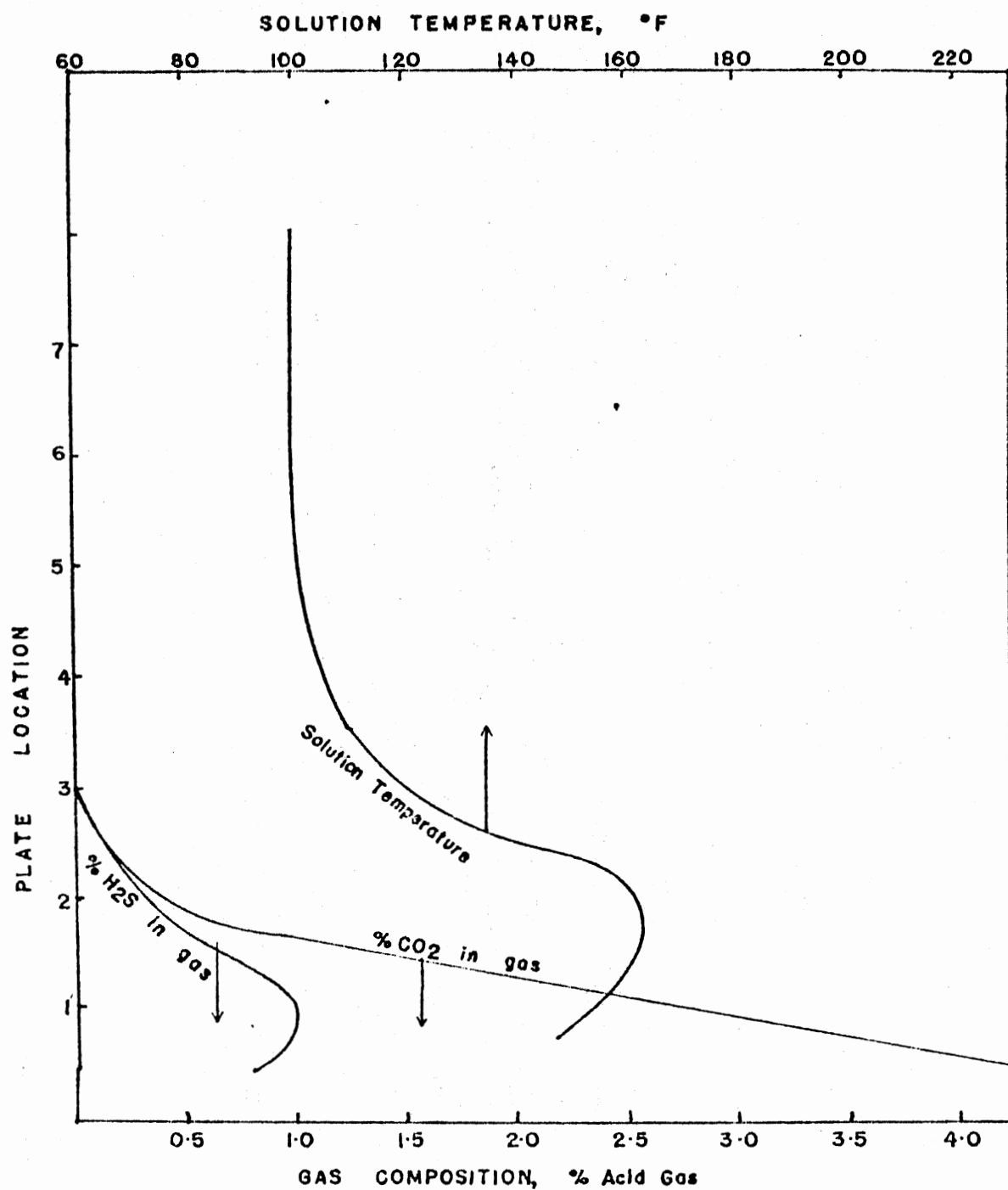


Figure 28. Temperature and Composition Profiles for Gas Treating Plant Absorber Handling a Gas Stream Containing a High Concentration of Acid Gas

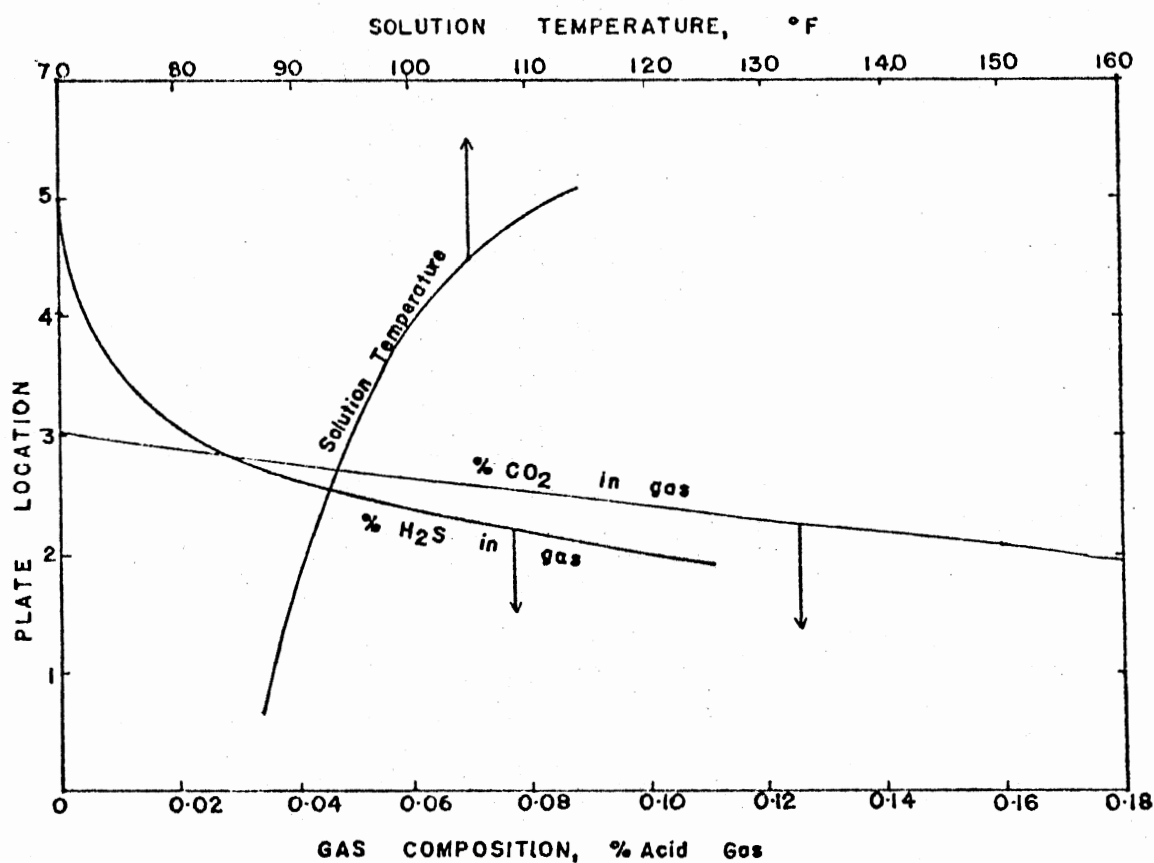


Figure 29. Temperature and Composition Profiles for Gas Treating Plant Absorber Handling a Gas Stream Containing a Low Concentration of Acid Gas

sented by Kohl and Riesenfeld (29). Kohl and Riesenfeld present test data for an ethanolamine absorber treating a gas at 540 psia containing 4 percent CO₂ and 0.8 percent H₂S, which provides inlet and effluent amine temperatures of 105 and 175 deg F, respectively whilst developing an internal temperature bulge to 230 deg F at a point a few plates above the bottom. Also, the reported profiles were made on towers handling a mixture of glycol and amine, and may or may not be exactly typical of an amine contactor. Nevertheless, the Amine Process Model calculations for the absorber show a similar trend in temperature and concentration profiles.

When gas streams containing relatively large amounts of acid gases (over 5 percent) are purified, the quantity of solution required is normally so large that the purified gas is cooled by the lean solution at the top of the column to within a few degrees of the temperature of the lean solution. Nearly all of the heat of reaction is taken up by the solution, which leaves the column at an elevated temperature. Typical temperature and concentration profiles for an absorber of this type are shown in Figure 28. These temperature and concentration profiles are similar to the plant data presented by Kohl and Riesenfeld (29). The temperature "bulge" is the result of the inlet gas obtaining heat from the hot loaded amine near the tower bottom and then losing this heat to amine higher in the column. This serves to pre-

heat the amine coming down the column and allows the heat of absorption to take the amine to a still higher temperature. The amine is then cooled down to its effluent temperature on the lowest plates by losing heat to the gas, which will carry heat back up the column. This effect can increase the plate and amine requirement somewhat. Another aspect of a temperature bulge is that it seriously complicates a stage to stage calculation method.

When more dilute gases ($<0.5\%$ acid gas) are purified, the quantity of gas may be so large, relative to the mass of solution, that the heat capacity of the gas can be more important than that of the liquid, causing temperature to decrease downward. In this case the gas leaving the contact zone will carry more of the heat which is generated than will the solution. The temperature and concentration profiles are illustrated in Figure 29 where the solution is cooled to approximately the temperature of the incoming gas before it leaves the column. The calculated profiles are similar to those presented by Kohl and Riesenfeld for such a case.

Comparison of Regenerated Amine Loadings with Empirical Correlations

Fitzgerald and Richardson (59) have carried out a study based on plant data gathered from a dozen operating MEA treating units to determine the effect of H_2S to CO_2 ratio and regenerator heat input on the residual hydrogen sulfide and carbon dioxide content of the lean MEA solution. The parameter commonly used in the sour gas treating industry to express heat input to the regenerator is the stripping steam rate expressed in pounds of steam per gallon of lean amine circulated. It is also an indicator of the vapor-liquid traffic at the bottom of the regenerator. The Fitzgerald and Richardson correlations clearly demonstrate a trend towards increased stripping of hydrogen sulfide from the lean amine solution with decrease in the ratio of H_2S to CO_2 . These data also illustrate an apparent asymptotic limit to residual hydrogen sulfide stripping from MEA with increased regenerator heat input (49). Figure 30 shows comparisons for two of the commercial plants in Fitzgerald and Richardson's study. The Amine Process Model runs were made with five and six theoretical stages for each of the two plants. The trends shown are similar to those displayed by the Fitzgerald and Richardson correlation.

Figure 31 presents a cross plot of data illustrated in Figure 30, in a more usable form. Considering the large number of influencing variables, many of which escape proper

definition, these data correlate exceptionally well. Figure 31 predicts expected lean solution residual hydrogen sulfide content at any stripping steam rate, for average solution loadings, amine concentrations and regeneration temperatures and pressures encountered in MEA plants. The conclusions drawn from Figures 30 and 31 are summarized by Fitzgerald and Richardson (59).

As reported by Maddox (47), Fitzgerald and Richardson also studied the effect of steam stripping rate and H₂S to CO₂ ratio in the sour gas on the retention of CO₂ in the stripped amine solution. The CO₂ loading in the regenerated amine is only marginally influenced by H₂S to CO₂ ratios (in plant feed) when the ratio is small (<1.0). This asymptotic trend is illustrated by Figure 32. Figure 32 presents the correlation they derived from their studies on operating plants and the results obtained from the computer simulation model. Fitzgerald and Richardson corrected their plots to a reboiler temperature of 252 deg F, corresponding to an average regeneration pressure of 17 psig, while the Amine Process Model results are not. Nevertheless the agreement between calculated and correlated sets of data is excellent. The information provided by Figures 31 and 32 is vital to the process design of amine treating units.

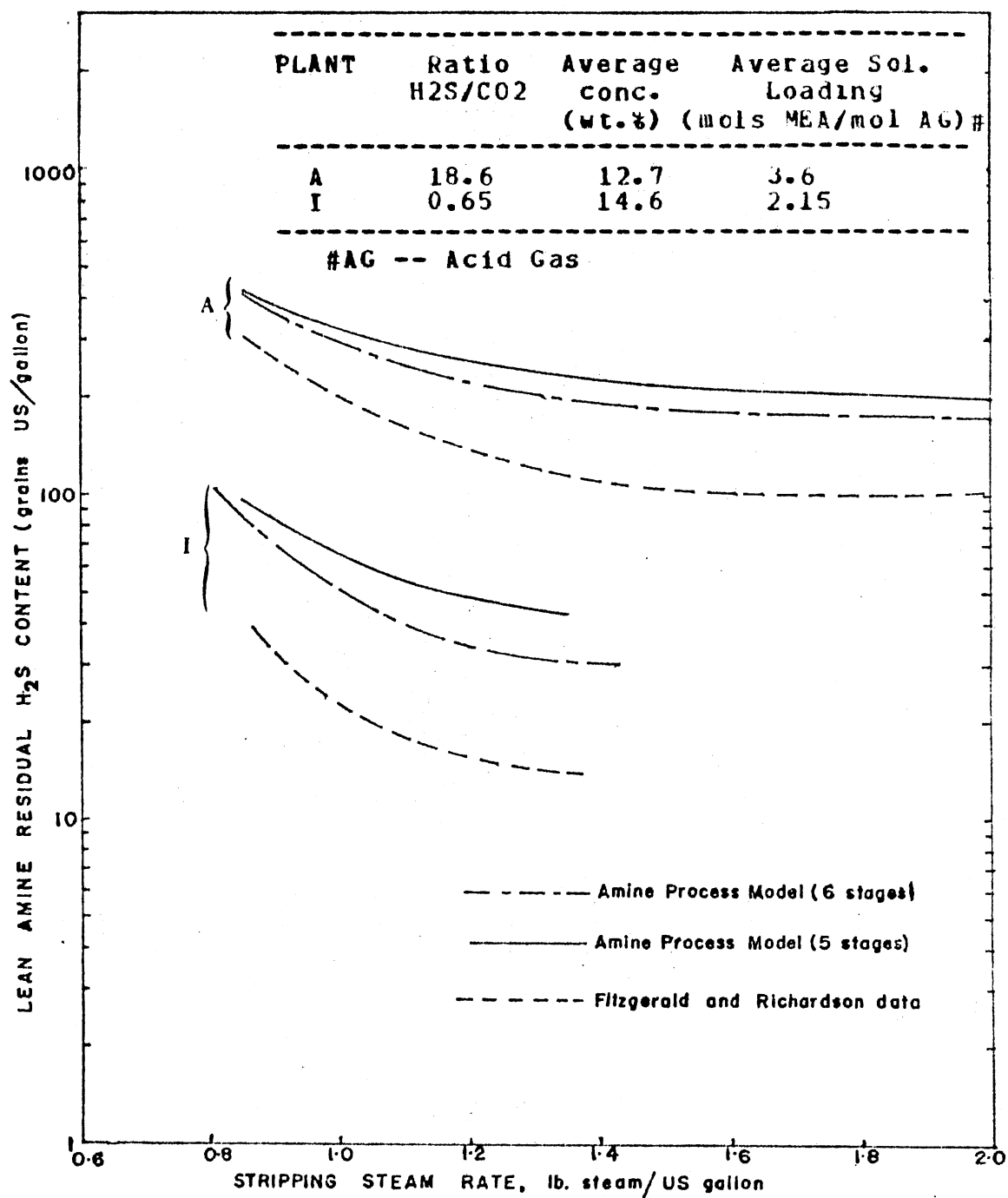


Figure 30. Effect of Acid-Gas Ratio on MEA Solution Stripping

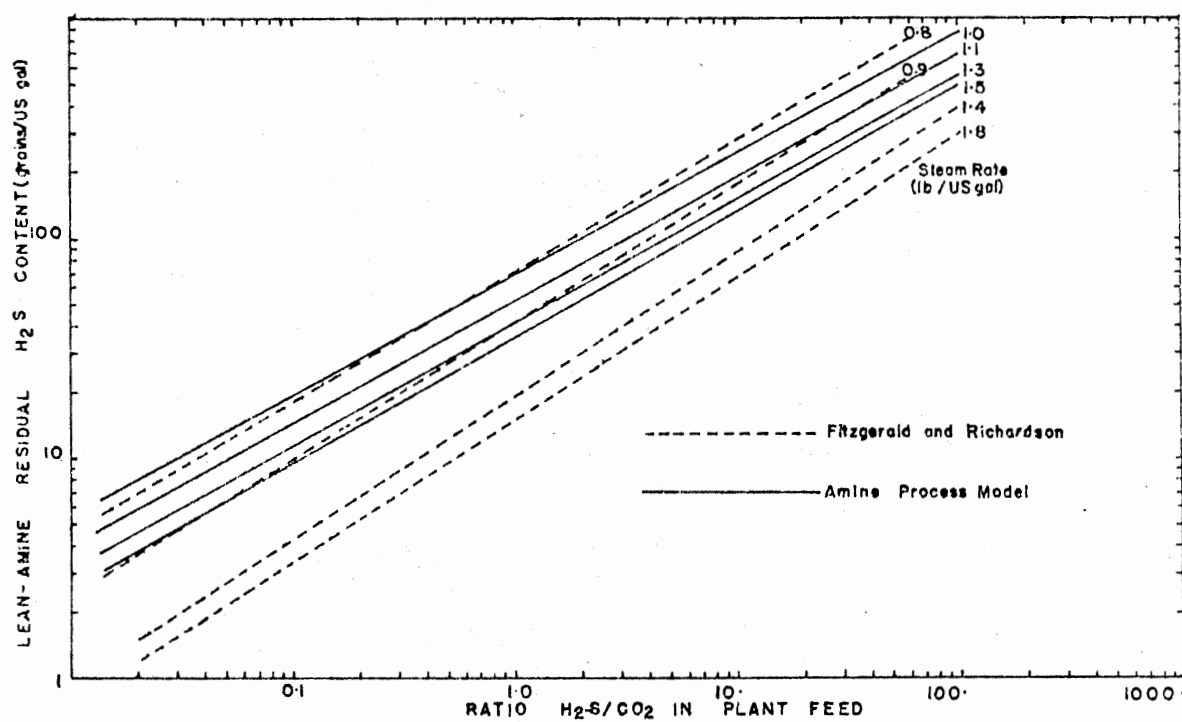


Figure 31. MEA Treating Limitations

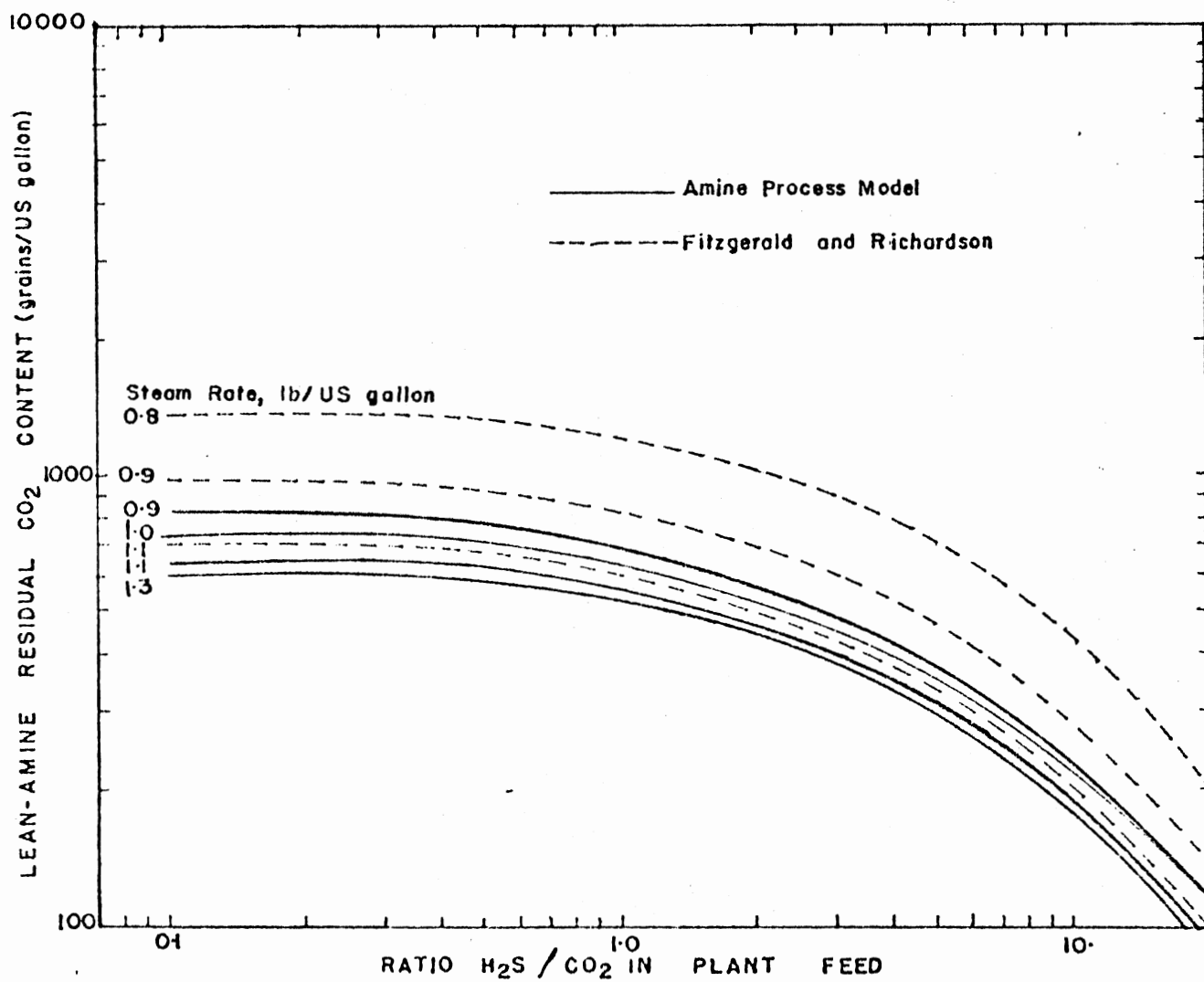


Figure 32. Trends Showing Expected CO_2 Retention in MEA Solutions (at Various Stripping Steam Rates)

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions can be drawn based on the results of this study:

1. The reaction equilibrium approach of predicting partial pressures of CO₂ and H₂S over CO₂-H₂S-Ethanolamine-Water systems is convenient and useful. The Kent-Eisenberg model, which uses the above approach, was extended to cover the amines not considered by the original authors.
2. A new model, the Acid-Gas Amine Equilibrium Model, based on the dominating reactions of an CO₂-H₂S-Ethanolamine-Water system has been developed.
3. The new Acid Gas-Amine equilibrium model is capable of predicting partial pressures of acid gas over ethanolamine solutions with fair accuracy. The new model performs as good as any existing in the literature and is in many cases more accurate.
4. Algorithms for carrying out process calculations of an amine contactor, regenerator, and flash drum have been presented.
5. A computer program which performs process calculations for a typical gas-sweetening plant was written and tested by data from several operating plants. The agreement between the calculated results and operating data is excellent. The mathematical relations adequately describe the significant process behavior.

6. The Amine Process Model was utilized to demonstrate the significant factors in the absorption and stripping of acid gases using ethanolamines.
7. The modular nature of the program makes it well suited to, and flexible enough for, simulating other configurations of gas sweetening units.
8. The Amine Process Model computer program provides a powerful tool for optimization and study of ethanolamine sweetening plant operations and design.

Recommendations

The following recommendations are made on the basis of the results of the Acid Gas-Amine Equilibrium Model:

1. The Acid Gas-Amine Equilibrium Model is based on two fitted constants K_1 and K_2 , which are derived by correlating the ternary systems (H₂S-Amine-H₂O and CO₂-Amine-Water), and consequently predict these data better. Almost always quaternary system data (H₂S-CO₂-H₂O-Amine) are used in process calculations. Therefore, when available, these quaternary system data should be fitted to derive constants K_1 and K_2 . Improved prediction capabilities can be expected for the mixed system. However, the prediction errors are correspondingly higher for the ternary system.
2. The sensitivity of the equilibrium models to K_1 and K_2 has been demonstrated. The values of these constants also depend on whether partial pressure data are fitted assuming loading or vice versa. An improved fit is also expected if smoothed data are used. Moreover, an investigation of how the closeness of fit criterion used reflects on the quality of fit obtained should be made. When partial pressure and acid gas loadings are simultaneously fitted, the use of weighting factors is recommended. Obviously, a comprehensive and systematic study of all

these factors can result in improved fits of data.

3. The major problem in correlating vapor-liquid equilibrium in aqueous solutions of weak electrolytes is the estimation of the activity coefficients of the ionic species. Although a number of models have been proposed, the determination of the parameters in a new case is not a simple matter. This problem occurs in the application of the fundamental thermodynamics to alkanolamine solutions containing H_2S and CO_2 . As and when these parameters become available correlation models can be subjected to a more rigorous thermodynamic approach.

The following recommendations are made with regard to the Amine Process Model:

1. The solubility data for methane and ethane in monoethanolamine and di-ethanolamine solutions are reported in the literature. The type and concentrations of amine, temperature, and presence of hydrogen sulphide and carbon dioxide affect the methane and ethane solubility. Knowledge of the amounts of hydrocarbon gas in the amine stream is necessary for a more complete and better design of the sweetening system and associated Claus sulfur recovery unit. This solubility effect needs to be included in the process calculations of the Amine Process Model.
2. The problem of recycle convergence has not been considered in the Amine Process Model. Cyclic processes involve the return of material and energy from a later point in the system to an earlier point and since the recycled stream may result in a change in the feed rate, composition, temperature or phase split to the different modules that have been previously calculated, the solution requires a reevaluation of the process system. While several recycle convergence acceleration algorithms are available, the modified Bounded Wegstein Method (55) is reportedly superior. It can result in reduction of computer time and process iterations.

3. The Amine Process model provides a powerful tool to study and optimize the ethanolamine sweetening processes. The effect of several process variables can be very easily assessed. Also, pertinent problems like the hydrogen sulfide selectivity of various ethanolamines can be investigated. A proper combination of theoretical contact stages, acid gas loadings and amine circulation rates can result in a selective H₂S removal process.
4. The potential of other design approaches to simulating the ethanolamine sweetening process should be explored. A kinetic approach whereby each stage is viewed as a backmix reactor incorporating residence times looks very favorable. For this type of approach a different kinetic model will have to be developed.

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APPENDIXES

APPENDIX A

PHYSICAL AND THERMAL PROPERTY DATA

CORRELATIONS

The calculations in this work employed physical and thermal properties available in various literature sources. Specifically vapor pressure, heat capacity and specific gravity data are required.

Vapor Pressure: The vapor pressure of the ethanolamines and water is estimated through use of the Antoine equation,

$$\ln P = A + B/(T + C)$$

where,

P = vapor pressure, mm Hg

T = temperature, deg C

and,

A, B, and C are constants obtained from Table XVIII

For DGA and DIPA the graphical data obtained were fitted using a non-linear regression technique.

Heat Capacity and Enthalpy: The values of heat capacity of water vapor and air/inerts are computed by use of the ideal-gas heat capacity equation. An integration of the ideal heat capacity equation provides the enthalpy for the gas. The constants for this equation are shown in Table XIX. The heat capacity for various concentrations of ethanolamine solutions are obtained as functions of temperature from Kohl and Riesenfeld (29).

Specific Gravity: The specific gravity data for the various ethanolamine solutions is obtained as function of

TABLE XVIII
CONSTANTS FOR ANTOINE EQUATION

	H2O	MEA	DEA	DIPA	DGA
A	18.3036	17.8174	18.704	16.492	16.916
B	3816.44	3988.33	5331.54	3492.66	4014.78
C	-46.13	186.22	173.3	132.42	141.72
Ref.	(67)	(67)	(11)	(29)	(29)

TABLE XIX
IDEAL GAS HEAT CAPACITY EQUATION CONSTANTS

$$C_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3$$

(Cp in cal. per gram mole K, T in deg K)

	A	B*103	C*105	D*109	Ref.
Water Vapor	8.22	.015	.134	-	(70)
Air	6.713	.0469	.1147	-.469	(69)
Methane*	8.2	1.307	.0875	-2.63	(69)

* -- temperature in deg C

temperature from Gas Conditioning Fact Book (68) and Kohl and Riesenfeld (29).

Heats of Reaction: The reaction heat of solution between acid-gas constituents and the absorbing solution is estimated by the method proposed by Crynes and Maddox (31). The method uses equilibrium partial pressure data for calculating the heat of reaction. The accuracy of this heat of reaction data is limited only by the accuracy and reliability of the equilibrium data used to derive the values.

The relationship used is,

$$\ln ppB/ppB_0 = HR/R(1/T_0 - 1/T)$$

where,

T is temperature in deg R.

ppB is partial pressure of a component,

R is gas constant

and,

0 represents an initial condition.

APPENDIX B

TYPICAL RESULTS OF PLANT SIMULATION

* NO DIAGNOSTICS GENERATED
 STATISTICS 001 DIAGNOSTICS THIS STEP :
 (DO YOU WANT TO RUN THE INTERACTIVE (TSO) VERSION?
 ENTER Y OR N)
 Y
 ENTER/REENTER OPTION:
 1=ABSORBER ONLY;2=REGENERATOR ONLY;3=FLASH ONLY;4=PLANT SIM)
 ?
 2
 (ENTER # STAGES IN REGENERATOR)
 ?
 3
 (ENTER AVERAGE PRESSURE (IN PSIA) IN REGENERATOR)
 ?
 22.7
 (A PRES DROP OF 5 PSI IS BEING ASSUMED ACROSS REGEN)
 (ENTER 1 IF CHANGE IS TO BE MADE; 0 IF NO CHANGE)
 ?
 0
 (ENTER STEAM RATE TO REBOILER (IN LBS STEAM/GAL SOL))
 ?
 1.5
 (ENTER AMINE TYPE USED IN THE SWEETENING)
 (1=MEA;2=DEA;3=DGA;4=DIPA)
 ?
 3
 (ENTER NORMALITY OF AMINE AND WT % AMINE)
 ?
 6.2
 ?
 60.
 (ENTER TEMP OF FEED (IN DEG F) TO REGEN)
 ?
 203.

(ENTER CO2 AND H2S LOADINGS(MOLE/MOLE AMINE)OF FEED)

?

.2299

?

.14

(IS A SIDE STREAM FROM REGEN INCLUDED?1=YES,0=NO)

?

0

(WANT TO CHANGE CONDENSER TEMP?)

(DEFAULT VALUE IS 35 DEG C (203 DEG F);1=YES,0=NO)

?

0

REGENERATOR SPECIFICATIONS :

=====

AMINE USED : DGA

NORMALITY OF AMINE USED = 6.20 N (OR 60.00 WT. PCT.)

AVERAGE OPERATING PRESSURE = 22.70 PSIA

TOP PRESSURE = 20.20 PSIA

BOTTOM PRESSURE = 25.20 PSIA

TEMPERATURE OF FEED = 95.00 DEG. C (OR 203.00 DEG. F)

LOADINGS OF FEED STREAM :

CO2 LOADING = 0.2299 MOLES CO2/MOLE AMINE
H2S LOADING = 0.1400 MOLES H2S/MOLE AMINE
AMOUNT OF STEAM TO REBOILER = 1.50 LBS. STEAM / GAL. AMINE
(OR 1.76 MOLE STEAM/MOLE AMINE)

TEMP OF REFLUX FROM CONDENSER
(SPECIFIED OR DEFAULT VALUE) = 95.00 DEG. C
(OR 203.00 DEG. F)

NUMBER OF STAGES FIXED/CALCULATED = 3

SIDESTREAM FROM STAGE 0 FROM TOP (NOT COUNTING CONDENSER)
SIDESTREAM SPLIT RATIO = 0.0 LB. MOLES REMOVED/LB. MOLES REMAINING

BASIS FOR REGEN CALCULATIONS: 1 LB. MOLE AMINE IN FEED

*****SUMMARY OF REGENERATOR CALCULATIONS*****

STAGE # 1

TEMPERATURE OF STAGE 105.37 DEG. C (OR 221.67 DEG. F)

STAGE PRESSURE = 20.20 PSIA

LOADINGS OF LIQUID ENTERING STAGE :

CO2 LOADING = 0.22990 MOLES CO2/MOLE AMINE
H2S LOADING = 0.14000 MOLE H2S / MOLE AMINE

LOADINGS OF LIQUID LEAVING STAGE :

CO2 LOADING = 0.23513 MOLES CO2/MOLE AMINE
H2S LOADING = 0.03121 MOLES H2S/MOLE AMINE

TOTAL LIQUID LEAVING STAGE = 4.89407 LB. MOLES

VAPOR CONCENTRATIONS (LEAVING STAGE) :

CO2 = 0.1400 LB. MOLES
H2S = 0.1389 LB. MOLES
STEAM = 0.5400 LB. MOLES
TOTAL VAPOR LOADING = 0.8190 LB. MOLES

MOLES STEAM/MOLE ACID GAS IN VAPOR = 1.94

+++++

STAGE # 2

TEMPERATURE OF STAGE 116.15 DEG. C (OR 241.07 DEG. F)

STAGE PRESSURE = 22.70 PSIA

LOADINGS OF LIQUID ENTERING STAGE :

CO2 LOADING = 0.23513 MOLES CO2/MOLE AMINE
H2S LOADING = 0.03121 MOLE H2S / MOLE AMINE

LOADINGS OF LIQUID LEAVING STAGE :

CO2 LOADING = 0.16233 MOLES CO2/MOLE AMINE
H2S LOADING = 0.00578 MOLES H2S/MOLE AMINE

TOTAL LIQUID LEAVING STAGE = 4.89407 LB. MOLES

VAPOR CONCENTRATIONS (LEAVING STAGE) :

CO2 = 0.1454 LB. MOLES
H2S = 0.0301 LB. MOLES
STEAM = 1.0779 LB. MOLES
TOTAL VAPOR LOADING = 1.2535 LB. MOLES

MOLES STEAM/MOLE ACID GAS IN VAPOR = 6.14

+++++

STAGE # 3

TEMPERATURE OF STAGE 122.32 DEG. C (OR 252.18 DEG. F)

STAGE PRESSURE = 25.20 PSIA

LOADINGS OF LIQUID ENTERING STAGE :

CO2 LOADING = 0.16233 MOLES CO2/MOLE AMINE
H2S LOADING = 0.00578 MOLE H2S / MOLE AMINE

LOADINGS OF LIQUID LEAVING STAGE :

CO2 LOADING = 0.08954 MOLES CO2/MOLE AMINE
H2S LOADING = 0.00109 MOLES H2S/MOLE AMINE

TOTAL LIQUID LEAVING STAGE = 4.89407 LB. MOLES

VAPOR CONCENTRATIONS (LEAVING STAGE) :

CO2 = 0.0728 LB. MOLES
H2S = 0.0047 LB. MOLES
STEAM = 1.7594 LB. MOLES
TOTAL VAPOR LOADING = 1.8368 LB. MOLES

MOLES STEAM/MOLE ACID GAS IN VAPOR = 22.71

+++++

*** REGENERATOR CALCULATIONS END FOR 3STAGES*****

((DO YOU WANT TO CONTINUE?) 1=YES,2=NO)

?

1

ENTER/REENTER OPTION:

1=ABSORBER ONLY;2=REGENERATOR ONLY;3=FLASH ONLY;4=PLANT SIM)

?

1

(ENTER AMINE TYPE USED IN THE SWEETENING)

(1=MEA;2=DEA;3=DGA;4=DIPA)

?

3

```

(ENTER NORMALITY OF AMINE AND WT % AMINE)
?
6.2
?
60.
(ENTER ABSORBER PRESSURE(IN PSIA))
?
914.7
(ENTER 1 IF # STAGES ARE TO BE CALCULATED
2 IF # STAGES ARE TO BE FIXED AND RESIDUE GAS COMPOSITION IS TOBE COMPUTED)
?
2
(ENTER # OF STAGES(INTEGER))
?
3
(ENTER 1 IF AMINE CIRC RATE IS TO BE FIXED)
      2 IF MIN. AMINE CIRC RATE IS TO BE CALCULATED)
?
1
(ENTER OPERATING AMINE CIRCULATION RATE)
?
.3633
(ENTER INLET GAS TEMPR(DEG C)
AND INLET GAS COMP.(IN MOLE FR.) OF CO2 AND H2S RESP.)
?
35.
?
5.
?
5.
(ENTER INLET AMINE TEMP(IN DEG C);)
      CO2 AND H2S LOADING )
?
40.

```

?
.09
?
.0011
(ENTER MURPHREE STG EFF.(IF ANY) FOR CO2 AND H2S RESP)
?
100.
?
100.

THE RIGOROUS CALCULATIONS PROGRAM CONVERGED

TOTAL NUMBER OF EQUILIBRIUM STAGES SPECIFIED/COMPUTED = 3
MINIMUM AMINE CIRCULATION RATE = 0.2204LB MOLES AMINE/LB MOLES GAS IN
OPERATING AMINE RATE = 0.3633LB MOLES AMINE/LB MOLES GAS IN

SUMMARY OF FLASH/EQUILIBRIUM ABSORBER CALCULATIONS

INLET SPECIFICATIONS MADE :

INLET GAS COMPOSITION : CO2 = 5.00PCT
H2S = 5.00PCT
INLET AMINE LOADING : CO2 = 0.090MOLE/MOLE AMINE
H2S = 0.001MOLE/MOLE AMINE
EFFLUENT GAS PURITY : CO2 LESS THAN 0.00PCT
H2S LESS THAN 0.00PCT
ABSORBER PRESSURE = 915.PSIA
INLET GAS TEMPERATURE = 35.0DEG C
INLET AMINE TEMPERATURE = 40.0DEG C
NORMALITY OF AMINE USED = 6.2N (OR 60.00WT. PERCENT)
HEAT CAPACITY OF AMINE = 0.92BTU/DEG F-LB SOLN
HEATS OF ABSORPTION : CO2 = 850.BTU/LB
H2S = 674.BTU/LB
MURPHREE STAGE EFFICIENCY : CO2 = 100.00PERCENT
H2S = 100.00PERCENT

STAGE NUMBER : 1

TEMPERATURE OF STAGE = 71.6DEG C

USING MURPHREE STAGE EFFICIENCY : CO2 = 100.PERCENT

H2S = 100.PERCENT

PARTIAL PRESSURE OF GAS IN: CO2 = 2364.53MM.HG (OR 0.05000MOLE/MOLE GAS IN)

H2S = 2364.53MM.HG (OR 0.05000MOLE/MOLE GAS IN)

PARTIAL PRESSURE OF GAS OUT : CO2 = 8.78MM.HG (OR 0.00017MOLE/MOLE GAS IN)

H2S = 197.26MM.HG (OR 0.00377MOLE/MOLE GAS IN)

GAS LOADING OF ENTERING AMINE : CO2 = 0.0905MOLE/MOLE AMINE

H2S = 0.0115MOLE/MOLE AMINE

GAS LOADING OF LEAVING AMINE : CO2 = 0.2276MOLE/MOLE AMINE

H2S = 0.1387MOLE/MOLE AMINE

STAGE NUMBER : 2

TEMPERATURE OF STAGE = 43.2DEG C

USING MURPHREE STAGE EFFICIENCY : CO2 = 100.PERCENT

H2S = 100.PERCENT

PARTIAL PRESSURE OF GAS IN: CO2 = 8.78MM.HG (OR 0.00017MOLE/MOLE GAS IN)

H2S = 197.26MM.HG (OR 0.00377MOLE/MOLE GAS IN)

PARTIAL PRESSURE OF GAS OUT : CO2 = 0.01MM.HG (OR 0.00000MOLE/MOLE GAS IN)

H2S = 0.37MM.HG (OR 0.00001MOLE/MOLE GAS IN)

GAS LOADING OF ENTERING AMINE : CO2 = 0.0900MOLE/MOLE AMINE

H2S = 0.0011MOLE/MOLE AMINE

GAS LOADING OF LEAVING AMINE : CO2 = 0.0905MOLE/MOLE AMINE

H2S = 0.0115MOLE/MOLE AMINE

STAGE NUMBER : 3

TEMPERATURE OF STAGE = 40.3DEG C

USING MURPHREE STAGE EFFICIENCY : CO2 = 100.PERCENT

H2S = 100.PERCENT

PARTIAL PRESSURE OF GAS IN: CO2 = 0.01MM.HG (OR 0.00000MOLE/MOLE GAS IN)

H2S = 0.37MM.HG (OR 0.00001MOLE/MOLE GAS IN)

PARTIAL PRESSURE OF GAS OUT : CO2 = 0.00MM.HG (OR 0.00000MOLE/MOLE GAS IN)

H2S = 0.03MM.HG (OR 0.00000MOLE/MOLE GAS IN)

GAS LOADING OF ENTERING AMINE : CO2 = 0.0900MOLE/MOLE AMINE

H2S = 0.0011MOLE/MOLE AMINE

GAS LOADING OF LEAVING AMINE : CO2 = 0.0900MOLE/MOLE AMINE

H2S = 0.0011MOLE/MOLE AMINE

40.03221

((DO YOU WANT TO CONTINUE?) 1=YES,2=NO)

?

2

READY

APPENDIX C

CONVERGENCE TECHNIQUES

In the case of a non-linear relation or procedure, implicit in the system variables being solved for, an iterative technique must be used. The Newton-Raphson method was suitably modified for use.

Figure 33 shows the graph of an error function, E , defined as the difference between the quantity computed from the calculation procedure minus the quantity assumed versus the guessed(assumed) values of the quantity. The answer to the problem is the value of the assumed quantity at which this error function goes to zero. The Newton-Raphson method is a convergence accelerator which is based on two initial guesses for the quantity being solved for and a linear extrapolation for the error function computed from these two guesses. This extrapolation gives the next value of the variable to be assumed. The general recursive relation is therefore:

$$E_{n+1} = 0 = E_n + (T_{n+1} - T_n)dE_n/dT$$

and,

$$dE_n/dT = (E_n - E_{n-1})/(T_n - T_{n-1})$$

so that,

$$T_{n+1} = T_n - E_n(T_n - T_{n-1})/(E_n - E_{n-1})$$

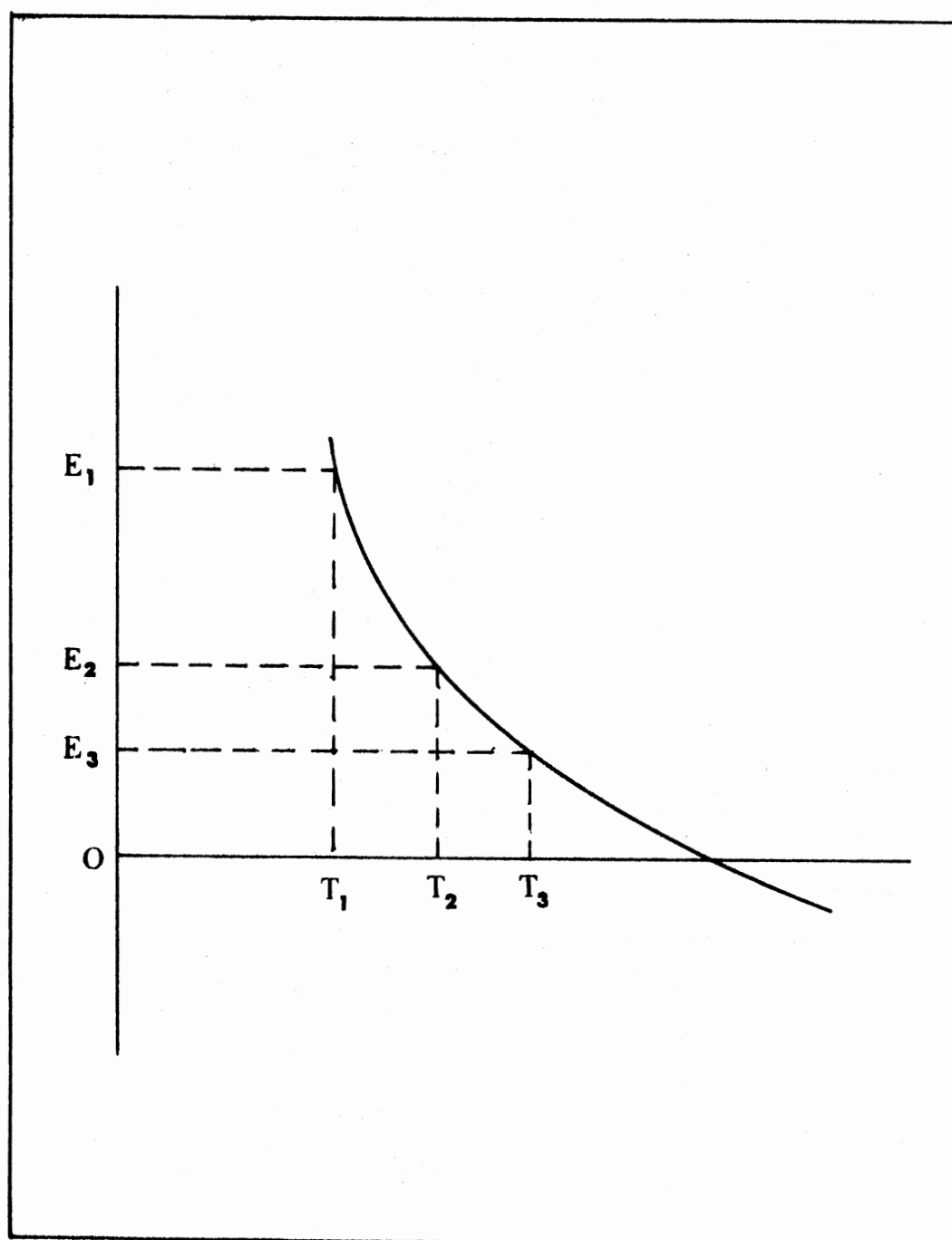


Figure 33. Newton-Raphson Convergence

2
VITA

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