

EXPERIMENTAL EQUILIBRIUM AND MODELING FOR
THE ABSORPTION OF ACID GASES IN
DIETHANOLAMINE SOLUTIONS AT
LOW AND HIGH PARTIAL
PRESSURES

By

ERARDO MARIO ELIZONDO VILLARREAL

Ingeniero Quimico

Universidad Autonoma de Nuevo Leon

Monterrey, Mexico

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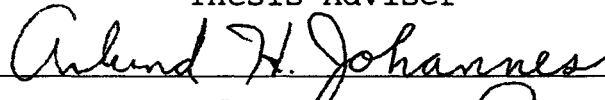
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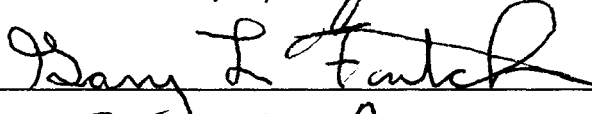
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Thesis Approved:



Thesis Adviser









Dean of the Graduate College

PREFACE

An experimental apparatus is developed to measure the equilibrium solubility of acid gas in diethanolamine solutions at low partial pressures. A direct measurement is made of the differential pressure between an equilibrium cell and a reference cell. Carbon dioxide and hydrogen sulfide equilibrium solubilities were obtained at acid gas partial pressures below 11 psia down to about 0.003 psia at 80, 150 and 240°F and 20, 35 and 50% by weight diethanolamine aqueous solutions. A consistency test is developed and shown to apply in the full range of partial pressures where chemical reactions dominate. Predictions of equilibrium acid gas partial pressures were improved and good results when modeling plant data were obtained.

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CHAPTER I

INTRODUCTION

Natural gas, refinery gas, and synthesis gas usually contain undesirable compounds like hydrogen sulfide (H_2S), carbon dioxide (CO_2), and water vapor (H_2O). In most cases these materials must be removed before the gas can be transported and sold.

Acid gases such as H_2S and CO_2 can cause corrosion in process equipment and pipelines. H_2S is particularly troublesome because of its wide occurrence and toxicity. CO_2 can be tolerated if the gas does not contain water vapor. The combustion products of H_2S , sulfur dioxide, and sulfur trioxide are atmospheric pollutants, and, on a mass basis, the harmful effects are comparable to those of hydrocarbons and nitrogen oxide (33). Environmental regulations in combination with exploitation of poorer crudes and natural gas resources make the removal of acid gases (gas sweetening) more important than ever.

There are several processes to sweeten gas streams, however, the most widely used in the gas industry are the alkanolamine (amine) processes. They are used mainly for purifying gas streams with small to medium amounts of acid

gases or for follow-up sweetening in conjunction with bulk removal processes (45, 32).

The first process using aqueous alkanolamine solutions was developed by Bottoms (8), who used triethanolamine for sweetening natural gas. Amines of commercial importance are monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and glycol amine (MEA or DEA with glycol to sweeten and dehydrate the gas simultaneously) (45, 32). Monoethanolamine and diethanolamine are widely used, and are non-selective removing both H_2S and CO_2 (45). MEA reacts irreversibly with carbon disulfide and carbonyl sulfide, causing solids buildup in the MEA solution. DEA reacts reversibly with them, and the products of these reversible reactions will be released with acid gases in the flash gas (64). This fact favors the use of DEA for sweetening refinery and manufactured gas streams (45). MEA solutions are more corrosive than most amine solutions for MEA concentrations higher than 20 weight percent and for high acid gas loadings. However, MEA solutions are preferred for gas streams with low concentrations of H_2S and CO_2 and essentially no carbonyl sulfide and carbon disulfide (32). DEA has a lower vapor pressure than MEA, implying less loss for a given operating temperature. After regeneration, aqueous DEA solutions have lower concentrations of acid gases than MEA solutions (45). These advantages of DEA over MEA make DEA the choice for sweetening of

high pressure sour natural gases with high concentrations of acid gases, with or without carbonyl sulfide and carbon disulfide (32). The sweet gas will meet pipeline specifications (one-quarter grain of H_2S per 100 standard cubic feet of gas (45)).

The equilibrium solubility of H_2S and CO_2 in the amine is required to obtain good design and operation of industrial sweetening units. The sweet gas specification represents a H_2S partial pressure of 0.20 mm Hg (0.0039 psia) for an amine contactor at 1000 psia (45). In addition, the presence of CO_2 in the amine solution affects the partial pressure of H_2S . As a result, experimental equilibrium data at low partial pressure for H_2S -aqueous DEA solutions and CO_2 -aqueous DEA solutions is essential.

This study was undertaken to obtain experimental equilibrium data on the solubility of H_2S and CO_2 in aqueous DEA solutions at low partial pressure. The systems studied were:

1. CO_2 -DEA (for 20%, 35%, and 50% by weight DEA)
 - (a) 80°F (26.67°C)
 - (b) 150°F (65.56°C)
 - (c) 240°F (115.56°C)
2. H_2S -DEA (for 20%, 35%, and 50% by weight DEA)
 - (a) 80°F (26.67°C)
 - (b) 150°F (65.56°C)
 - (c) 240°F (115.56°C)

A procedure to correlate the experimental information obtained in combination with available literature data at high partial pressures of H_2S and CO_2 in aqueous DEA solutions will be presented and tested to establish a model for the CO_2 - H_2S -aqueous DEA systems.

The apparatus used is a modification of that of Bhairi (5), to measure solubilities corresponding to acid gas partial pressures in the order of 0.20 mm Hg (0.0039 psia). The method used to calculate acid gas loadings is modified by assuming ideal gas under the low pressures considered.

CHAPTER II

LITERATURE SURVEY

The equilibrium solubility data at low partial pressure of acid gas in aqueous DEA solutions is presented. A brief description of experimental techniques that have been used is given. Different correlating models and reaction mechanisms are summarized.

DEA Data

Bottoms (8) was the first to publish solubility data for CO_2 and H_2S in aqueous DEA solutions at low partial pressures. His plots can be read to as low as 0.20 psia. Mason and Dodge (47) worked with CO_2 down to 0.19 psia at four different DEA concentrations and temperatures. Lee et al. (36, 37, 38) obtained experimental data over a range of temperatures, DEA concentrations, and from relatively low partial pressure (0.27 psia) to high partial pressure of acid gas. Of the other experimental data published below 0.27 psia, Lawson and Garst (35) and Lal et al. (34) studied one DEA concentration; Murzin and Leites (49) data for CO_2 have to be read from small scale plots; Atwood et al. (3) reported only three or four points for each tempera-

ture; and Leibush and Shneerson (42) covered two amine concentrations and three temperatures for H_2S only. Table I summarizes the experimental solubility data at low partial pressure of acid gas found in the literature for DEA. Table I shows there is a lack of experimental data in the low partial pressure range.

Experimental Techniques

There are two basic types of experimental methods used to determine the solubility of acid gases in aqueous alkanolamine solutions, the saturation, or open system method and the closed system. The saturation method uses a series of saturators immersed in a constant temperature bath. The saturators contain amine at the desired concentration. A carrier gas with acid gas, or a mixture of acid gases, is bubbled in the amine solution. Equilibrium is reached when there is no change in outlet gas composition as checked by Orsat analysis (3, 47), mass spectrometry (48), or gas chromatography (27). Liquid samples are then drawn for analysis. This method has been used for low to medium partial pressures.

The closed system uses an equilibrium cell placed in a constant temperature bath. Lee et al. (37, 38) used a magnetic pump to recirculate the vapor phase and improve mixing in the cell. Bhairi (5) used a shaking bath. Lee et al. (36) and Lawson and Garst (35) used magnetic stirrers. Most researchers (36, 35, 37, 38) feed the amine solution

TABLE I
LITERATURE SURVEY OF SOLUBILITY DATA
LOW PARTIAL PRESSURE OF ACID GAS
DEA AQUEOUS SOLUTION

Author	Acid Gas	Normality (Weight %)	Temperature °F	Lowest Pressure Psia
Bottoms (8)	H ₂ S, CO ₂	(50)	77, 95, 113, 131	0.20, 0.20
Mason and Dodge (47)	CO ₂	0.5, 2.0, 5.0, 8.0	32, 77, 122, 167	0.190
Lee et al. (36)	CO ₂	0.5, 2.0, 3.5, 5.0	77, 122, 167, 212, 248	0.27
Atwood et al. (3)	H ₂ S	(10, 25, 50)	80, 140	0.009
Lawson and Garst (35)	H ₂ S, CO ₂	(25)	100, 125, 150, 175, 200, 225, 250	2 x 10 ⁻⁴ , 0.29
Leibush and Shneerson (42)	H ₂ S	0.97, 2.0	59, 77, 122	0.001
Murzin and Leites (49)	CO ₂	0.5, 1.0, 2.0, 5.0, 8.0	77, 122, 167, 212, 248	0.004
Lal et al. (34)	H ₂ S, CO ₂	2.0	104, 212	0.0014, 0.0061
Lee et al. (37, 38)	H ₂ S	0.5, 2.0, 3.5, 5.0	77, 122, 167, 212, 248	0.350

after the cell is purged with an inert gas. The acid gas is then injected to the desired pressure. Equilibrium is reached when the cell pressure is constant. Liquid and vapor samples are then taken for analysis. Liquid samples are analyzed by evolving the gas with the addition of an excess of a strong acid and heating. The gas evolved is measured with a calibrated burette . When H_2S is present, an oxidizing agent is used in excess (iodine solution) and the excess titrated with standard solution (sodium thiosulfate). Vapor samples are analyzed using gas spectrometry (35) or gas chromatography (3, 37, 38).

Bhairi (5) developed a new technique using the closed system. The equilibrium cell is evacuated and fed several times with the acid gas under study to eliminate air from the system. An initial amount of acid gas is fed, then the amine solution is injected. Equilibrium is reached when the pressure stops decreasing. Acid gas loading is determined by material balances from the initial and final quantities in the vapor phase. This technique does not require analysis when working with a single acid gas.

Models and Reaction Mechanisms

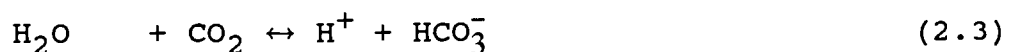
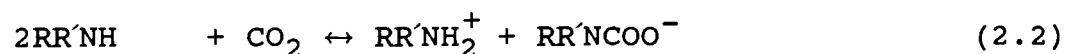
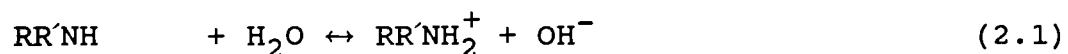
Two approaches are available, the equilibrium models and the mass transfer models. Different reaction mechanisms are used by different authors to specify the system and determine the unknowns involved.

Equilibrium Models

The use of equilibrium models has been the most successful technique to correlate and predict the partial pressure of acid gases above alkanolamine solutions. Basically, the technique requires postulating a set of reactions to satisfy the stoichiometry. The pseudo equilibrium constants or equilibrium constants for the reactions are then combined with necessary thermodynamic constraints to provide a correlating model for the equilibrium solubility data.

Atwood et al. (3) developed a method using the "mean ionic activity coefficient." They assumed that the activity coefficients of all ionic species were equal. They applied the method to H_2S in aqueous amine solutions and stated that their method may serve as a guide for engineering calculations. The assumption of equal activity coefficients is applicable to low ionic strength only, which is not the case for most acid gas-amine systems.

Klyamer et al. (31) generalized the Atwood et al. model for H_2S-CO_2 - aqueous amine solutions. They postulated the following reactions:

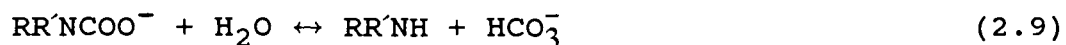
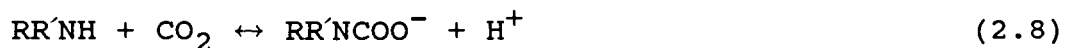




where R stands for $-\text{CH}_2-\text{CH}_2-\text{OH}$ and R' for $-\text{CH}_2-\text{CH}_2-\text{OH}$ to represent DEA or $-\text{H}$ to represent MEA.

The equilibrium constants for these seven reactions in combination with a charge balance (electroneutrality), mole balances, and Henry's law to relate gas and liquid phase concentrations of H_2S and CO_2 form the set of equations to chemically describe the system. To solve for the unknowns, the equilibrium constants for the reactions, the Henry's law constants as well as the mean ion activity coefficient (which is dependent upon ion concentration) and the ratio between the activity of un-ionized amine to the activity of water, must be known. Klyamer et al. studied MEA aqueous solutions, took equilibrium constants from the literature, and used the mean ionic activity coefficient and the ratio of activity of un-ionized amine to that of water from Atwood et al. (3). Comparisons with experimental data have been made by Lee et al. (40, 41), who concluded that the Klyamer et al. model is not in agreement with their experimental results over the complete range of conditions within the precision of their data.

Danckwerts and McNeil (16) developed a model for solution of carbon dioxide into aqueous amine solutions. Their set of reactions was (2.3) to (2.5) plus:



They used pseudo equilibrium constants corrected for the effects of ionic strength, Henry's law, a charge balance, and mole balances. When this model was used to predict equilibrium partial pressures, substantial deviations from experimental data were found (29).

Kent and Eisenberg (29, 30), extended and modified the Danckwerts and McNeil work. They proposed the set of reactions (2.3) to (2.7) and (2.9) plus:



and Henry's law for H_2S and CO_2 :

$$P_{\text{H}_2\text{S}} = H_{\text{H}_2\text{S}} [\text{H}_2\text{S}] \quad (2.11)$$

$$P_{\text{CO}_2} = H_{\text{CO}_2} [\text{CO}_2] \quad (2.12)$$

Kent and Eisenberg accepted literature values of the equilibrium constants for reactions (2.3) to (2.7) and forced the amine pseudo equilibrium constants (reactions (2.9) and (2.10)) to fit CO_2 -aqueous amine and H_2S -aqueous amine experimental equilibrium data. The fitted pseudo equilibrium constants exhibited an Arrhenius dependence with temperature. The model was extended to predict H_2S - CO_2 -aqueous amine systems. Comparisons with experimental data for these systems indicated reasonable predictions. Lee et

al. (40, 41) found disagreement with their experimental results especially at high partial pressure of acid gas, suggesting that Henry's law using fugacities should be employed.

Comparisons (50) between the Klyamer et al. and the Kent and Eisenberg models showed that both methods consistently underestimate the partial pressure of H_2S , while better predictions were obtained for CO_2 in aqueous MEA systems. In the low partial pressure range, the Kent and Eisenberg model was consistently closer to experimental (27). Batt et al. (4), using the Kent and Eisenberg model, improved the predictions for MEA and DEA systems and extended the model to DGA and DIPA. Loh (43) extended it for MDEA. Comparisons of the improved predictions and extensions to other amines with experimental and plant data indicated good agreement.

Deshmukh and Mather (21) proposed a model based on reactions (2.1), (2.8) and (2.3) to (2.7) for which they used equilibrium constants. The activity coefficient and molality of the species are required. For the vapor-liquid equilibrium of acid gases, they used the fugacity coefficient, calculated by the Peng-Robinson equation of state, and the Henry's law constant in molality units. For water, the vapor-liquid equilibrium was included through the fugacity coefficient, setting the water activity coefficient to unity and neglecting the effect of pressure on the fugacity of pure liquid water. Electroneutrality and mole

balances were considered. They calculated the activity coefficients with the Debye-Huckel expression presented by Edwards et al. (24):

$$\ln \gamma_i = \frac{-Az_i^2 I^{0.50}}{1 + Ba I^{0.50}} + 2 \sum_{j \neq i} \beta_{ij} m_j \quad (2.13)$$

where:

- γ_i = activity coefficient of species i.
- A = proportionality factor related to the dielectric constant of the solvent.
- z_i = charge number of species i.
- I = ionic strength $\equiv 0.5 \sum_i m_i z_i^2$.
- m_i = molality of species i.
- β_{ij} = specific interaction parameter between i and j.
- Ba = constant = 1 if I is in molality units.

The interaction parameters, β_{ij} , were curvefitted by least squares to experimental data from single acid gas-aqueous MEA data (39, 40) assuming that only $RR'NH_2^+$, $RR'NCOO^-$, HCO_3^- , and HS^- were present in significant amounts to be considered. The interaction parameters for CO_2 , H_2S , OH^- , H^+ , $S^{=}$, $CO_3^{=}$, H_2O and $RR'NH$ were neglected. Values for the equilibrium constants were taken from the literature. The model was extended to H_2S-CO_2 - aqueous MEA. They stated that agreement of predicted partial pressures with experi-

mental values was much better than models proposed previously.

Maddox et al. (46) proposed a model involving reactions (2.3) to (2.7) and (2.9), (2.10); Henry's law corrected by ionic strength as suggested by Silvester and Pitzer (58) was applied to equations (2.11) and (2.12); electroneutrality and mole balances were used. They first used the pseudo equilibrium constants corrected by ionic concentration effects for single and double charged ions given by Davies (20). However, predicted values were not in agreement with experimental; then, they defined an ionic correction factor as a function of ionic strength, one for protonation of amine and one for carbamate formation. These correction factors were obtained from equilibrium data for pure H_2S - aqueous amine and pure CO_2 - aqueous amine. All the other reactions involved were corrected by Davies' corrections. The predicted values were relatively good for mixtures of acid gases and aqueous MEA systems.

Planche et al. (53) presented a model based on the same reactions as the Kent and Eisenberg model. They considered the equilibrium constants for the reactions as a function of the activity coefficients. The expressions for the equilibrium constants were taken from Kent and Eisenberg's model. The Henry's law constants were obtained from Edwards et al. (23). Their model was proposed for only low partial pressures of CO_2 and H_2S . Accordingly, the fugacities were set to one for all volatile species. Evaluation

of the activity coefficients was done based on an equation of state developed by them. Experimental data were used to adjust the parameters involved. The calculation of the real concentrations in the liquid phase was based on the minimization of the Gibbs energy in which the variation of activity coefficients with concentration was neglected. The model predictions were compared with Lal et al. (34) experimental data. They concluded that the vapor-liquid equilibrium was enhanced, but the poor accuracy of the experimental data put a limit on the comparisons. They stated that the most significant parameters were precise chemical reaction constants and good values of the Henry's law constants.

In principle, the model proposed by Planche et al. is using the Kent and Eisenberg equilibrium constants, even though the equilibrium constants for carbamate formation and protonation of the amine were curvefitted to experimental data. This curvefitting procedure already accounted for non-idealities in the system. In addition, Planche et al. also curvefitted their parameters to experimental data. They then evaluated the activity coefficients. However, they should have taken all the equilibrium constants from non-curvefitted expressions and curvefitted their parameters to experimental data.

Tamcej and Otto (59) used a modified Kent and Eisenberg approach. The equilibrium constants for protonation of amine and carbamate formation were curvefitted to exper-

imental single acid gas solubility data as a function of temperature, solution loading, and amine concentration. Good predictions were reported.

As has been presented, there are mainly two types of equilibrium models, those based on pseudo equilibrium constants and those based on equilibrium constants. In both types, a set of reactions is proposed and vapor-liquid equilibrium for acid gases or acid gases and water is considered. The most recent models (21, 29, 46) involve curvefitting to single acid gas-aqueous amine experimental data. The curvefitting allows one to extend the predictions to $\text{H}_2\text{S}-\text{CO}_2$ - aqueous amine systems with good results. From these models, only the one by Kent and Eisenberg has been extended to practically all the amines of industrial interest. This is because of the simplicity involved in approaching the description of the acid gas-aqueous amine system.

Mass Transfer Models

The mass transfer models are based on the assumption that there is no vapor-liquid equilibrium between the bulk phases. Equilibrium is assumed only at the interface. As a result, a diffusional process is established due to the difference in concentration within each phase. Acid gases will transfer to the interface, then to the liquid phase. The models require a theory for the diffusional process.

Two film, penetration, and surface renewal theories all have been used. The two film theory says that the mass transfer coefficient is proportional to the diffusion coefficient. The penetration and surface renewal theories say that the mass transfer coefficient is proportional to the square root of the diffusion coefficient. None of these theories take into account interfacial turbulence regarded as eddy diffusion (61). These type of models need not only the equilibrium solubility data, but also estimation of the mass transfer coefficients for H_2S and CO_2 in a reacting system and kinetic constants for the reactions involved in the mechanism chosen.

Ouwerkerk (51) used the steady state two film theory of Whitman to evaluate the absorption kinetics of H_2S alone and the surface renewal theory of Danckwerts for the absorption of CO_2 .

The reaction he considered for H_2S was:



which is instantaneous, so that equilibrium is attained everywhere in the liquid phase. The molar flux for H_2S , $J_{\text{H}_2\text{S}}$ was expressed as:

$$J_{\text{H}_2\text{S}} = \frac{k_{1,s}}{E_s} ([\text{H}_2\text{S}]_i - [\text{H}_2\text{S}]_b) \quad (2.15)$$

where: $k_{1,s}$ = mass transfer coefficient in the liquid phase for H_2S .

- E_s = relative penetration depth in the film.
 $[H_2S]$ = concentration of H_2S .
 i,b = interface, liquid hulk.

The penetration depth, E_s , is the distance from the interface where the reaction takes place. He assumed their value was very small and approximated the molar flux as:

$$J_{H_2S} = k_1 \chi_{s,i} [RR'NH] \quad (2.16)$$

- where:
- $\chi_{s,i}$ = fraction of amine converted by H_2S .
 $[RR'NH]$ = total amine concentration initially.
 k_1 = mass transfer coefficient in the liquid phase.

Equation (2.16) plus the equilibrium constant for reaction (2.14) gave close agreement with experimental data for 2M DEA at 25°C.

For CO_2 he assumed the only reaction with primary or secondary amines was reaction (2.2). This reaction was considered pseudo-first-order at an amine concentration equal to the interfacial value. Then from the surface renewal theory and assuming fast reaction takes place at low CO_2 partial pressure, the molar flux for CO_2 , J_{CO_2} became:

$$J_{CO_2} = (k[RR'NH]_b D_c)^{0.05} p_{ci}/H_c \quad (2.17)$$

where: k = reaction rate constant for (2.2).

$[RR'NH]_b$ = total amine concentration in the liquid bulk.

D_C = diffusion coefficient of CO_2 in the liquid.

p_{Ci} = partial pressure of CO_2 at interface.

H_C = Henry's law constant, CO_2 .

At high CO_2 pressure, absorption with instantaneous reaction predominates:

$$J_{CO_2} = 0.50 k_1 [RR'NH]_b \quad (2.18)$$

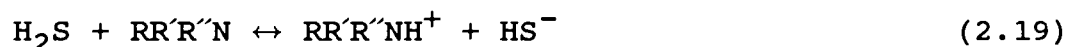
Close agreement of (2.17) and (2.18) with experiment was reported. The individual mass transfer coefficients, k_g and k_l , and the interfacial area per tray and per unit of bubbling area, a' , were measured experimentally for a trayed column 11 cm in diameter. The air- CO_2 -2M DIPA system was used to measure a' . The air- CO_2 -0.20M DIPA system was studied to measure $k_l a'$. The air- SO_2 -2M DIPA system was studied to measure $k_g a'$. These systems were studied in a search for selective absorption of H_2S .

After the experimental determinations, the application for simultaneous absorption of H_2S and CO_2 in DIPA was done in the 11 cm trayed column. The set of equations describing the system involves the molar fluxes for each acid gas to the interface and from it to the reaction front in the liquid, the electroneutrality equation, the amine balance

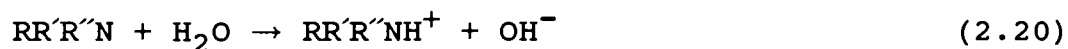
equation and the pseudo equilibrium constant for reaction (2.14). Ouwerkerk assumed that all of the absorbed CO_2 is converted in the liquid film; therefore, there is no CO_2 in the liquid bulk. The predictions for the 11 cm contactor, matched experimental results. Based on results obtained, a contactor of 8.50 m was reported successfully designed for a Claus Off-Gas Treating Process.

The approach given by Ouwerkerk allowed for solution algebraic equations rather than differential. There is no indication about calculating the diffusion coefficient of CO_2 in the liquid phase. In estimating the mass transfer coefficient in the liquid phase, reaction (2.2) was considered irreversible. As a result, the mass transfer model used for the interpretation of experimental data neglected the reversibility.

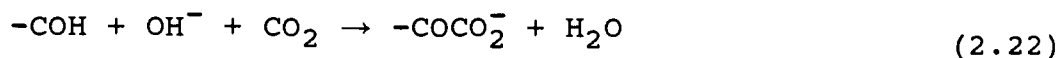
Cornelissen (15) applied the two film theory with linearized concentration profiles. He stated that this model is not very realistic but is far simpler than the Higbie penetration theory. The model was applied to tertiary amines as an extension of Ouwerkerk's work (51). The reaction with H_2S used was:



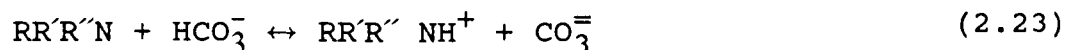
The reactions considered for CO_2 were reaction (2.3) plus:



and the reaction of CO_2 with hydroxyl groups of the alkanolamine to form alkyl carbonate:



which was incorporated into the rate constant of (2.21). When $\text{pH} > 9$ the bicarbonate/carbonate equilibrium was considered:



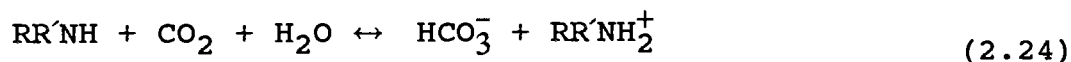
R'' is an alkanol group. The Henry's law constants, and the liquid and gas side mass transfer coefficients were obtained experimentally. The mass transfer coefficients were converted on the basis of both, k_g and k_l , being proportional to the square root of the diffusion coefficient as suggested by Danckwerts (19). Liquid phase diffusion coefficients were estimated by a method presented by Akgerman and Gainer (1). The method of Wilke and Lee (65) was used to estimate the diffusion coefficients in the gas phase. Rate constants for reactions (2.3) and (2.21) were from Pinsent et. al. (52). Rate constants for reactions of CO_2 with various alkanolamines were obtained experimentally. Equilibrium for H_2S - amine was determined experimentally at different temperatures and molarities.

The set of equations that describes the system includes the absorption flux for H_2S and CO_2 as function of the overall and individual mass transfer coefficients and driving forces; the electroneutrality equation in which the

hydrogen ion concentration was neglected; the amine balance; the H_2S and CO_2 balances in which the concentration of CO_2 in the bulk was neglected and the pseudo equilibrium constants for the reactions involved. The method described was applied to a tray in conjunction with a separate algorithm for the iterative tray by tray calculation for a 0.11 m diameter contactor equipped with valve trays. Good results were reported. The method provided the basic for the design of commercial-scale contactors for selective absorption of H_2S . Results were not reported.

The method proposed by Cornelissen even though it uses the film theory, evaluates the mass transfer coefficients as the penetration and surface renewal theories do. Neglecting the CO_2 and hydrogen ion concentration might be acceptable at very low loadings. There is no information on which tertiary amine the model was applied in the pilot contactor.

Cornelisse et. al. (14) used the film theory for the gas phase and the penetration theory for the liquid phase. They proposed reactions (2.2) and (2.14) plus the bicarbonate formation as:



They considered (2.24) contribution only in the liquid bulk.

According to the Higbie penetration theory, unsteady state mass transfer equations were established for CO_2

reaction balance, total CO_2 , H_2S , amine and acid gas balances. They assumed the bulk of the liquid to be in equilibrium for a given loading of H_2S and CO_2 . Then mole balance equations were set for H_2S , CO_2 and amine. Pseudo equilibrium constants for reactions (2.2) and (2.14) were considered. The charge balance took into account the electrically charged species in reactions (2.2), (2.14) and (2.24). The boundary conditions included equal transfer rates at the gas and liquid sides of CO_2 and H_2S ; no amine, no HS^- , no carbamate can pass the interface. They used the three point backward scheme with the parabolic differential equations. This procedure gave a set of linear algebraic equations which were solved by using the three diagonal matrix algorithm. The values for liquid and gas mass transfer coefficients, Henry's law and equilibrium constants were obtained from the literature. The diffusion coefficients were all taken equal, allowing comparison with the results of previous works based on different transfer models. Agreement was within 7% when compared with the approximate solutions of Ouwerkerk (51) and Cornelisse et. al. (13) under the assumptions of pseudo irreversible reaction for CO_2 and instantaneous reversible reaction for H_2S .

Astarita and Savage (2) presented a simplified thermodynamic model for the system CO_2 - H_2S - aqueous MEA solutions at very low acid gas loadings. They based their model in reactions (2.2) and (2.19) with R' and R'' substituted by $-\text{H}$. They assumed that both reactions were instantaneous so

there would be chemical equilibrium at every point in the liquid phase. In addition, all diffusion coefficients were equal. The analysis was based upon the two film theory which gives the same results as the penetration theory when all diffusion coefficients are equal. Equilibrium constants, Henry's law constants, equilibrium partial pressures versus loading and diffusion coefficients were taken from the literature. The results obtained were within 5% of the values from Kent and Eisenberg (29).

Haimour and Sandall (25), developed a model for the absorption of acid gases in aqueous DEA solutions. Their model was recommended for DEA concentrations greater than 1M and was applied to 15% by weight DEA solution. The penetration theory was used. They considered reactions (2.2) and (2.14) and assumed that both reactions were irreversible. Second order kinetics for the CO_2 -DEA reaction (first order with respect to both CO_2 and DEA) and instantaneous reaction for H_2S with DEA were assumed. The unsteady state diffusion equations were established considering a moving boundary within which CO_2 and H_2S are not reacting, only diffusing. The system of equations was solved numerically using a finite difference method. The diffusion coefficient of CO_2 in DEA solutions was obtained by using the N_2O analogy. This analogy assumes that the ratio of the diffusion coefficient of CO_2 to that of N_2O in water and in solutions having different DEA concentrations, is constant. A similar assumption for the diffusion coef-

ficient of H_2S was made. The solubility of free CO_2 in aqueous DEA was taken from the literature and divided by the solubility of CO_2 in pure water under similar conditions. Then the ratio for CO_2 was assumed to be applicable to the solubility of free H_2S in aqueous DEA. They presented a parametric analysis and concluded that to obtain high selectivity towards H_2S , short contact times and low temperature are required. This model does not take into account the reversibility of the reactions involved, nor the electroneutrality of the solution.

Haimour et. al. (26) applied the two film theory to model the absorption of acid gases in aqueous MDEA solutions. The physical properties and kinetic rate parameters required were measured in their laboratory. The reactions considered were (2.19) and the summation of reactions (2.20) and (2.21). In these reactions, R'' is substituted by $-CH_3$. The reactions were assumed irreversible. CO_2 was assumed to undergo a second order reaction with MDEA. Steady state diffusion equations were established. The rate at which MDEA diffuses from the liquid to the interface was set equal to the rate of H_2S diffusion from the interface to the liquid. This assumption neglects the contribution of CO_2 in the process of MDEA diffusion. According to their boundary conditions, there will not be free H_2S in the liquid bulk. This is because they neglected reversibility in the reaction, as a result, their model may be applied for the lean end of industrial con-

tactor. Test of this model with industrial data was not presented, a parametric analysis was given instead. Their results indicate that higher selectivity for H_2S is obtained in contactors having short contact times, operating at low temperature and using concentrated MDEA solutions.

Tomcej and Otto (59) proposed three options for mass transfer models. The Murphree vapor efficiency, the vaporization efficiency and the use of mass transfer coefficients. The three options are related. The Murphree vapor efficiency E_{mv} for a component i in stage j is defined as:

$$E_{mv} = \frac{Y_{ij} - Y_{ij+1}}{Y_{ij}^* - Y_{ij+1}} \quad (2.25)$$

where: Y_{ij} = actual mole fraction in the vapor.
 Y_{ij}^* = mole fraction in the vapor which
 is in equilibrium with a liquid
 of a mole fraction X_{ij} .
 Y_{ij+1} = actual mole fraction in the vapor
 coming in.

The vaporization efficiency \mathcal{E} for a component i in stage j is:

$$Y_{ij} = \mathcal{E}_{ij} K_{ij} X_{ij} \quad (2.26)$$

where: K_{ij} = equilibrium ratio for i .

The overall gas-phase mass transfer coefficient for absorption, K_{og} , is defined as a function of the individual gas and liquid mass transfer coefficients, k_g and k_l , as:

$$\frac{1}{K_{og}} = \frac{1}{k_g} + \frac{H}{E k_l} \quad (2.27)$$

where H is the Henry's law constant and E the correction factor which takes into account the turbulence regarded as eddy diffusivity and the reaction in the liquid phase. When complete mixing is assumed on the stage, E_{mv} is related to K_{og} by:

$$E_{mv} = 1 - \exp(-za K_{og} P/G) \quad (2.28)$$

where: z = height of liquid on stage.

a = interfacial area per unit volume.

P = total pressure of equilibrium stage.

G = molar flow rate of gas per unit cross-sectional area of tower.

Tomcej and Otto suggested that the designer could draw upon experience and using equation (2.28) to simulate the system. Examples using (2.28) were not presented.

Katti and Langfitt (28) proposed a mass transfer model for the system H_2S - CO_2 - aqueous MDEA using the film theory. The liquid phase composition was calculated using the Deshmukh and Mather (21) approach, already described. The reactions considered were (2.3) to (2.7) and (2.20). The binary interaction parameters required in (2.13) were

curvefitted using experimental data from Chakravarty (10). The equilibrium constants for the reactions were taken from the same source. A separate model and different set of parameters were developed for low acid gas loading.

The absorption process was assumed to be governed by reactions (2.19) and the summation of (2.20) and (2.21), with R" representing $-\text{CH}_3$. Reversibility for the CO_2 -MDEA reaction was neglected. The reaction rate constants were taken from Yu et al. (66). The reaction for H_2S -MDEA was assumed instantaneous, which means equilibrium everywhere in the liquid film. The mass transfer coefficients and interfacial areas for tray columns were obtained from purely physical correlations, and were empirically corrected based on plant data comparisons for the system. They assumed the correction factors obtained to be applicable under all sets of operating conditions. Their model was successfully tested against industrial data on various contactors. An interesting aspect is that the kinetic study by Yu et al. (66) involves a correction factor extracted from vapor-liquid equilibrium data available in the literature. This correction factor was obtained for the equilibrium partial pressure as a function of CO_2 reacted, instead of using the Henry's law constant, the equilibrium constant for the protonation of amine and the first dissociation constant of carbonic acid.

Tomcej et al. (60) proposed a mass transfer model based on a modified Murphree vapor efficiency defined as

the ratio of the moles of component i leaving stage j in the vapor phase to the moles of component i leaving stage j if it were equilibrium. Material and energy balances in addition to a set of stage efficiency relationships form the nonlinear algebraic equations to be solved. Estimation of the modified Murphree efficiency involves the solution of a differential material balance on the tray and estimation of the overall mass transfer coefficient by equation (2.27). The reactions considered for primary and secondary amines were (2.2), (2.14) and (2.21). The mechanism for reaction (2.2) was that proposed by Danckwerts (18). For tertiary amines reaction (2.19), the summation of (2.20) and (2.21) plus (2.21) itself were taken. Reaction rate constants for CO_2 in different amines were obtained experimentally. The N_2O analogy was used for Henry's law constant and the diffusion coefficient for CO_2 in MDEA solutions. They only presented a parametric study and no comparisons with industrial data.

Sardar et. al. (55, 56, 57) developed a mass transfer model for acid gases with aqueous MEA, DEA or MDEA using the film theory. The Deshmukh and Mather (21) approach was used when calculating the liquid phase composition and equilibrium at the interface. The reactions taken for MEA and DEA were (2.2) to (2.7) and the reverse of (2.10). The set of reactions for MDEA was (2.3) to (2.7) and the reverse of (2.10) modified for MDEA. Binary interaction parameters for (2.13) and equilibrium constants for the

reactions were obtained from Chakravarty (10). A general description was given with respect to evaluating mass transfer coefficients, and material and energy balances for each phase. No information was presented about which reactions were considered to dominate the absorption process, nor from which source the reaction rate constants were taken for them. The Henry's law constant was corrected by ionic strength according to Danckwerts (19). Trayed and packed column were handled.

Comparisons with plant data for MEA regenerator, MDEA contactor, MDEA regenerator, an integrated (contactor and regenerator) MDEA plant and integrated CO_2 -DEA and CO_2 -MEA plants were made. Satisfactory predictions were presented. There are two interesting points to mention. First, for regeneration their model predicts almost equilibrium temperature (within 0.5°F difference) for the bulk phases, even though the assumption of equilibrium temperature at the interface was made. Second, for one of the two MDEA contactors presented, they found that by increasing by 5% the gas-side mass transfer coefficient for H_2S , they would meet plant data. For that contactor, H_2S was absorbed in the upper half, with negligible absorption of H_2S in the bottom. No H_2S profile was shown after increasing the gas-side mass transfer coefficient.

Chakravarty et. al. (11) proposed a mass transfer model for absorption of CO_2 in blended aqueous MEA-MDEA. The Deshmukh and Mather (21) model was used for vapor-

liquid equilibrium calculations. Binary parameters needed in (2.13) for various ion-ion and molecule-ion interactions were fitted to experimental data. Their basic approach was to fit this model to all the data on single-acid gas single-amine systems, then extend the model to mixed solvents. For the CO_2 -MEA-MDEA system, the reactions taken were (2.2) to (2.5) and (2.20). Their model involved material balances on each amine, an electroneutrality equation, CO_2 balance and equilibrium relationships for each reaction. These equations should be solved together with phase equilibrium equations. They used the film theory and assumed that the rate of diffusion of the acid gas through the liquid film was equal to the rate of consumption by reaction. They presented correction factors for the mass transfer coefficient in the liquid phase (enhancement factors) for MEA/MDEA blends at total 30% by weight, under contactor and regenerator conditions. Then suggested that blended amines are a potential improvement, since advantages of each amine for absorption as well as desorption can be taken without the disadvantages of either. Interaction parameters between ion-ion and molecule-ion in the blends cannot be obtained from single acid gas-amine systems, therefore they must have been assumed. However, there is no comment about that in the article.

Vickery and Weiland (62) extended the work of Chakravarty et al. (11) to acid gases in blended aqueous MEA-MDEA and DEA-MDEA. They assumed "reasonable" values

for the interaction parameters present only in mixed amine systems and required when calculating activity coefficients by equation (2.13). They indicated that the equilibrium pressures did not change by more than 2% when the additional interaction parameters were neglected. The reactions considered were (2.3) to (2.8), the reverse of (2.10) and



for the protonation of MDEA. They simulated blends containing 3.5 molar total amine. Their parametric analysis shows that the use of MEA in blends with MDEA reduces the equilibrium pressures of CO_2 over loaded solutions, compared to MDEA alone. The presence of H_2S has little effect on the reduction of CO_2 equilibrium pressure. In DEA-MDEA blends, their predictions indicate small differences with respect to MEA-MDEA blends, even for a 1M DEA contribution in the blend.

Recently, Vickery et al. (63) extended the work for acid gases in blends of aqueous DGA-MDEA and DIPA-MDEA. They called it the "rate approach" instead of the "non-equilibrium models" as was initially introduced. In this paper they compared their predictions with plant data for a DEA-MDEA blend. Deviations for sweet gas composition are 5.42% for CO_2 and 154% for H_2S . For the loading in the rich amine the deviations are 8.4% for CO_2 and 1% for H_2S . Evidently there is a problem when predicting H_2S in the

sweet gas. For the regenerator, deviations for the off gas are 2.2% for CO_2 and H_2S . Deviations for the lean solution loading are -100% for H_2S and -59% for CO_2 . The lean solution loadings do not represent "limit of measurability" as the authors suggested because in 1972 Lee et al. (36) were able to experimentally determine CO_2 loadings less than 0.02 and in the experimental work presented in this thesis, values in that order were easily obtained. In 1950 Leibush and Shneerson (42) reported experimental loadings less than 0.004. The contactor and regenerator were simulated independently with the deviations reported above; therefore, their mass transfer model needs to be improved if good predicted values are to be obtained for an integrated plant.

Blauwhoff (6) developed a mass transfer model for correlating the solubility of acid gases in aqueous DIPA and aqueous MDEA solutions. The reactions considered for acid gases in aqueous DIPA were (2.3) to (2.7), (2.9) and (2.14), for aqueous MDEA were (2.3) to (2.7), (2.19) and the summation of (2.20) and (2.21). Reaction rate constants for (2.9) and the summation of (2.20) and (2.21) were given. These reactions were assumed to be second order, first order with respect to CO_2 and amine. Thermal equilibrium between gas and liquid leaving the tray was assumed. The liquid phase composition, including the free H_2S and CO_2 was calculated by using equilibrium constants from the open literature for the reactions involved. A

charge balance, CO_2 , H_2S , and amine balances were also included. The calculation of the activity coefficients used the extended Debye-Huckel relation given by Davies (20):

$$\log \gamma_i = -A z_i^2 [I^{0.50}/(1+I^{0.50}) - 0.2I] \quad (2.30)$$

where: γ_i = activity coefficient of species i .

A = constant in Debye-Huckel relation.

I = ion strength $\equiv 0.50 \sum_i m_i z_i^2$.

m_i = molality of species i .

z_i = charge number of species i .

The Henry's law constants were corrected by ionic strength according to Danckwerts (19). Gas phase fugacities were calculated by the Soave-Redlich-Kwong equation of state. Blauwhoff used the penetration theory with the numerical solution method for simultaneous mass transfer and interactive reversible reactions developed by Cornelisse et al. (14). High pressure mass transfer coefficients and interfacial areas were extrapolated from correlations derived at atmospheric pressure by assuming a penetration theory dependance of k_1 and k_g on the diffusion coefficient. The interfacial areas were assumed independent of pressure and temperature. Their calculational procedure sets H_2S pipeline specification, and when CO_2 concentration in the sweet gas does not deviate more than 5% in consecutive iterations, convergence

comparisons were reported. A parametric analysis was presented.

In summary, most of the mass transfer models presented used the Whitman's two film theory to represent the concentration distribution and calculate variables involved. Cornelisse et al. (14), Haimour and Sandal (25) and Blauwhoff (6) used the Higbie penetration theory considering a more realistic approach to represent the diffusional process. Ouwerkerk (51) used the two film theory for H_2S and the Danckwerts surface renewal theory for CO_2 . The mass transfer coefficients in most of the models were obtained from the literature; experimental evaluations were made by three sources (15, 26, 51); Katti and Langfitt (28) applied corrections empirically obtained from plant data; Blauwhoff (6) converted the mass transfer coefficients found in the literature by assuming a penetration theory dependency on the diffusivity. The rate constants required for the CO_2 reactions with the amines considered were obtained experimentally by four sources (15, 26, 51, 60), the others used literature data; however, those by Katti and Langfitt (28) involved a correction factor obtained from literature acid gas equilibrium solubility data. The mass transfer coefficients and experimental determination of rate constants need the diffusion coefficients, which in turn cannot be measured directly due to the reactions, then the N_2O analogy is used (7). Recently, Versteeg (61) showed that to determine reaction rate constants for CO_2

and amines, the mass transfer models applied to study the experimental data should not neglect reaction reversibilities, as has been done, since this effect can affect the results substantially.

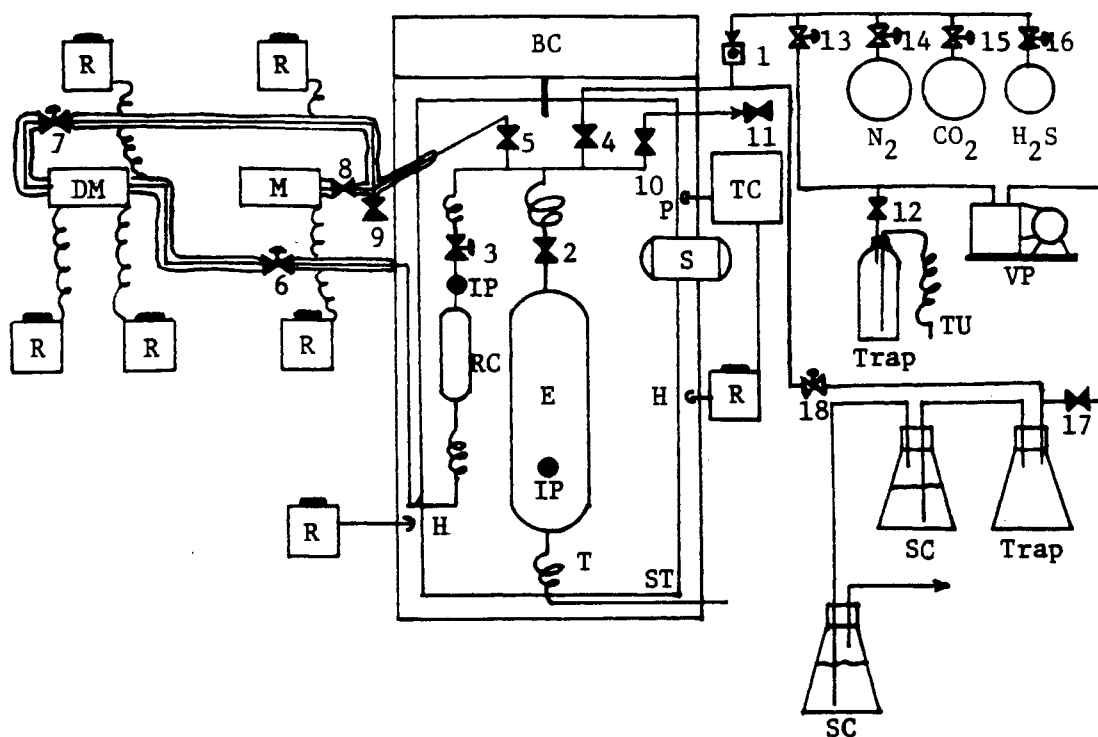
From all the mass transfer models, some have been applied to industrial scale with limited success: Ouwerkerk (51) in a DIPA contactor; Katti and Langfitt (28) in two MDEA contactors; Sardar et al. (55) in a packed MEA regenerator, two MDEA contactors and a MDEA regenerator; Sardar et al. (56, 57) in a CO₂-MEA integrated plant (contactor and regenerator packed) and a CO₂-DEA integrated plant contactor and regenerator, both trayed; Vickery et al. (63) using DEA-MDEA blends in an independent contactor and an independent regenerator, predictions for H₂S were poor and for CO₂ acceptable in the contactor but poor in the lean side of the regenerator, even though the plant was not simulated fully integrated.

The mass transfer models need to be improved, especially in the manner of obtaining the mass transfer coefficients that account for interfacial turbulence, reliable kinetic data and mechanisms. These factors constitute the bottleneck, and the break-through might be obtained when a better understanding in these fields arise.

CHAPTER III

EXPERIMENTAL APPARATUS

The apparatus used here is shown in Figure 1 and is that of Bhairi (5), modified to measure solubilities in the low acid gas partial pressure range. It consists of two double ended stainless steel cells, an equilibrium cell and a reference cell. The assembly is immersed in an oil shaker bath. The reference cell is used to compensate for the vapor pressure of the solution with an inert gas alone or an inert gas and aqueous DEA solution. The differential pressure between the two cells allows the determination of total pressure in the equilibrium cell, then by subtracting the vapor pressure of the DEA solution, the final amount of acid gas is calculated. Manometers and gas feed lines are attached to one of the two ports of the cells. The differential manometer increases the accuracy of the reading by a factor of at least 12 with respect to the mercury manometer. Differential pressures are read to 0.052 mm Hg (0.001 psia). Injection ports for liquid feed are available in both cells. Detailed description and specifications are presented in the next paragraphs.



Numbers indicate valve numbers

E	Equilibrium Cell	T	Thermocouple
RC	Reference Cell	R	Rheostat
BC	Bath Controls	H	Immersion Heater
M	Mercury Manometer	S	Stirrer
DM	Differential Manometer	ST	Shaker Tray
IP	Injection Port	VP	Vacuum Pump
TC	Temperature Controller	TU	Tygon Tubing
P	Probe	SC	Scrubber

	Needle Valve
	Ball Valve
	Diaphragm Valve
	Micro-Metering Valve

Figure 1. Schematic Diagram of Apparatus Used

Constant Temperature Shaker Bath

The shaker bath is made by Precision Scientific, G.C.A. Corporation, Model 50 Cat. #66802, 9 gallon capacity. A built-in variable speed tachometer allows oscillations from 20 to 200 cycles per minute for the shaker tray. A 3-position drive hub provides for stroke lengths of 0.50, 1.00 and 1.50 inches. A solid state built-in proportional temperature controller is included. The sensitivity is ± 0.07 at 100°F and $\pm 0.20^{\circ}\text{F}$ at 150°F . The temperature uniformity is $\pm 0.15^{\circ}\text{F}$ at 100°F and $\pm 0.45^{\circ}\text{F}$ at 150°F . The overall controlling range is from 9°F above room temperature to 212°F .

An independent temperature controller made by Omega, Model D921T06A20-E607 with a temperature range of 0 to 650°F , is available to improve the control and expand the temperature range. The unit responded to a temperature change of $\pm 0.25\%$ of span. An electric stirrer is also used to improve temperature uniformity in the bath. An extra immersion heater made by A-Tech, Model G11EX4A, manually controlled, is used for high temperature. Polyalkylene glycol, supplied by Union Carbide is the bath fluid.

Equilibrium and Reference Cells

The equilibrium and reference cells are made by Whitey of 304 stainless steel. The nominal volumes are 1000 cc and 40 cc. The small volume for the reference cell allows to have little amount of water in the vapor phase when

aqueous DEA solution is injected to it. The gas line is connected to one of the two 1/4" ports of both cells. An injection port for liquid feed in the equilibrium cell is adapted right above the cell. The reference cell has the injection port for the liquid right next to it. A calibrated copper-constantan thermocouple is installed inside a 1/8" 316 stainless steel closed end tube made by Omega which extends 6" inside the equilibrium cell. Another calibrated copper-constantan thermocouple is placed in the glycol bath near the reference cell. The volumes of the cells, lines, valves and all the connections in the assembly were determined by displacement of distilled water at a known temperature (see Appendix B). The thermocouples were calibrated against a platinum resistance thermometer which was calibrated by the National Bureau of Standards, the calibration information is presented in Appendix C. Thermocouples were recalibrated periodically.

Manometers

Two 50 in type U-tube manometers Model 10AA25WM-50 from Meriam Instrument Company were used. One filled with mercury and the differential with diethylene glycol. The mercury manometer is connected to the equilibrium cell and the differential manometer, to the equilibrium cell and the reference cell. The manometers can be read to an accuracy of 0.025 in with a cathetometer. This represents 0.635 mm Hg (0.012 psia) for the mercury manometer and 0.052 mm

Hg (0.001 psia) for the differential manometer. The internal volume of the U-tubes was measured by displacement of distilled water using the 50cc calibrated burette. The volumes are needed when calculating the total volume in the equilibrium cell side and the reference cell side. The volumes depend upon the position of the manometric liquids. In addition, the inside diameter of the U-tubes was measured with a vernier as a double checking of the internal volumes.

Gas Distribution System

The system is made up of CO₂, H₂S, CH₄ (or N₂) cylinders. Each cylinder is equipped with a pressure regulator and a 1/8" needle valve leading to the assembly. The desired pressure in the system is attained by admitting gas through a micro-metering valve made by Whitey catalog SS22RS2.

The gas line in the system is connected to a 1/3 HP Welch Duo-Seal vacuum pump. The lowest pressure attainable is 0.010 Torr. The oil is changed at least every two months.

A scrubbing system is connected to the discharge of the vacuum pump. Two scrubbers in series charged with about 20% by weight sodium hydroxide solution are used to absorb most of the gases.

Liquid Feed Systems

Liquid feed systems consist of independent injection ports for the equilibrium cell and the reference cell. The injection ports are adapted CAJON ultra torr 316 SS reduction from 1/4" to 1/8" tube. A septum F-174, 2-2731, 11 mm from Supelco is installed on the 1/4" side.

Syringes marketed as Multifit and Micromate were calibrated using distilled water and the calibrated burettes. The syringes are used to inject the liquid. The calibration procedure and volumes are given in Appendix D.

Auxiliary Equipment and Materials

A potentiometer made by Leeds and Northrup Co. Model 8686 is used to read the millivolts in the thermocouples. An ice bath is the reference side of the thermocouples. The range is from -10.0 to 100.1 millivolts with the smallest subdivision being 0.005 mv. The error is 0.03% when reading below 6 mv. The reading at 240°F is 4.9875 mv for the equilibrium cell thermocouple.

A digital thermometer made by Omega, Model 2160A type T is used with another copper-constantan thermocouple as a quick check when controlling the temperature in the lines and the oil bath.

Rheostats made by Superior Electric Co., 110 V, 10A, 1.10 KVA are used with heating tapes to control the temperature in the lines. A pair of rheostats from the same company are used with immersion heaters to control the temper-

ature in the oil bath. The heating tapes are made by Sargent Welch (Briskheat 3/4"). Three 4 foot long tapes were used to heat the tubes of manometers. Two heating tapes, Briskheat 1/2" 4 foot long, heated the stainless steel tube lines and valves connecting the manometers to the bath.

An electronic balance made by Mettler, model P1210 is used to prepare the aqueous amine solutions, 0.001 gr can be read. A magnetic stirrer made by E. H. Sargent and Co. Model S76490 is used when mixing the cool boiled distilled water and amine to prepare the aqueous amine solutions.

The use of coils 1/16" stainless steel tubing permitted the shaking of the cells without affecting the lines leading to the U-tube manometers and to the gas feed.

The fittings, ball valves and diaphragm valves are all stainless steel, 1/8", made by Parker C.P.I.

The DEA was obtained from Kodak at 98.5% minimum purity. The diethylene glycol (DEG) for the differential manometer was from Sargent Welch 98% minimum purity.

Hydrogen sulfide and carbon dioxide were purchased from Matheson with 99.5% purity. Methane was from Matheson, 99% purity and nitrogen from Sooners, 98% minimum purity.

All the materials were used as received without further purification.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The experimental techniques and calculating procedure are presented in this chapter.

Experimental Technique

The operational procedure is initiated by cleaning the equilibrium cell and the 124 glass beads, 1/8 in in diameter, which are used to improve the mixing inside the cell. Only distilled water is used in cleaning. Then the cell is vacuum dried for about 20 minutes and the beads are dried. The cell with the beads inside is reinstalled. The next steps are (see Figure 1):

1. Evacuate the system at room temperature. Connect tygon tubing to valve 11, open valves 2 to 8, 10 to 12 and 17, valves 1, 9 and 13 are closed. Turn on vacuum pump. After 30 minutes close valves 4, 10 and 11, turn off vacuum pump and check for leaks using the differential manometer. Close valve 3 to isolate the reference cell side and see which side is leaking. Close valve 2 to isolate equilibrium cell. Adjust connections or septums in the injection ports as needed.

2. Pressurize the system using CH_4 (or N_2). Open valves 3, 2 and 4. Regulate the delivery pressure for CH_4 (or N_2) to about 50 psia or less if possible. Open needle valve 14 at a minimum, then by using micro-metering valve, valve 1, very slowly start feeding CH_4 (or N_2). Check the feeding rate watching the differential manometer. Pressurize up to 12 in of mercury gauge. Then close valves 1, 14 and 4. Check for leaks using the differential manometer and valves 3 and 2 as in step 1.

3. Set temperature controller at 150°F . Turn on the heating tapes for tubes and fittings and control this temperature 8°F above the set point.

4. After 150°F is reached, close valve 17 and release the gauge pressure through the scrubbers with valves 4 and 18 open. Then close valves 4 and 18 and evacuate the system following step 1. Pressurize the system again as described in step 2.

5. Set temperature controller at 212°F and heating tapes accordingly. When this temperature is reached, release the gauge pressure as in step 4 then evacuate the system as in step 1. This step will eliminate the water. If the final desired equilibrium temperature is 240°F , then set temperature at 250°F and evacuate the system when attained.

6. Set desired equilibrium temperature and the heating tapes. Check for leaks when this condition is obtained (the system must keep the vacuum).

7. Admit CH_4 (or N_2) into the system. Open valves 3, 2 and 4. Open valve 14 and feed the gas slowly by using valve 1. Set desired pressure then close valves 1, 14 and 4. After the system stabilizes, the temperature, manometric and barometric pressures are read and recorded. The desired pressure should consider the vapor pressure of the solution and the initial pressure of acid gas.

8. Isolate the reference cell by closing diaphragm valves 3 and 7.

9. Evacuate the equilibrium cell side. With tygon tubing connected to valve 11, open valve 17 and turn on the vacuum pump. Open valves 13, 12, 11, 1, 4 and 10. Evacuate for 20 minutes then close valves 1, 4, 13, 10 and 11 and turn off vacuum pump.

10. Admit acid gas CO_2 (or H_2S) to the equilibrium cell. Open valves 4, 15 (or 16) and control feeding rate with valve 1. Then close valves 1, 15 (or 16) and 4.

11. Repeat steps 9 and 10 to insure that no CH_4 (or N_2) is present.

12. Adjust pressure in equilibrium cell to that of step 7 minus the vapor pressure of amine solution.

13. Wait until the system stabilizes and the temperature, manometric and barometric pressures are read and recorded.

14. Inject desired amount of amine with calibrated syringe through the injection port in the equilibrium cell and open valve 7. As a double checking, weight the syringe

in the Mettler balance before and after injection to obtain amount injected.

15. When the differential manometer stops changing, equilibrium is attained. Then record the temperature, manometric, differential and barometric pressures.

16. With valve 7 remaining open, inject more amine solution to obtain another equilibrium measurement. Steps 14 and 15 are repeated. The limit of injections per run depends on the 50 in of differential manometric liquid, the starting point in step 7 and the amount of amine injected.

17. When a run is completed, equate pressures in both cells by opening valve 3. If the system is under vacuum, pressurize it to atmospheric with N_2 or CO_2 , open valves 4, 14 and 1. Keep an eye on the differential manometer while feeding. Then close valves 1, 14 and 4. If the system is under pressure, release it through valves 4 and 18, with valve 17 closed. Then close valves 18 and 4 when atmospheric pressure is attained.

If H_2S is in use, when the system is under vacuum, air is admitted in the system. Close valves 3 and 7 and open valve 9 (or 10 and 11). When atmospheric pressure is reached close valve 9 (or 10 and 11) and evacuate the equilibrium cell as in step 1. When the system is under pressure, this is released through valves 4 and 18, with valve 17 closed. Then valves 18 and 4 are closed when atmospheric pressure is reached and the system is evacuated as in step 1. Admission of air and evacuation are repeated at

least three times to ensure minimum H_2S when the cell is opened to the atmosphere.

18. Disconnect and wash the equilibrium cell and beads. With valves 9, 10, 11 and 12 open and vacuum pump on, the lines are rinsed with distilled water. The equilibrium cell with the beads in is ready to start another run.

There is an alternative procedure that can be used. In step 7 the reference cell is pressurized without taking into account the vapor pressure of the solution. Then steps 8 through 11 are followed and step 12 is modified by adjusting the pressure in the equilibrium cell to that of the 7 here. Then follow step 13, and step 14 is modified as:

14. Inject desired amount of amine with a calibrated syringe through the injection port in the equilibrium cell and inject 2 ml of amine solution to the reference cell. Then open valve 7. Then follow steps 15 to 18. In this alternative operational procedure, since amine solution is injected in both cells, the vapor pressure of the solution is available in both cells, however, step 18 is modified by disconnecting the reference cell and cleaning it and its 5 beads.

The experimental techniques presented were first tested with the determination of the vapor pressure of water at each temperature of interest. In fact, this experimental determination helped to set the controls for

the bath, temperature controller and the heating tapes with their rheostats.

Calculating Procedure

The calculating procedure to obtain the solubility of an acid gas in an amine solution is based on a mass balance. The cell volumes, gas temperature, differential pressure, manometric and barometric pressures before and after injection of amine solution and the amount of amine injected allow calculation of the amount of acid gas dissolved in the amine solution. Since low partial and total pressures are involved, ideal gas is assumed in the calculations.

In addition to the information already mentioned to calculate the solubility, the amine solution vapor pressure at the equilibrium temperature is required. In this work, the vapor pressure was measured experimentally for each weight percentage of amine solution at each temperature of interest. The experimental results for the vapor pressure are given in Tables XXI and XXII Appendix E. The density of the amine solution is needed too and was obtained from Maddox (45), values are reported in Table XXIV Appendix E.

Some additional assumptions made in the calculations are: the liquid is incompressible; the liquid volume does not change with acid gas solubility; expansion of liquid and equilibrium cell with temperature is negligible under working conditions; water was eliminated from the system

before starting a run by following the experimental techniques already described.

A sample calculation is presented in Appendix F. The density of the differential manometric liquid, diethylene glycol, was taken from Campbell (9); the equation used is given in Appendix E.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

A Consistency Test for Data on Equilibrium Between Acid Gases and Ethanolamine Solutions

Edwards et al. (24) presented a thermodynamic framework for calculating vapor-liquid equilibrium of dilute solutions of volatile weak electrolytes. Ammonia, carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen cyanide were considered. The last two dissociate directly in the solution; the others must react with water before they can dissociate.

The Edwards et al. (24) work considered two descriptions of the weak electrolyte in solution. The macroscopic or stoichiometric, using bulk properties as reported by standard quantitative analysis, and the microscopic or molecular, recognizing dissociation in the liquid phase. The equations of phase equilibrium are:

Macroscopic:

$$y_A \phi_A^P = m_A \gamma_A^H a_A \quad (5.1)$$

Microscopic:

$$Y_a \phi_a P = m_a \gamma_a H_a \quad (5.2)$$

where: Y = vapor phase mole fraction.

ϕ = vapor phase fugacity coefficient.

P = pressure.

m = concentration, molality, moles per kilogram of water.

γ = molal activity coefficient.

H = Henry's law constant.

a = component, molecular.

A = component, stoichiometric or total,

$$m_A = m_a + 0.50 (m_+ + m_-).$$

m_+ = molality of cation.

m_- = molality of anion.

If dissociation in the vapor phase is negligible:

$$Y_A \phi_A P = Y_a \phi_a P \quad (5.3)$$

The stoichiometric standard state is defined as a hypothetical ideal dilute aqueous solution of undissociated A at system temperature and pressure and at unit molality, m_A , which gives:

$$H_A = H_a \quad (5.4)$$

Combining equations (5.1) to (5.4):

$$m_A \gamma_A = m_a \gamma_a \quad (5.5)$$

The molecular activity coefficient, γ_a , for a solution containing one or more electrolytes, is represented by equation (2.13) in Chapter II. In the case of a single weak electrolyte, the ionic concentration is very small, so:

$$\ln \gamma_a = 2\beta_{a-a}m_a \quad (5.6)$$

Edwards et al. (24) used the Henry's law constant as:

$$\ln H_a = \ln H_a^{(Pw)} + v_a^\infty (P-Pw)/(RT) \quad (5.7)$$

where: Pw = solvent saturation pressure at the system temperature.

v_a^∞ = partial molar volume of solute at infinite dilution.

R = gas constant.

T = absolute temperature.

Taking the logarithm of both sides of (5.2), substituting (5.6) and (5.7), and rearranging:

$$\ln(Y_a \phi_a^P / m_a) - v_a^\infty (P-Pw)/(RT) = \ln H_a^{(Pw)} + 2\beta_{a-a}m_a \quad (5.8)$$

Equation (5.8) is the equation of phase equilibrium for a single solute gas in water. Edwards et al. (24) used it to evaluate the Henry's law constant, $H_a^{(Pw)}$, and the molecule-molecule interaction parameter, β_{a-a} , by evaluating the left-hand side of (5.8) from experimental data. A plot of the left-hand side of (5.8) versus m_a gives a straight line with a Y axis intercept of $\ln H_a^{(Pw)}$ and a slope of $2\beta_{a-a}$.

An equation similar to (5.8) can be derived using the macroscopic definition of a weak electrolyte. Following a procedure similar to the one outlined above, the resulting macroscopic equation is:

$$\ln (P_A/m_A) = 2(\beta_{a-a}\gamma_A/\gamma_a)m_A + \ln[H_a\gamma_A/(\emptyset_a\gamma_a)] \quad (5.9)$$

Expressing the molality of the acid gas (CO_2 or H_2S) in the DEA solution in terms of the solution loading:

$$m_A = \beta/Q \quad (5.10)$$

where: $Q = (100 - \text{wt}\%)M_{\text{DEA}}/(1000 \text{ wt}\%)$.

M_{DEA} = molecular weight of DEA.

$\text{wt}\%$ = weight percentage of DEA.

β = loading, mole CO_2 or H_2S /mole DEA.

Substituting (5.10) into (5.9) and using common rather than Napierian logarithms:

$$\log(P_A/\beta) = [2\beta_{a-a}\gamma_A/(\gamma_aQC_1)]\beta + \log[H_a\gamma_A/(\emptyset_A\gamma_aQ)] \quad (5.11)$$

where: $C_1 = 2.30259$

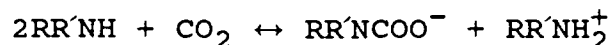
Equation (5.11) can be written as:

$$\log(P_A/\beta) = S\beta + I \quad (5.12)$$

Equation (5.12) will plot on semi-log coordinates as a straight line of slope S and Y axis intercept of I .

At low CO_2 partial pressures, carbamate formation dominates for DEA. Molecular CO_2 reacts directly with DEA,

the overall reaction (17,45) is represented as given in equation (2.2):

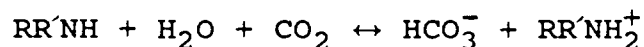


The equilibrium constant is:

$$K_{2.2} = K_{2.3} / (K_{2.9} \times K_{2.10}) \quad (5.13)$$

where: K = equilibrium constant for reaction number indicated by the subscript.

At high partial pressures, the bicarbonate forming reaction becomes important. Hydrated CO_2 reacts with DEA as given by equation (2.24):



The equilibrium constant is:

$$K_{2.24} = K_{2.3} / K_{2.10} \quad (5.14)$$

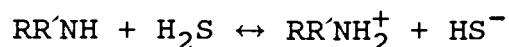
Values of the equilibrium constants calculated from the experimental data of this work are shown in Table II. $K_{2.2}$ and $K_{2.24}$ decrease when the temperature increases. The ratio $K_{2.2}/K_{2.24}$ decreases from 3.26 at 80°F to 2.07 at 240°F, indicating that bicarbonate forming reaction becomes more important as the temperature increases. $K_{2.2}$ and $K_{2.24}$ depend on $K_{2.3}$ and even the reverse of reaction (2.9) depends on the HCO_3^- formation which in turn is formed

TABLE II
EQUILIBRIUM CONSTANTS FOR THE SYSTEM
CO₂-H₂S-DEA AQUEOUS SOLUTIONS

T (°F)	80	150	240
Carbon Dioxide:			
K _{2.10}	0.4475×10 ⁻⁹	4.170×10 ⁻⁹	38.15×10 ⁻⁹
K _{2.9}	0.3065	0.3854	0.4836
K _{2.3}	475.2×10 ⁻⁹	548.8×10 ⁻⁹	354.9×10 ⁻⁹
K _{2.2}	3465	341.5	19.24
K _{2.24}	1062	131.6	9.303
Hydrogen Sulfide:			
K _{2.10}	0.4475×10 ⁻⁹	4.170×10 ⁻⁹	38.15×10 ⁻⁹
K _{2.4}	11.98×10 ⁻¹⁵	122.2×10 ⁻¹⁵	809.6×10 ⁻¹⁵
K _{2.6}	111.4×10 ⁻⁹	261.9×10 ⁻⁹	302.8×10 ⁻⁹
K _{2.14}	248.9	62.80	7.940
K _{5.16}	2.982×10 ⁻¹²	7.675×10 ⁻¹²	6.426×10 ⁻¹²

from reaction (2.3). As a result, the determining factor is $K_{2.3}$.

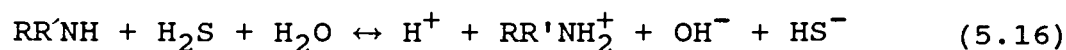
Molecular H_2S reacts directly with DEA (45) as given by reaction (2.14):



The equilibrium constant for this reaction is:

$$K_{2.14} = K_{2.6}/K_{2.10} \quad (5.15)$$

In aqueous solution, an overall reaction between the amine and H_2S can be regarded as:



The equilibrium constant is:

$$K_{5.16} = K_{2.4} \times K_{2.6}/K_{2.10} \quad (5.17)$$

Calculated values of $K_{2.14}$ and $K_{5.16}$ are also shown in Table II. Evidently, the presence of water is determining for $K_{5.16}$.

The foregoing shows clearly that the solubility of the acid gas (either CO_2 or H_2S) to form a weak electrolyte is the controlling mechanism in the reaction with alkanolamines.

Figure 2 shows $\log(P_A/\beta)$ as a function of β (loading) for CO_2 in 20% by weight DEA at 80 and 150°F. The experimental data follow the straight line. Tables III and IV (Appendix A) show the data. Similar plots were obtained

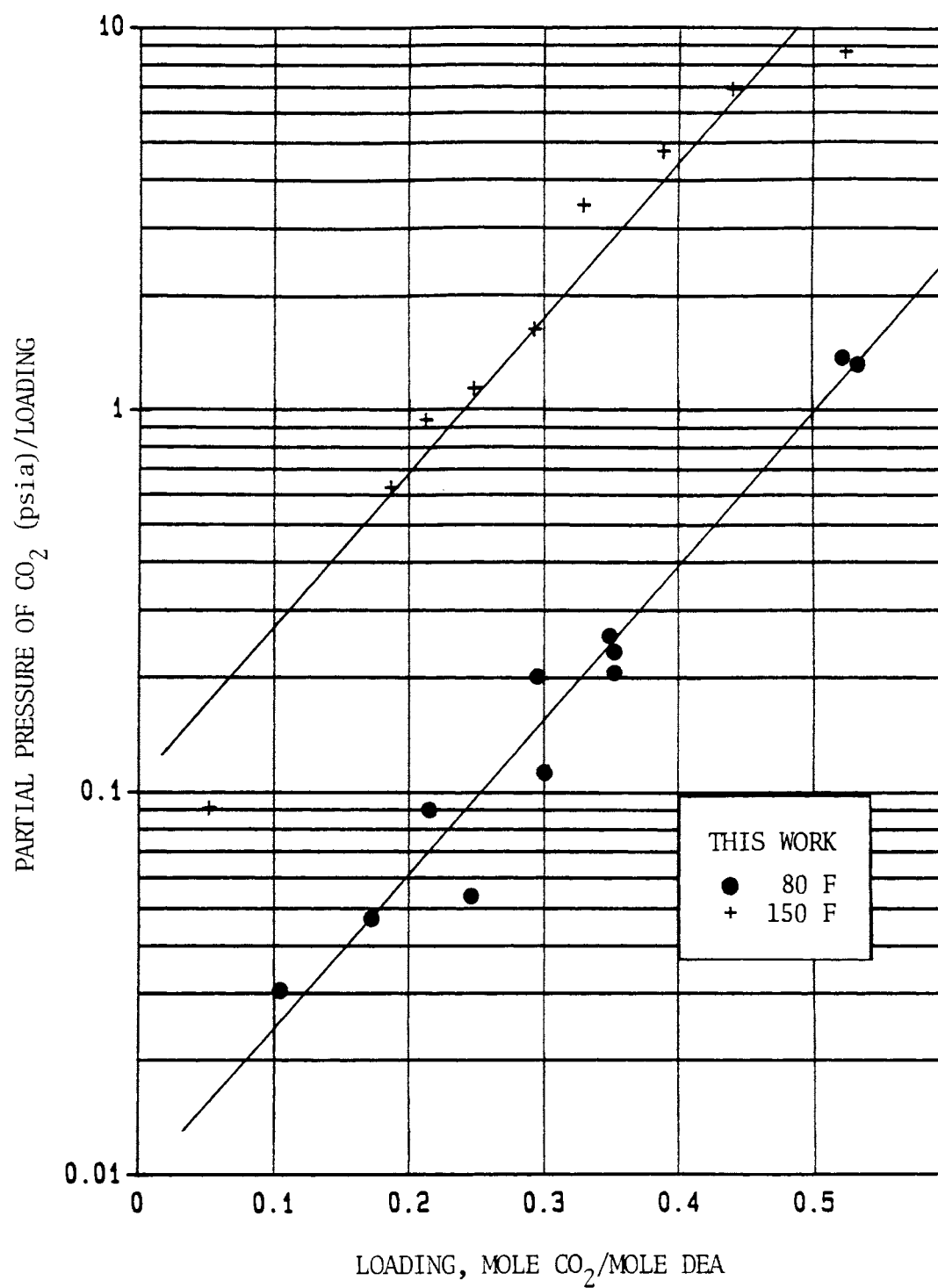


Figure 2. Solubility of CO₂ in 20% by Weight DEA Aqueous Solution, Data Consistency Test

for all the systems studied. The acid-gas aqueous amine systems behave according to equation (5.12), which justifies the plotting technique used to test data consistency.

Activity Coefficients for Water from
Data on Boiling Points of DEA
Aqueous Solution

The vapor pressures of DEA solutions and of water were measured using the two cell differential pressure apparatus. The experimental values are shown in Tables XXI and XXII (Appendix E). If the vapor phase over the amine solutions is assumed to be ideal and contains only water vapor, the activity coefficient for liquid water can be calculated. The calculated activity coefficients are shown in Table XIX (Appendix E) and Figure 3. At 80°F there is a definite curvature to the γ -mole fraction plot, but the line is almost straight for 150 and 240°F.

Activity coefficients were also calculated using DEA solution vapor pressures and H₂O vapor pressures read from Dow (22). These values are shown in Table XXIII (Appendix E). Comparison shows that all three sets of numbers, water vapor pressure, DEA solution vapor pressure and activity coefficients, are in good agreement.

In general, the activity coefficient for water in these systems is less than 1.0. The Dow values are slightly higher than 1.0 at 240°F. In the Deshmuk and

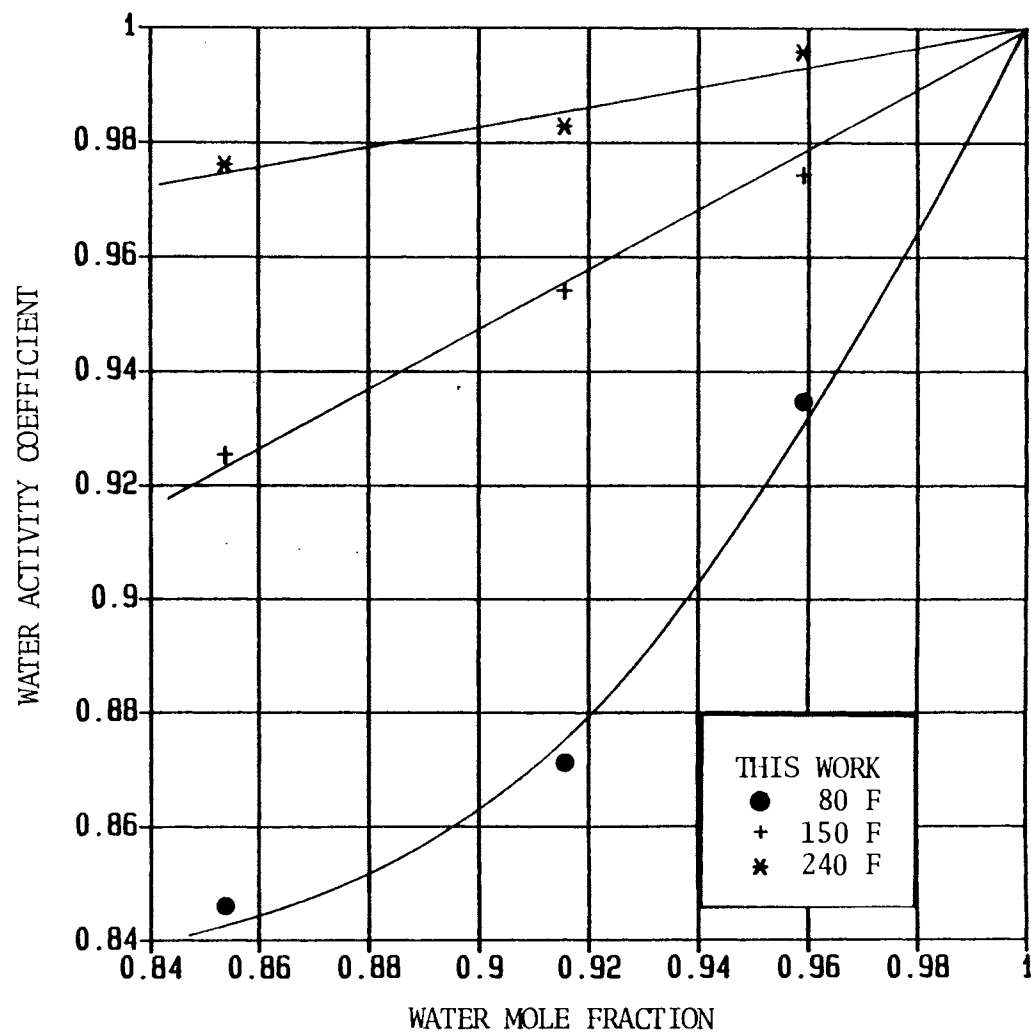


Figure 3. Activity Coefficient of Water in DEA Aqueous Solution

Mather (21) model, which is used by most of the mass transfer models presented in Chapter II, the activity coefficient of water is set to 1.0. This assumption will give an average error of -1.51% for 240°F, -4.88% for 150°F and -8.58% at 80°F. The maximum errors are at 50% by weight DEA. They are -2.40%, 7.50%, and -15.4% for 240, 150 and 80°F respectively. As shown in Table XIX (Appendix E) and Figure 3, the activity coefficients are closer to 1.0 as the temperature increases for a given DEA weight percentage. For a given temperature, the activity coefficient is closer to 1.0 as DEA concentration decreases.

Carbon Dioxide-Diethanolamine Equilibrium Data

The data for solubility of carbon dioxide (CO_2) in DEA aqueous solution are shown in Tables III to IX (Appendix A) and Figures 4 to 9. All the data show good internal consistency except for 20% by weight DEA at 240°F (Figure 5). Initial technical problems in controlling 240°F in the lines to avoid condensation are a reason for the scatter. The position of the injection port was initially beside the equilibrium cell (as for the reference cell, see Figure 1). After the injection port was relocated to right above the cell, the internal consistency for the 240°F was improved. Also, there is a greater internal deviation for the data taken early in the research and before the consistency checking procedure had been developed and implemented.

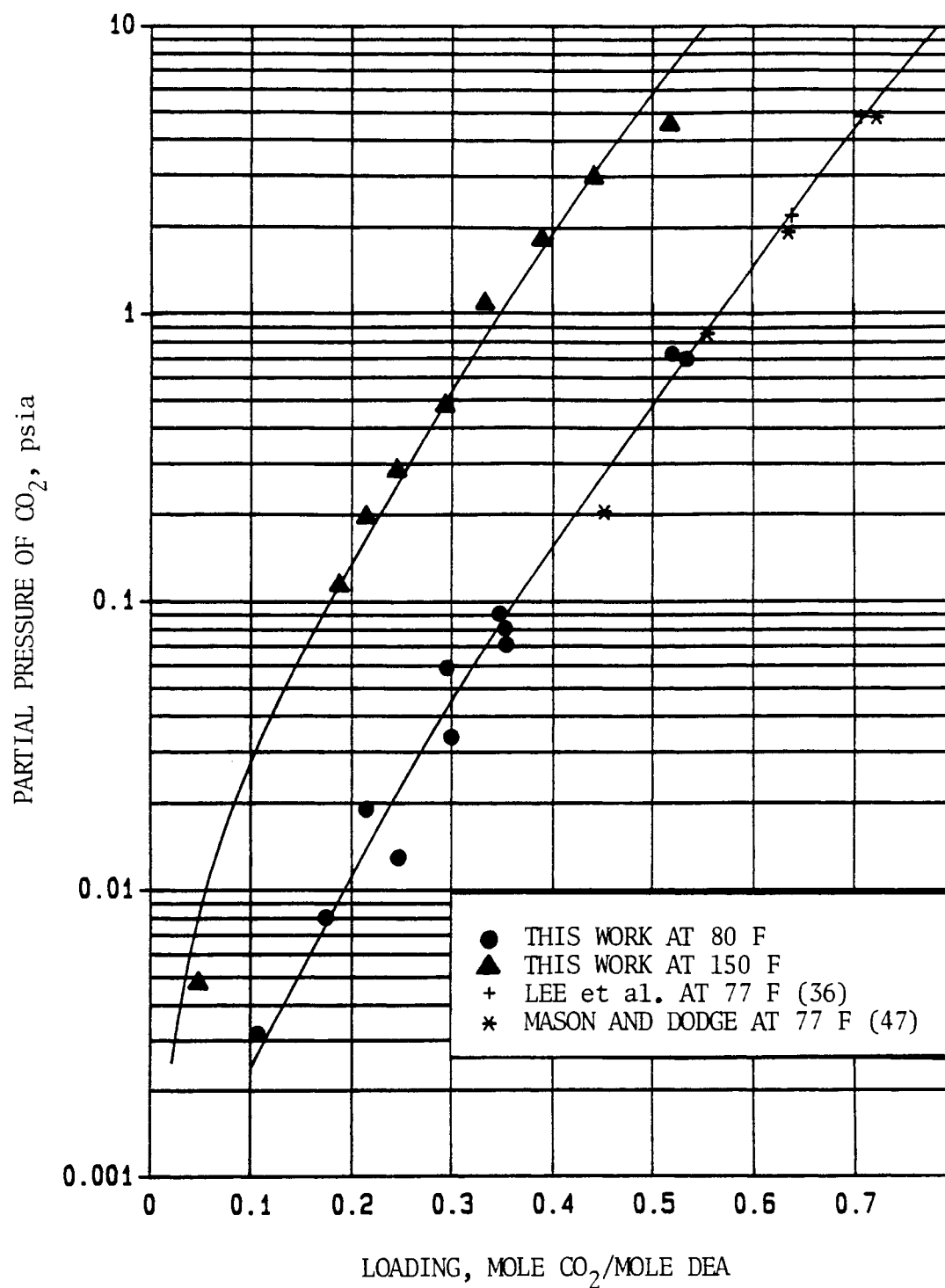


Figure 4. Solubility of CO₂ in 20% by Weight DEA Aqueous Solution at 80 and 150 F

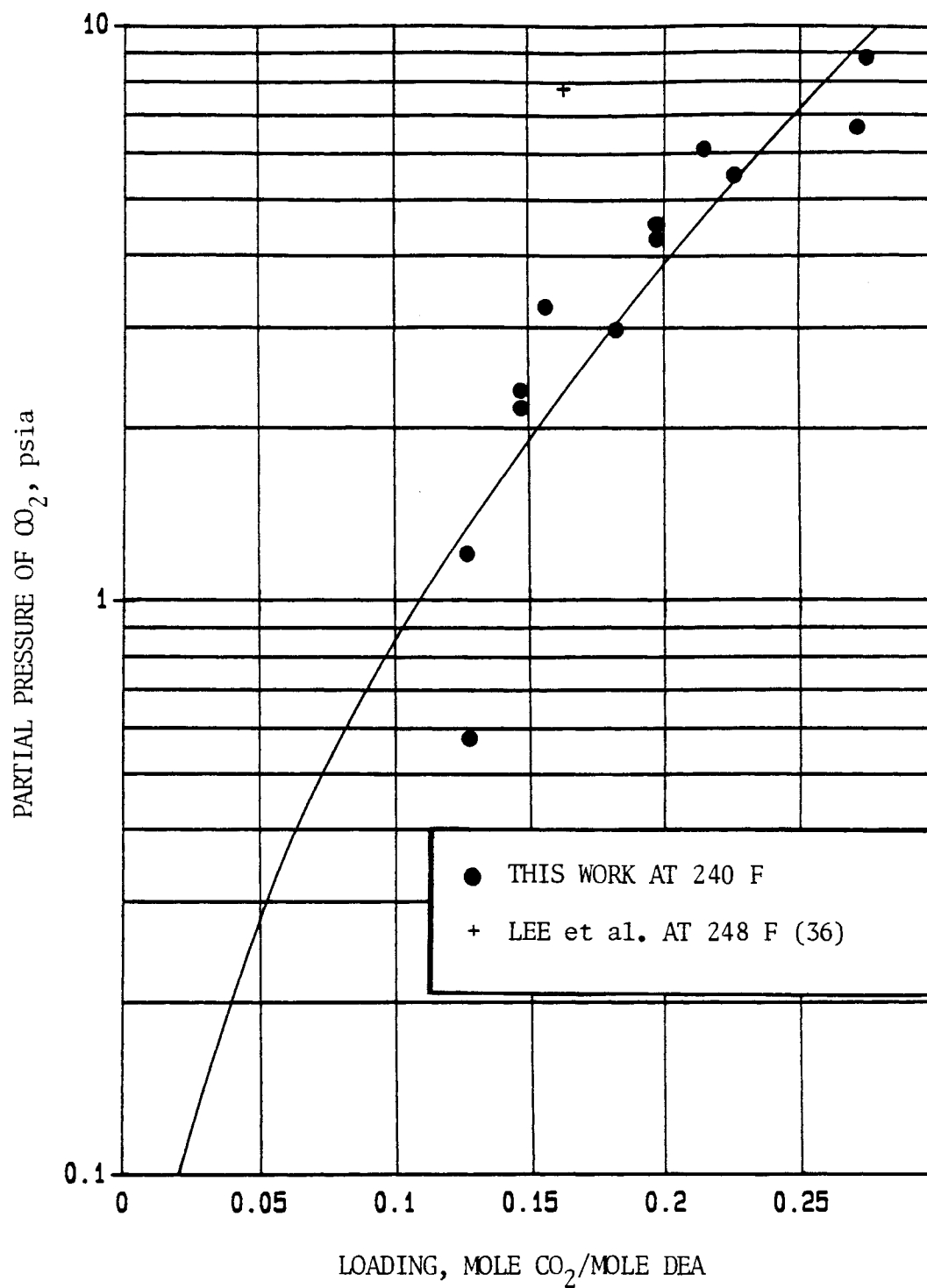


Figure 5. Solubility of CO₂ in 20% by Weight DEA Aqueous Solution at 240 F

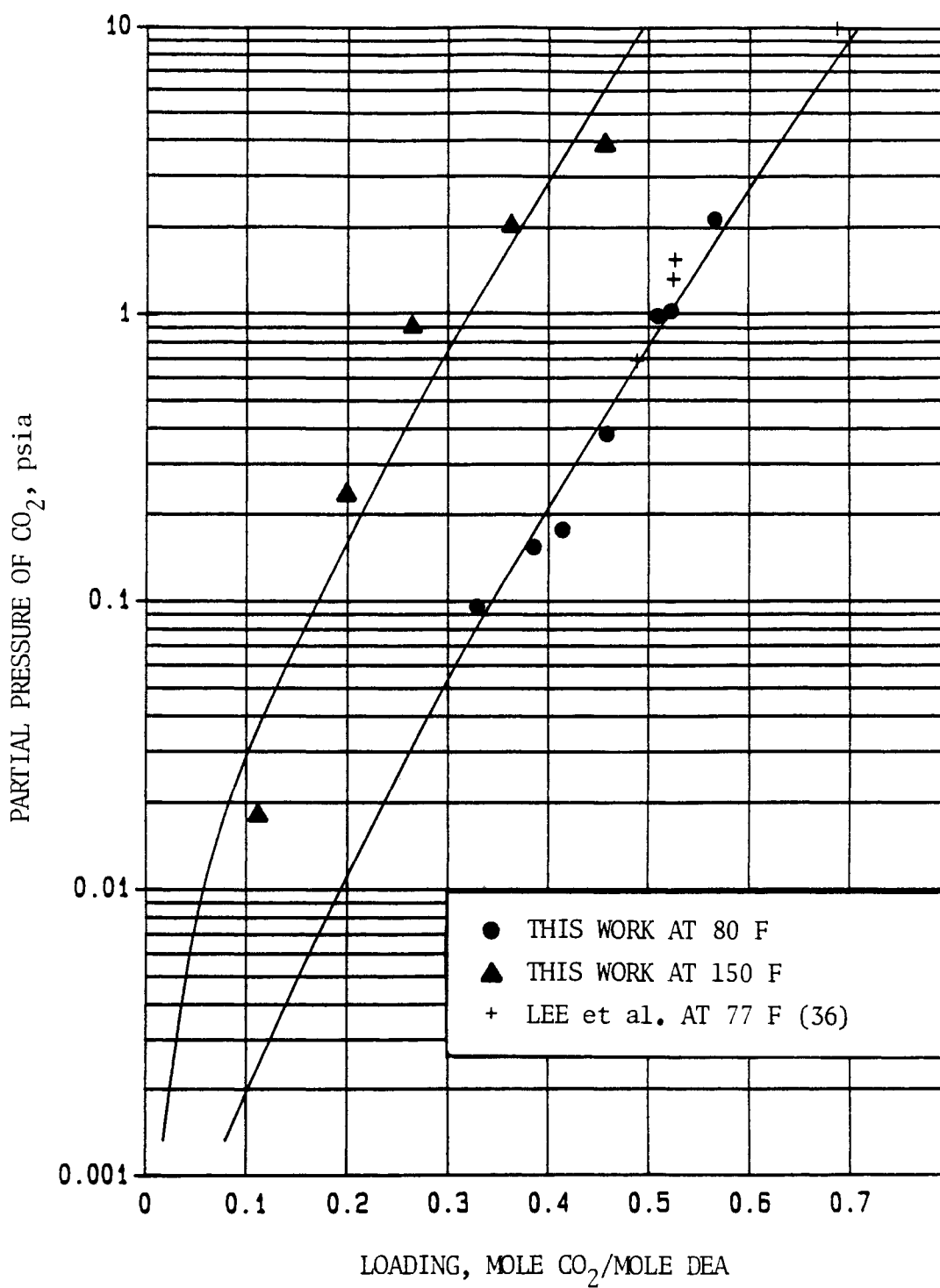


Figure 6. Solubility of CO₂ in 35% by Weight DEA Aqueous Solution at 80° and 150 F

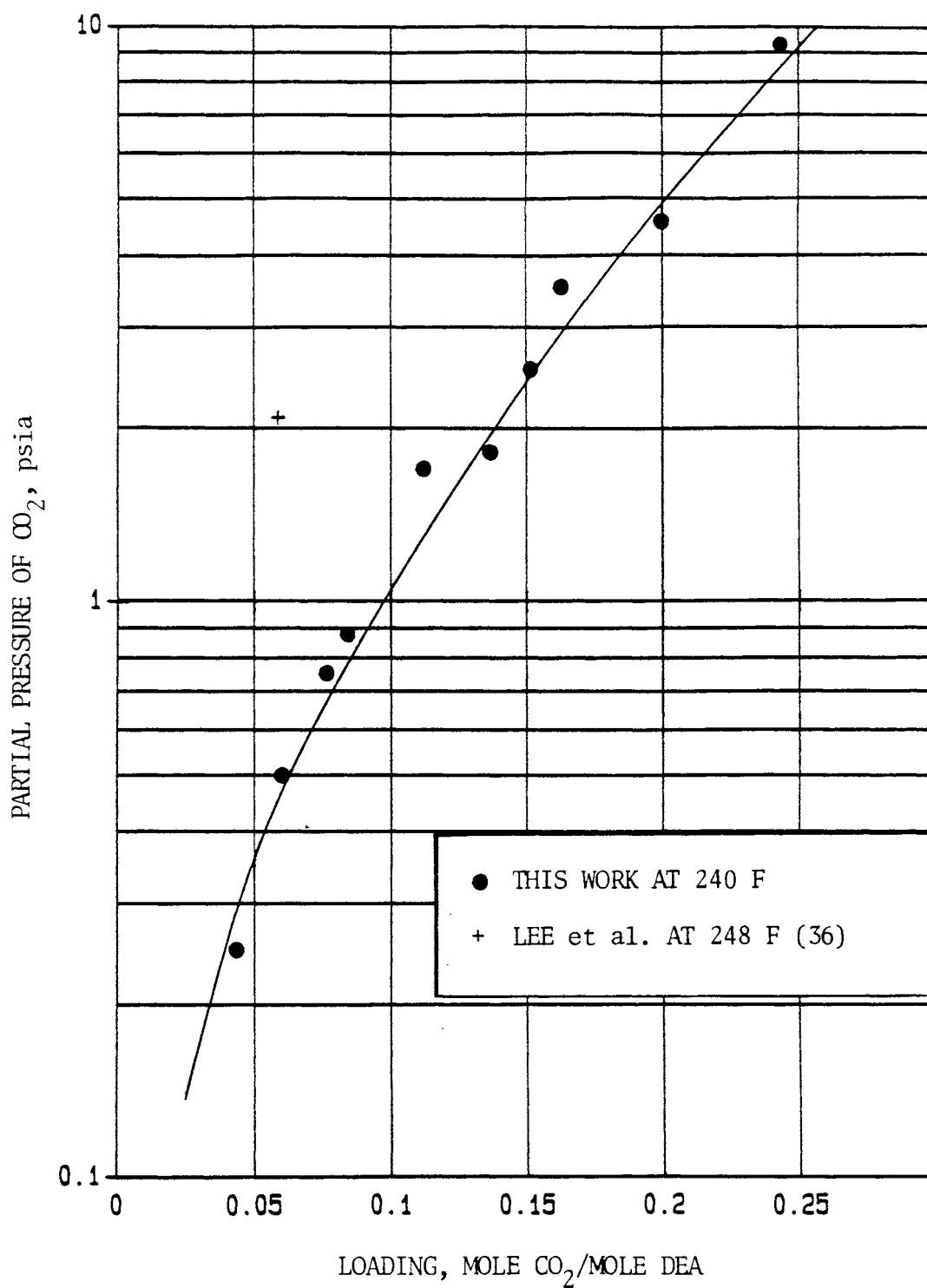


Figure 7. Solubility of CO₂ in 35% by Weight DEA Aqueous Solution at 240 F

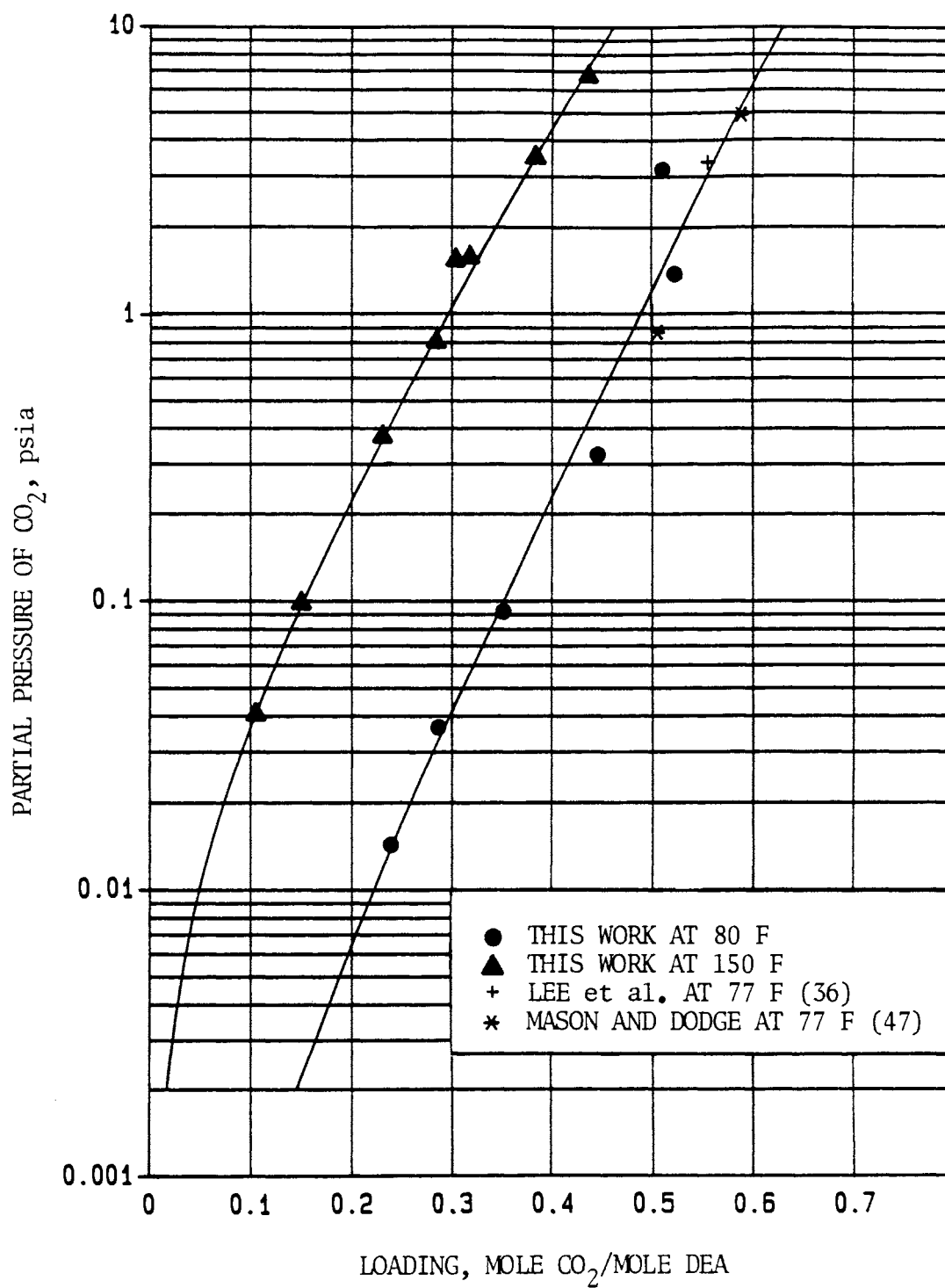


Figure 8. Solubility of CO₂ in 50% by Weight DEA Aqueous Solution at 80 and 150 F

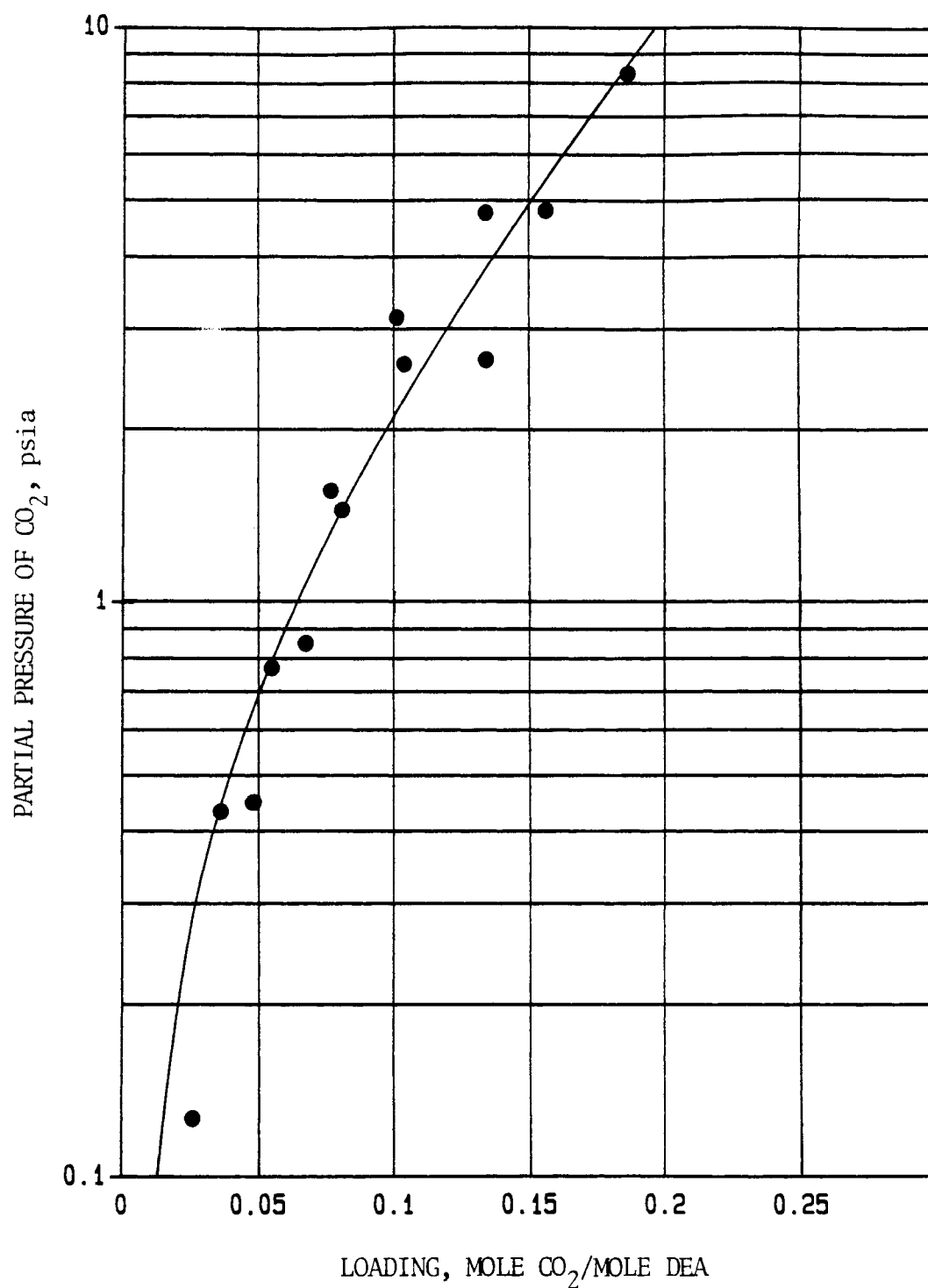


Figure 9. Solubility of CO₂ in 50% by Weight DEA Aqueous Solution at 240 F

Experimental data from Lee et al. (36) and Mason and Dodge (47) are available at low temperature and show good agreement with this work (Figures 4, 6, and 8). No literature data are available at 150°F. The data are consistent at 150°F although there is a little scatter at 35% DEA (Figure 6). Two experimental data points from Lee et al. (36) at 248°F are available and are in qualitative agreement with this work (Figures 5 and 7).

The smoothed curves for each DEA weight percentage are presented in Figures 10, 11 and 12. For a given DEA concentration, they show the change in equilibrium partial pressure with loading. At a given loading, they also indicate the increase in partial pressure with the temperature. For loadings greater than 0.15, there is a smooth change in partial pressure with loading at any of the temperatures and DEA concentrations studied. At loadings less than 0.15, the partial pressure changes rapidly. This is clearer as the temperature increases. The straight line equations (see Table XXV, Appendix G) describe the equilibrium solubility at very low loadings, say 0.001 mole of CO_2 per mole DEA. However, the equations cannot be used down to zero loading because of the log term. These equations can be used with more confidence in the low loading range due to the basis under which they are founded.

Figure 13 summarizes the smoothed curves for the equilibrium solubility of CO_2 in DEA solutions. The DEA weight percentage is used as parameter at each temperature. At

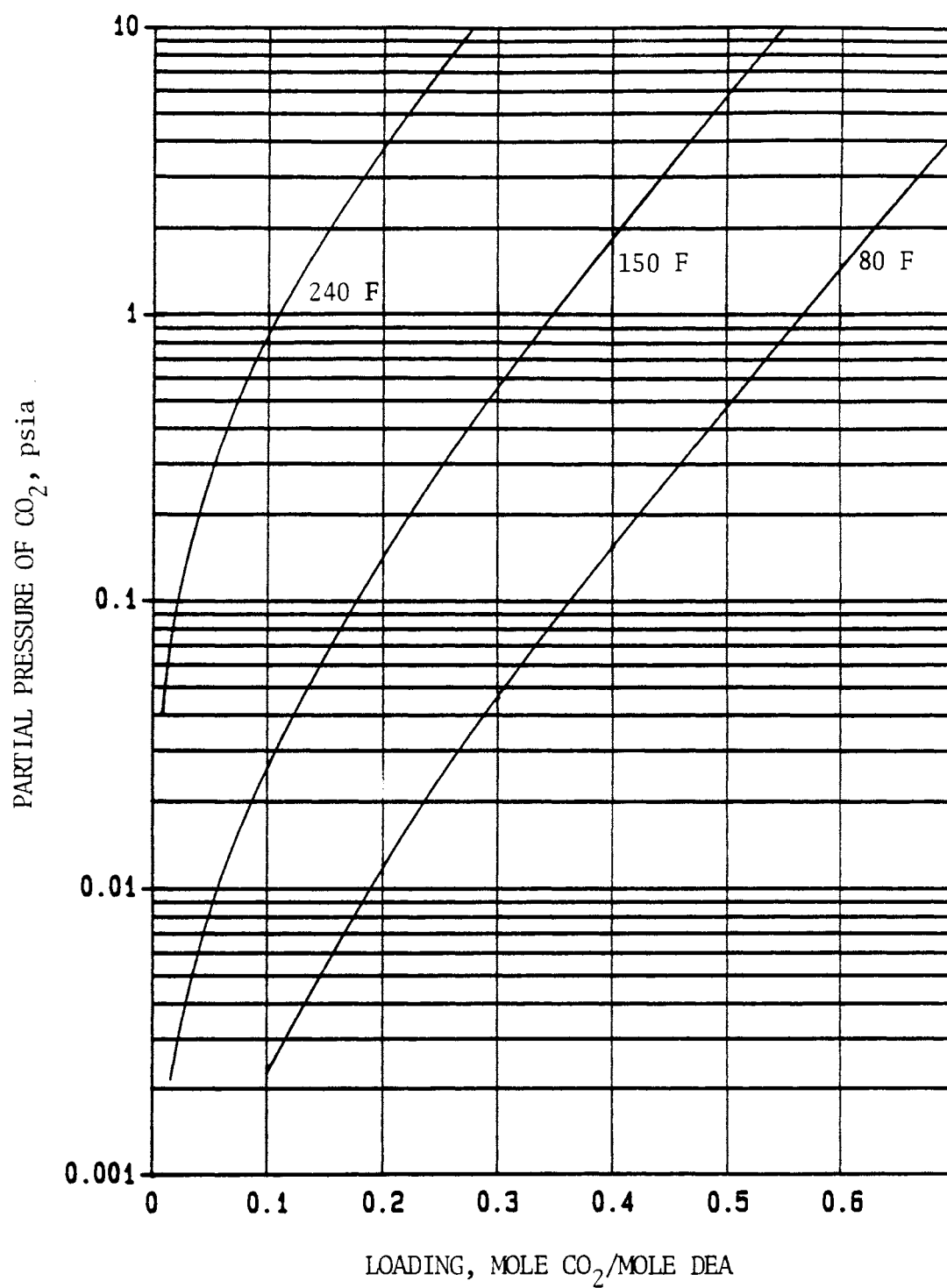


Figure 10. Solubility of CO₂ in 20% by Weight DEA Aqueous Solution, Smoothed Curves

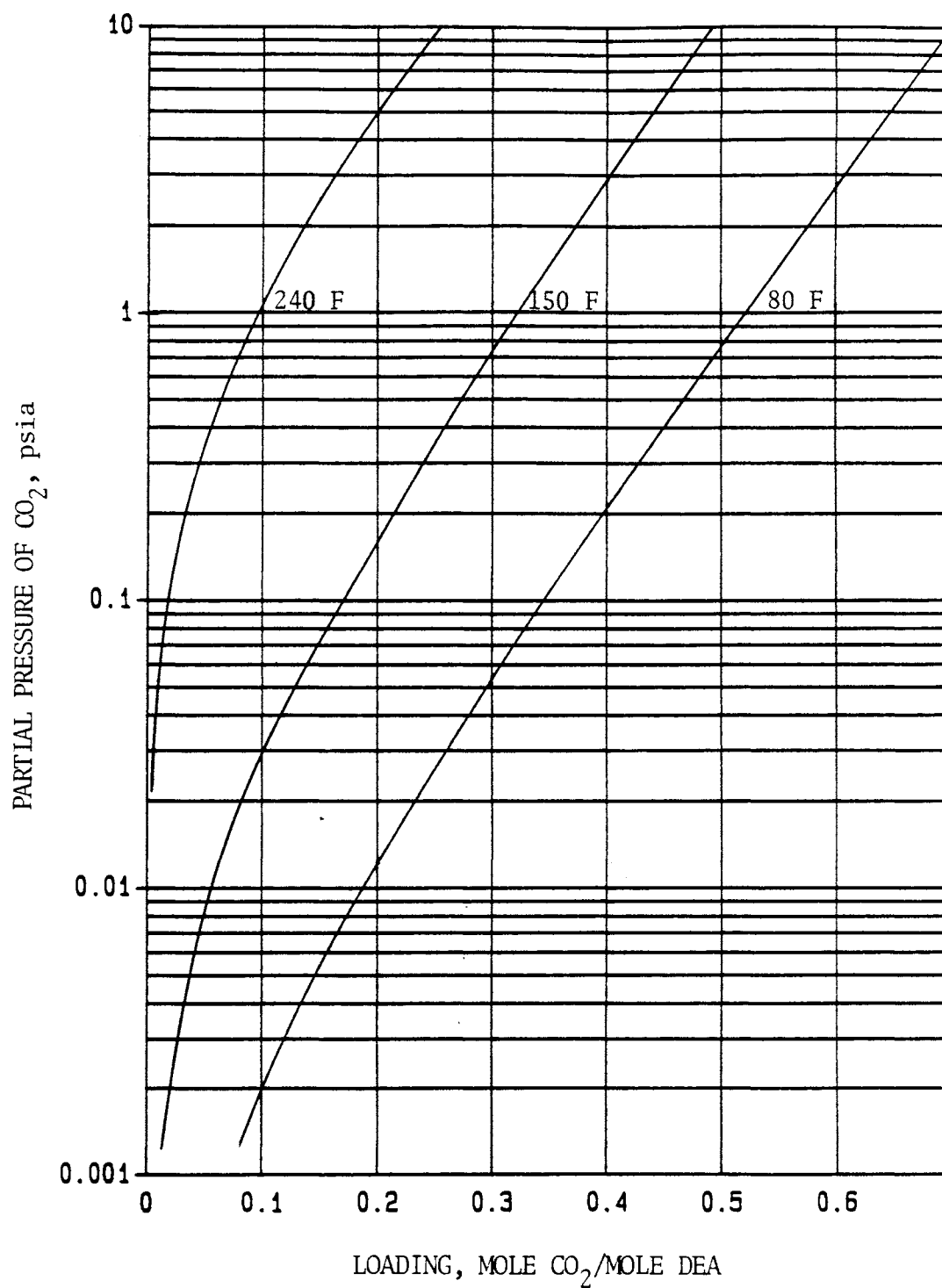


Figure 11. Solubility of CO₂ in 35% by Weight DEA Aqueous Solution, Smoothed Curves

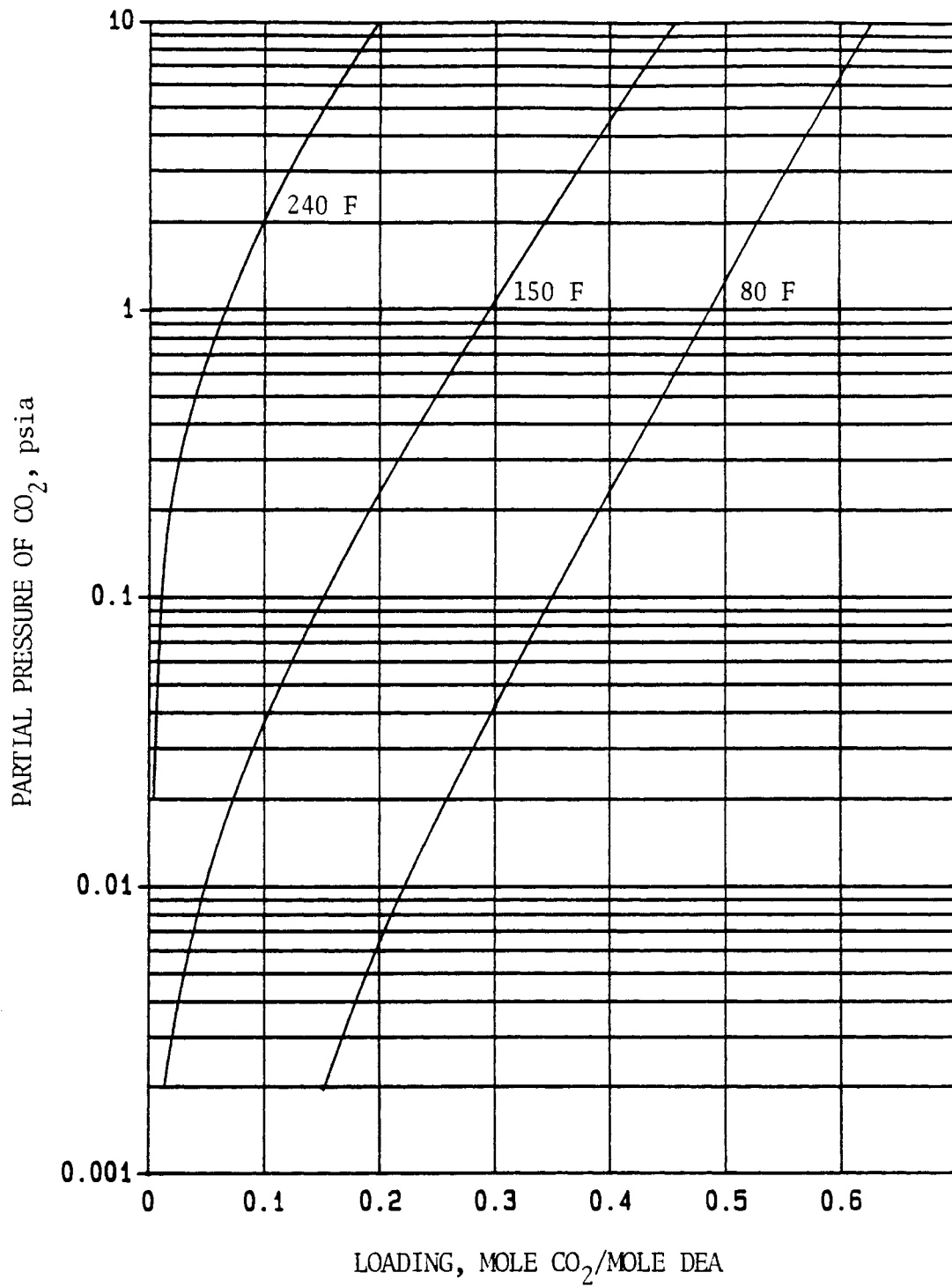


Figure 12. Solubility of CO₂ in 50% by Weight DEA Aqueous Solution, Smoothed Curves

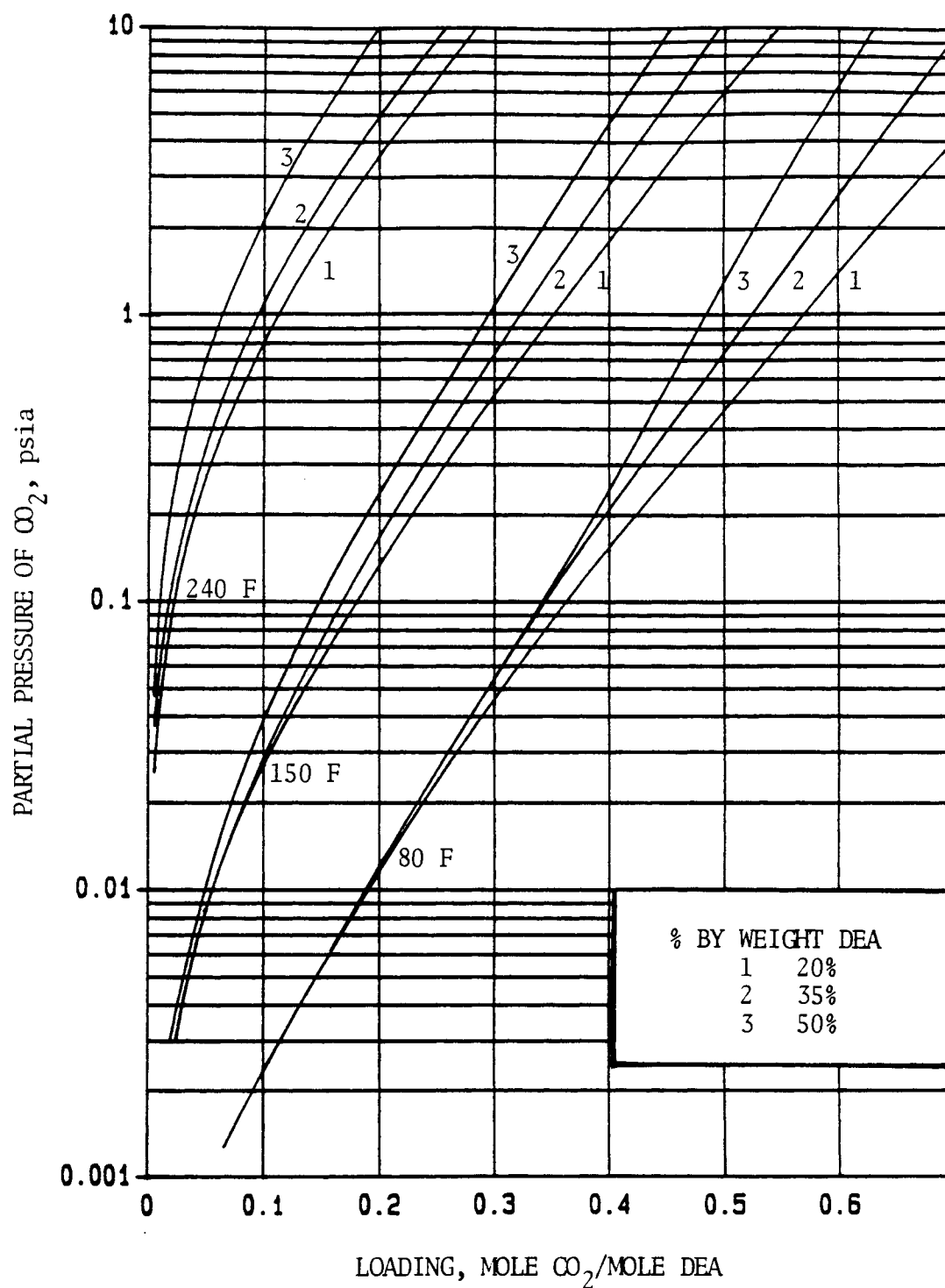


Figure 13. Solubility of CO₂ in DEA Aqueous Solution at 80, 150 and 240 F, Smoothed Curves

80°F, the smoothed curves for the three concentrations studied come together for loadings less than 0.20. The CO₂ partial pressure is 0.012 psia. This means that, within the accuracy of the experimental data, the DEA concentration makes no difference below this partial pressure. At low partial pressure and temperature, very small differences can be expected between the equilibrium values among the different DEA concentrations. Small differences in free CO₂ are also to be expected. This is because of Henry's law equation (2.12). If the partial pressures of CO₂ are very close among the amine concentrations at low temperature, then the free CO₂ will be very close. At 150 and 240°F, the three curves come together for loadings less than 0.02 and 0.01 respectively, which corresponds to partial pressures below 0.02 psia.

In Figure 13, the three weight percentages appear evenly distributed for 80 and 150°F. However, at 240°F the 35% DEA curve is shifted towards the 20% DEA curve. A possible explanation is that the equilibrium constants for the overall carbamate and bicarbonate formation reactions become close ($K_{2.2}$ and $K_{2.24}$ in Table II), making the equilibrium more dependent on DEA concentration.

Hydrogen Sulfide-Diethanolamine

Equilibrium Data

The experimental solubility of hydrogen sulfide (H₂S) in DEA aqueous solution is in Tables X to XV (Appendix A)

and Figures 14 to 19. Good internal consistency is shown by all the data. The data smoothed by Lee et al. (38) are in agreement with this work at 80°F, although the Lee et al. data are at 77°F (Figures 14, 16 and 18). At 240°F there is agreement for loadings less than 0.15. Above 0.15 higher loadings for a given partial pressure were obtained in this work (Figures 15, 17 and 19). The data from Lee et al. are at 248°F. There are no literature data at 150°F.

Figures 20, 21 and 22 summarize the smoothed curves obtained. There is a smooth change of partial pressure with the loading for loadings greater than 0.20. The partial pressure decreases rapidly for loadings less than 0.20 at any temperature and for all DEA concentrations.

Figure 23 is a composite of the smoothed curves obtained for the solubility of H_2S in DEA aqueous solution. At any temperature, the three DEA weight percentages appear evenly distributed and clearly separated. This figure shows the increase in the equilibrium partial pressure when temperature increases for a given DEA weight percentage. Experimentally, the time required to reach equilibrium with H_2S -DEA aqueous solution was much shorter than for CO_2 -DEA. This is because the H_2S -DEA reaction is instantaneous since it involves the transfer of a proton only (19). The experience acquired with the CO_2 -DEA systems permitted closer control resulting in less experimental scatter for the H_2S -DEA systems.

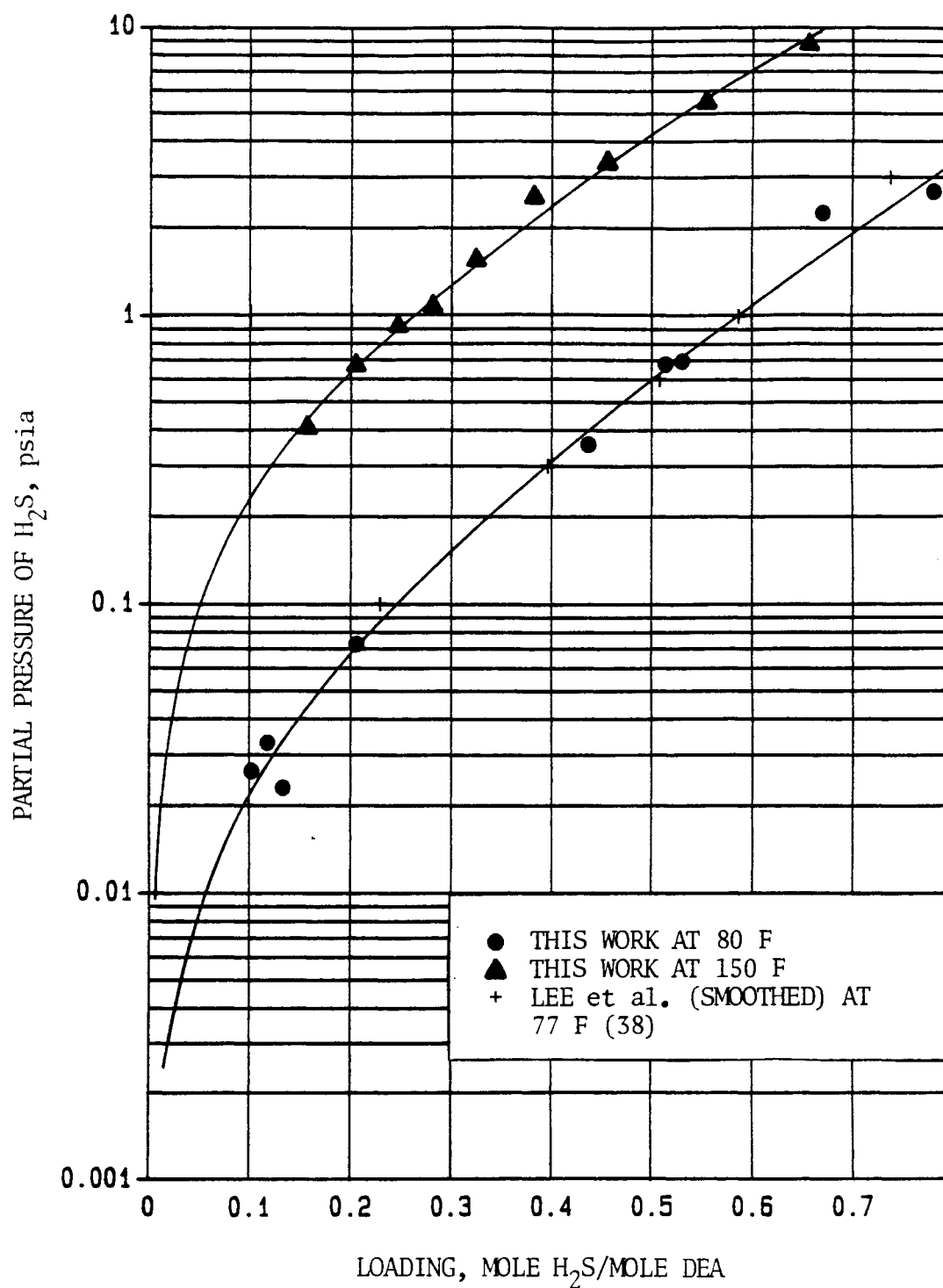


Figure 14. Solubility of H₂S in 20% by Weight DEA Aqueous Solution at 80 and 150 F

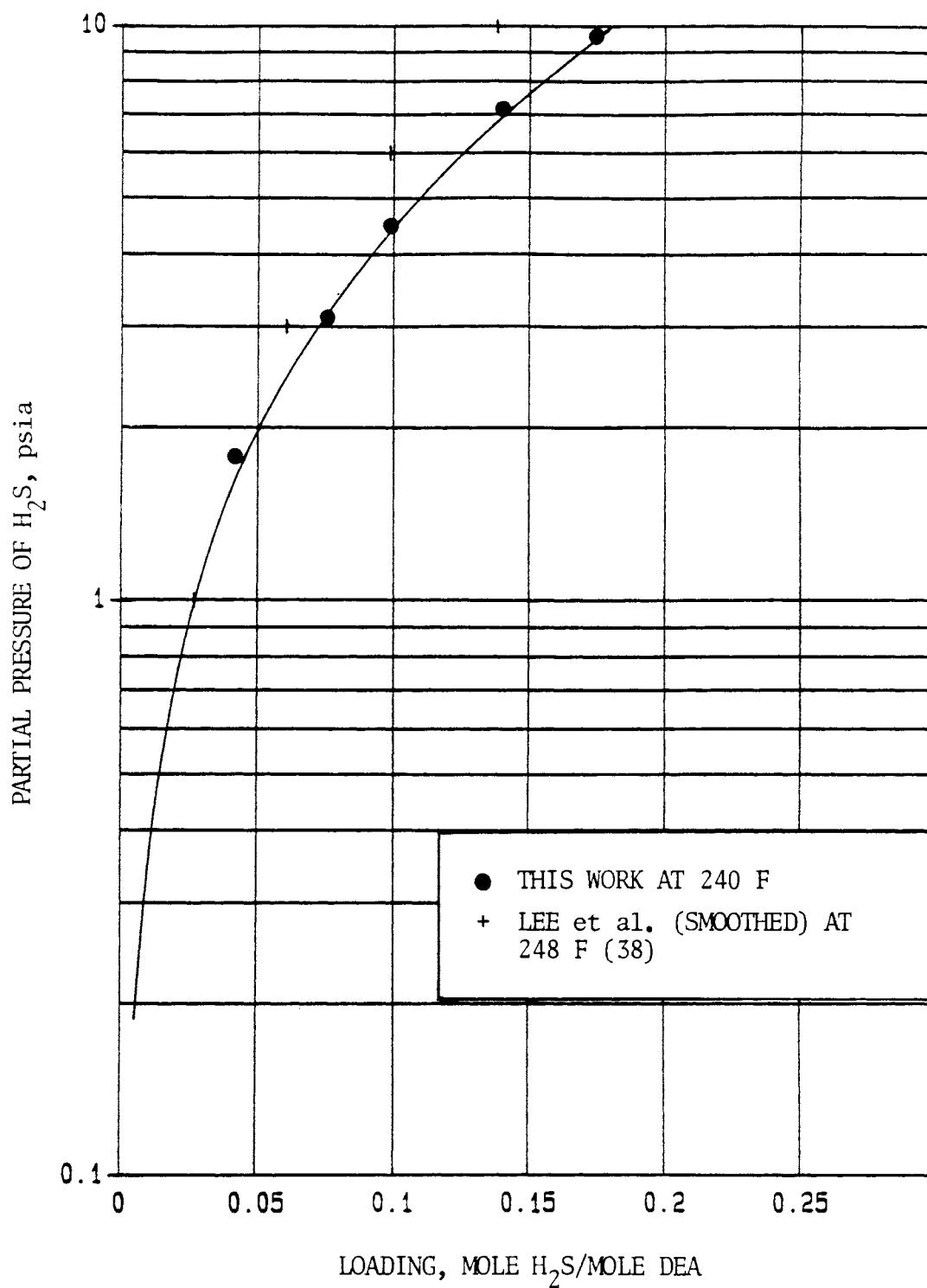


Figure 15. Solubility of H₂S in 20% by Weight DEA Aqueous Solution at 240 F

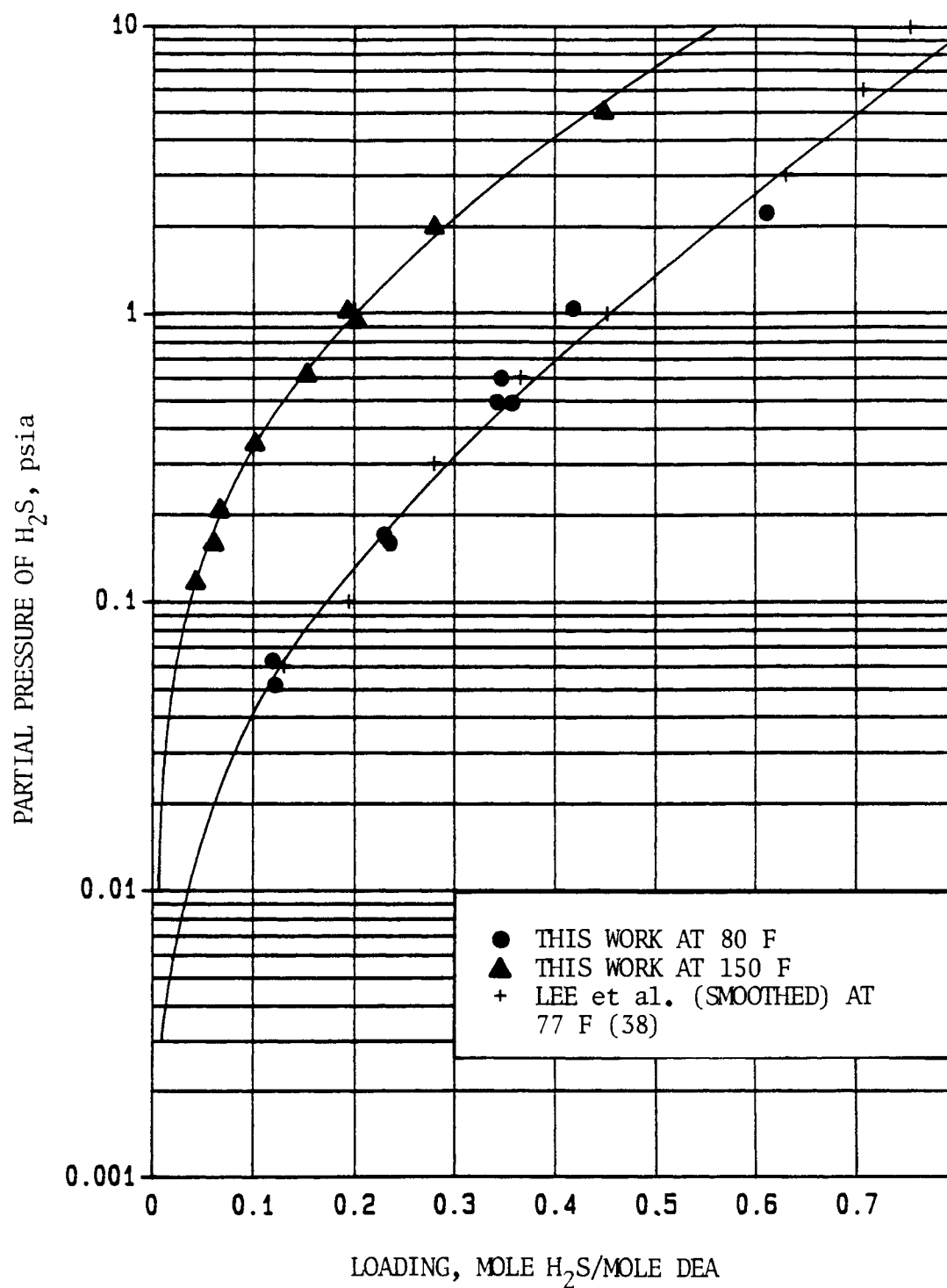


Figure 16. Solubility of H₂S in 35% by Weight DEA Aqueous Solution at 80 and 150 F

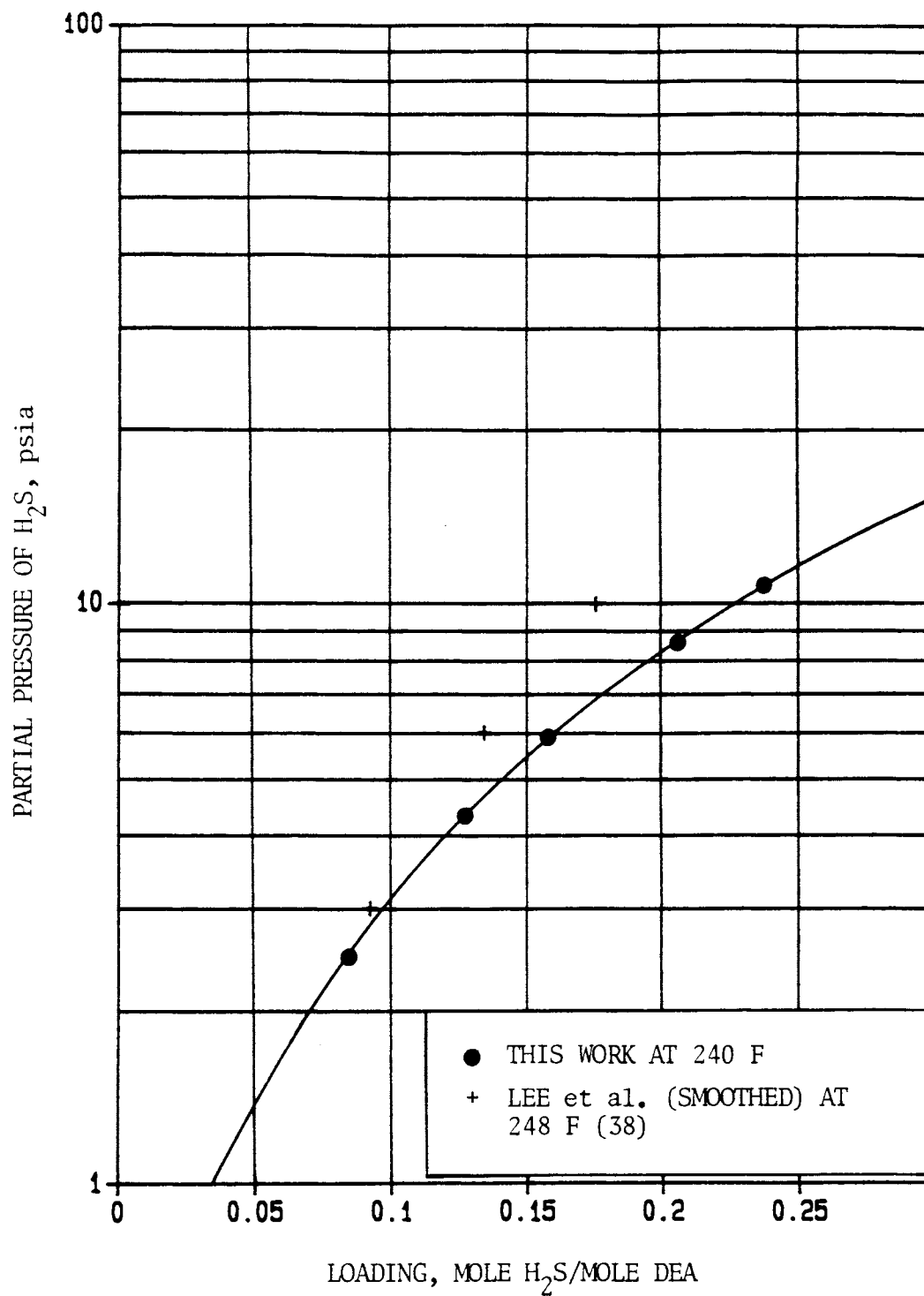


Figure 17. Solubility of H_2S in 35% by Weight DEA Aqueous Solution at 240 F

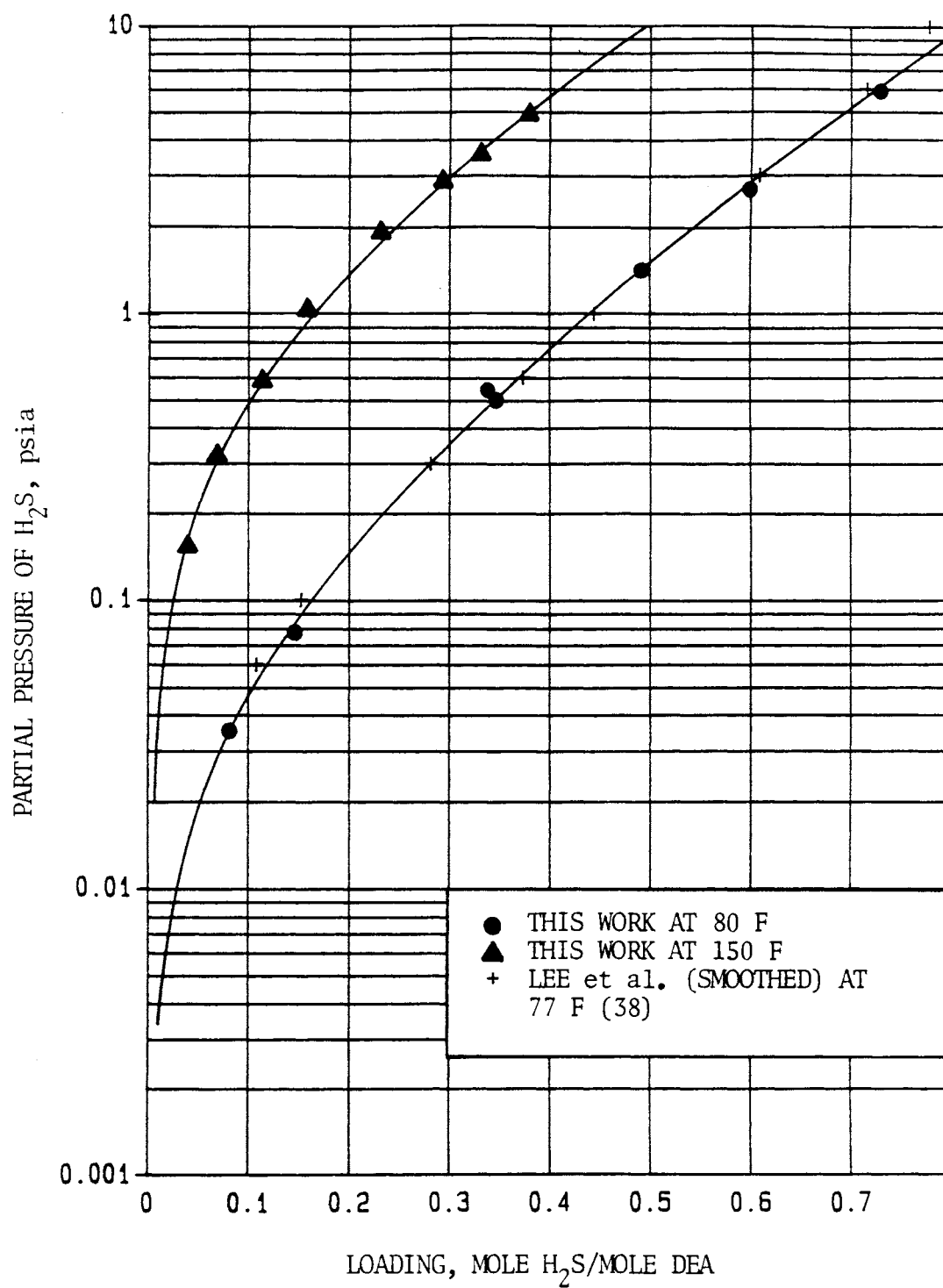


Figure 18. Solubility of H_2S in 50% by Weight DEA Aqueous Solution at 80 and 150 F

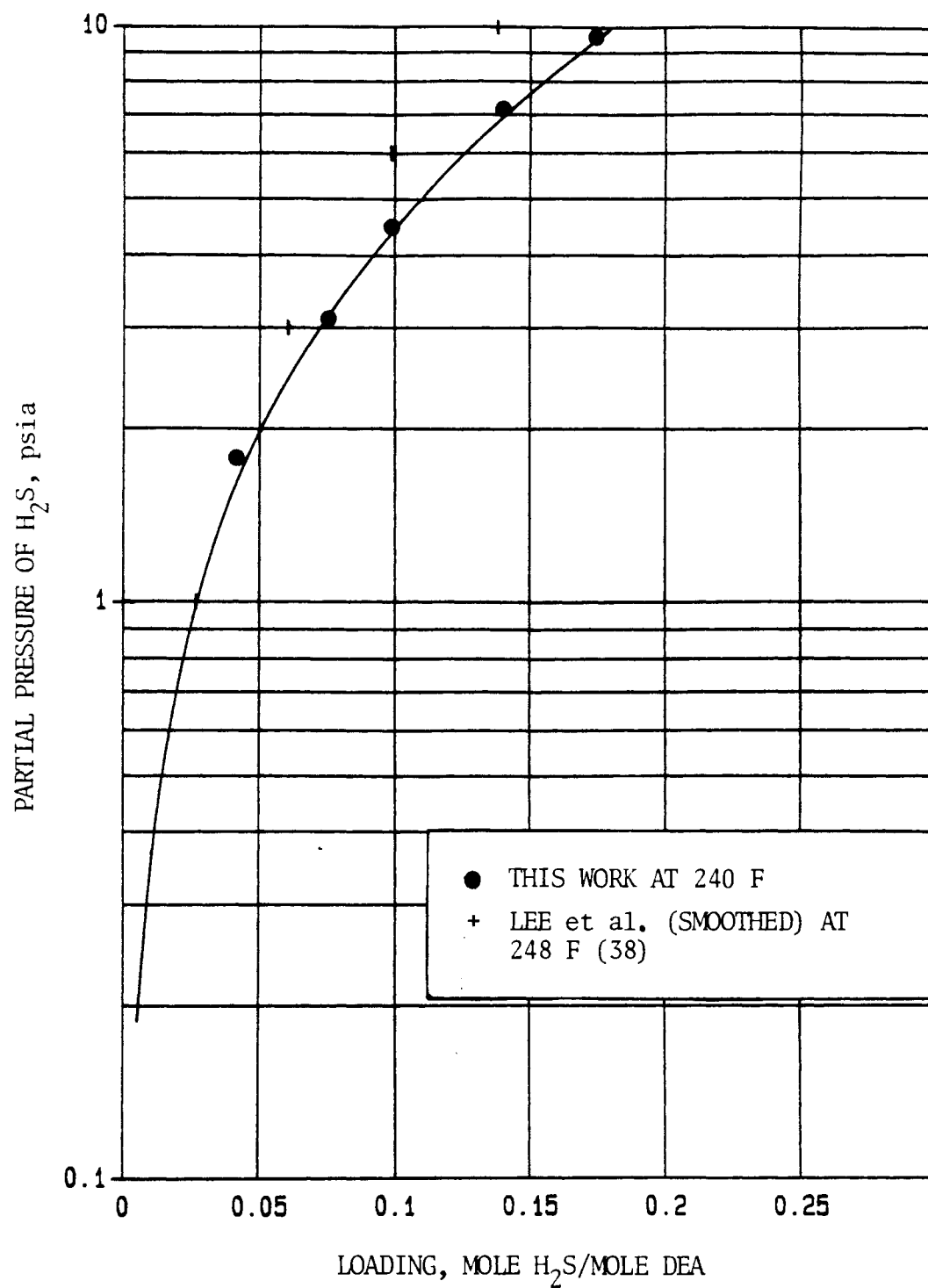


Figure 19. Solubility of H_2S in 50% by Weight DEA Aqueous Solution at 240 F

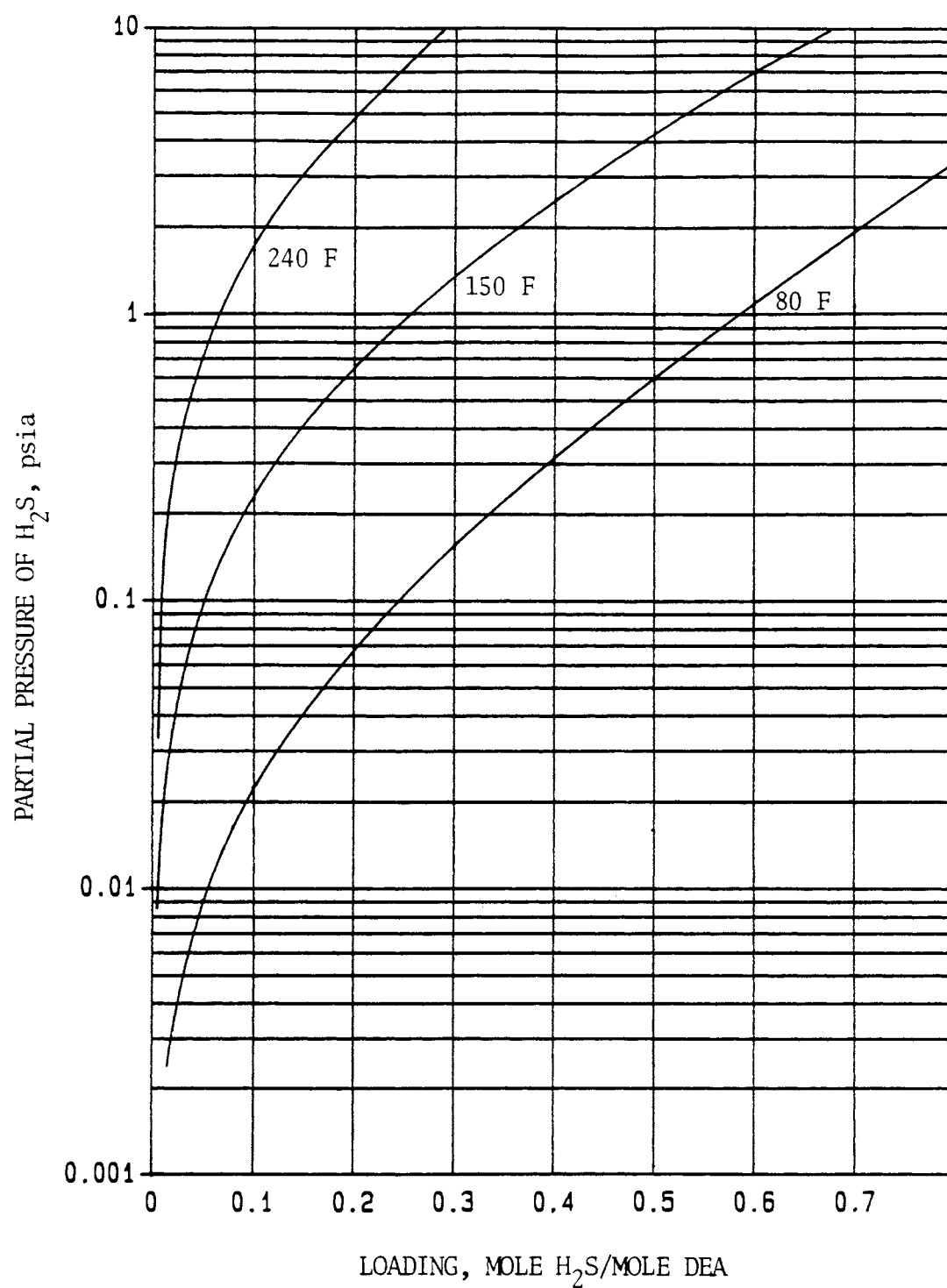


Figure 20. Solubility of H_2S in 20% by Weight DEA Aqueous Solution, Smoothed Curves

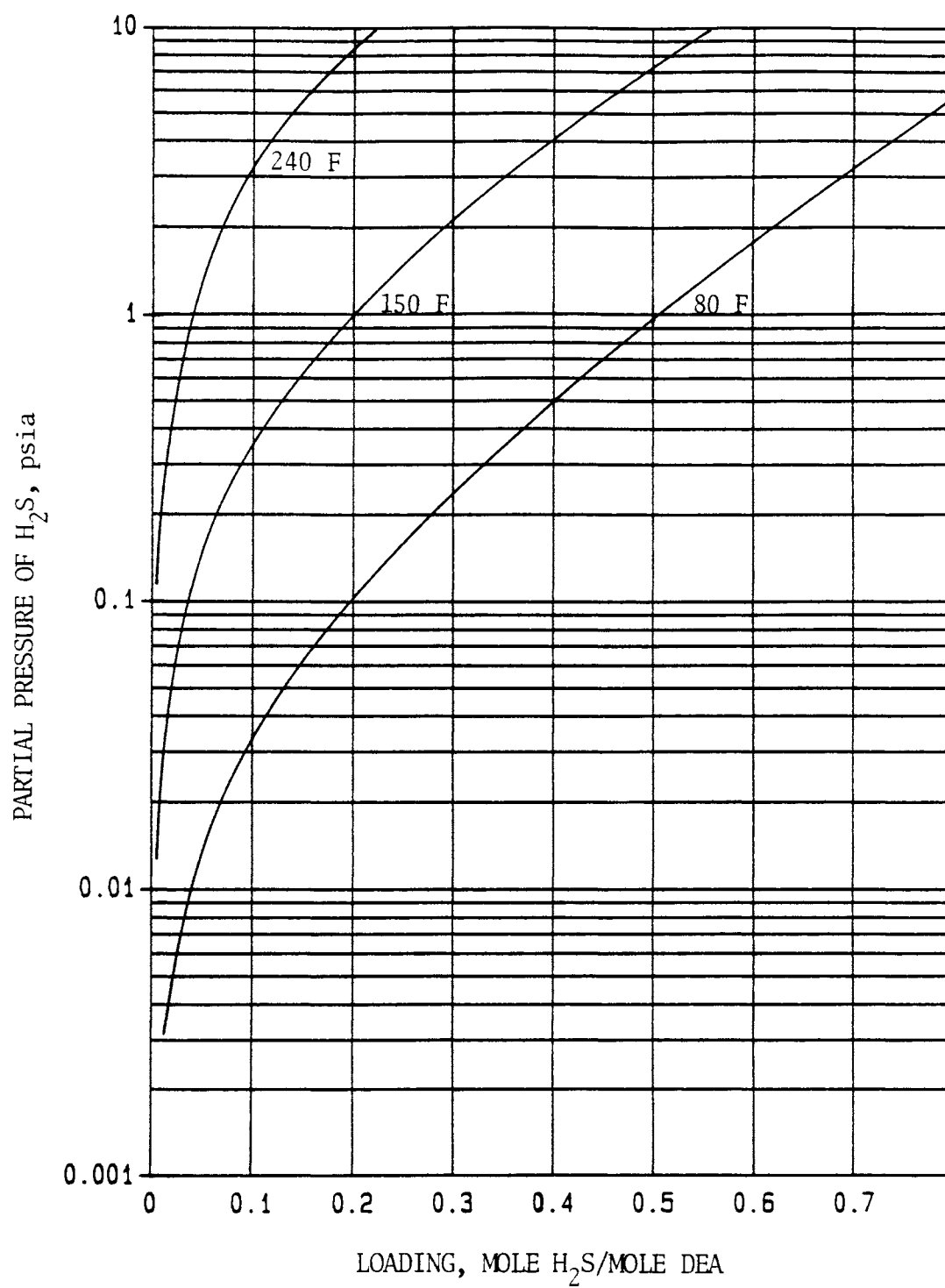


Figure 21. Solubility of H_2S in 35% by Weight DEA Aqueous Solution, Smoothed Curves

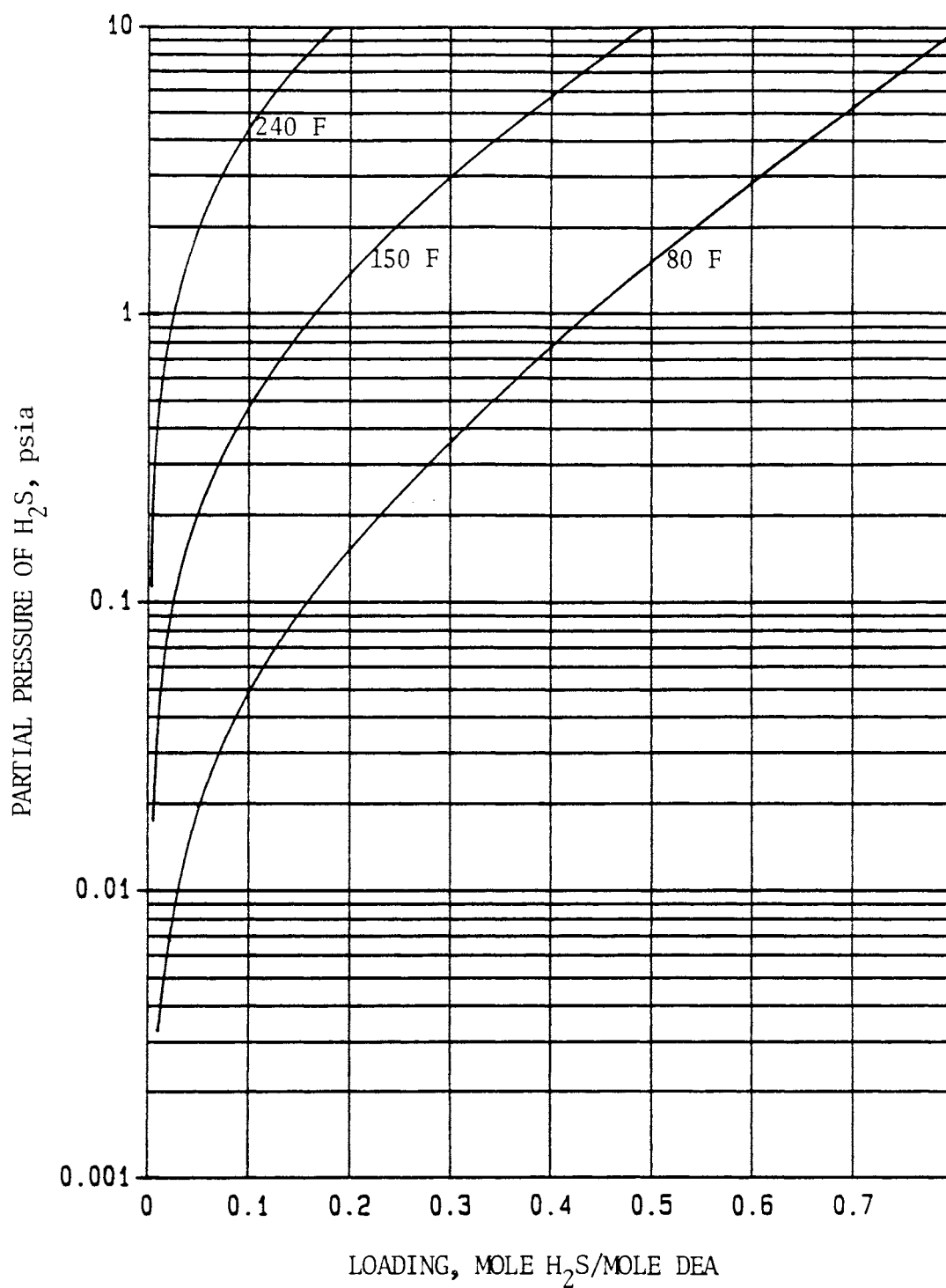


Figure 22. Solubility of H_2S in 50% by Weight DEA Aqueous Solution, Smoothed Curves

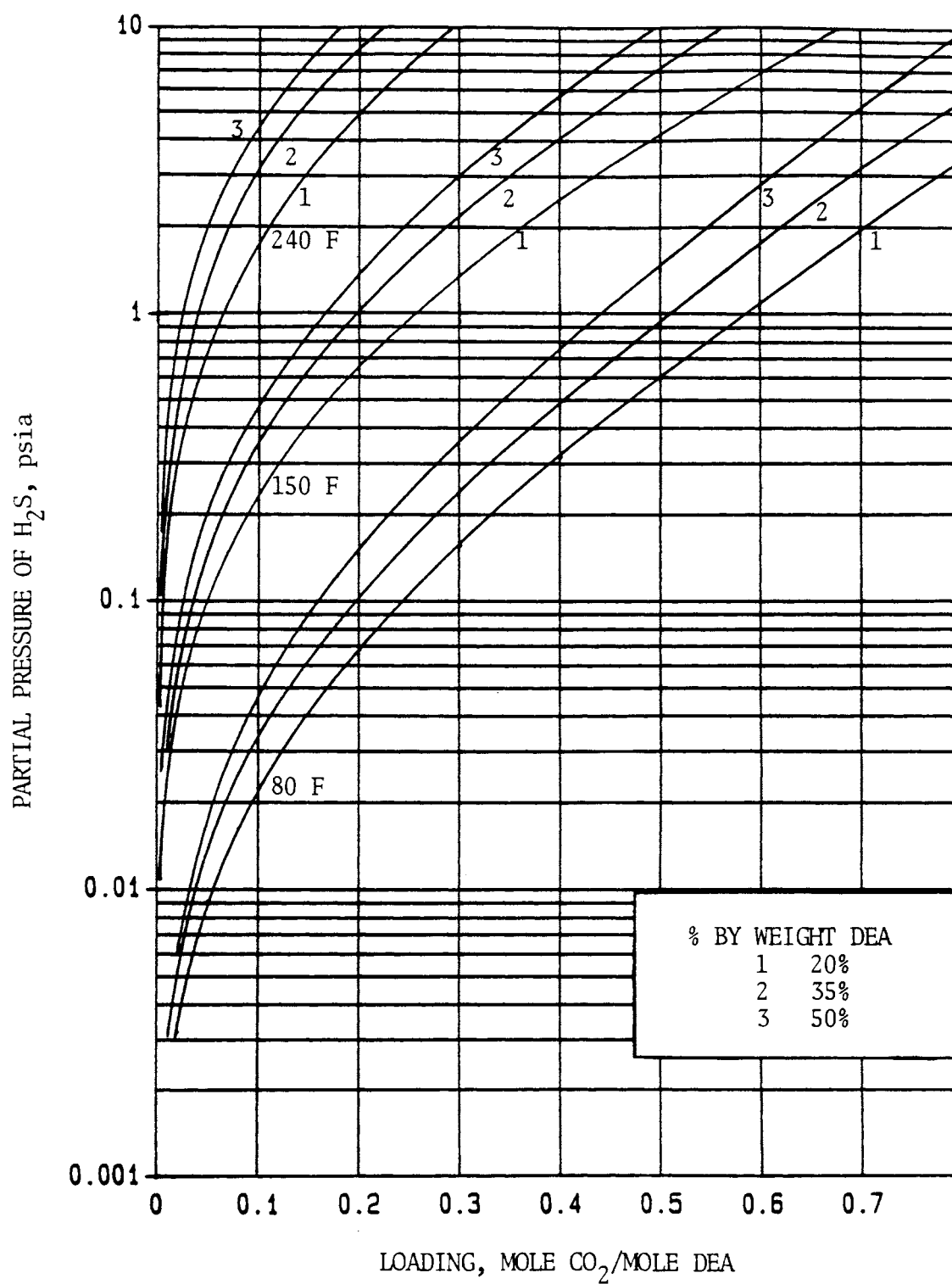


Figure 23. Solubility of H_2S in DEA Aqueous Solution at 80, 150 and 240 F, Smoothed Curves

The smoothed curves obtained for the equilibrium solubility of CO_2 and H_2S in 20% DEA at 80 and 150°F are presented in Figure 24. At 80°F, for acid gas partial pressures higher than approximately 0.80 psia, the CO_2 partial pressures are higher than H_2S . Below 0.80 psia, the H_2S partial pressure is higher than CO_2 . Similar behavior is seen for 150°F. The intersection is at around 3.5 psia. The same behavior was observed for 35% DEA and 50% DEA. This reinforces the internal consistency of the data taken.

In Figure 25, smoothed lines for the equilibrium solubility of CO_2 and H_2S in 20% DEA at 240°F are shown. In this case, the intersection point is at around 7 psia. Above this acid gas partial pressure, the CO_2 partial pressure is higher than H_2S . Below, the opposite occurs. Similar behavior was found for 35% DEA and 50% DEA, supporting the consistency of the experimental data taken.

In the last two sections, the experimental data have been presented. Most of the data sets have little or no data scatter and are internally consistent. Good agreement with available literature data was shown. An error analysis (Appendix J) indicates that the deviation for the partial pressure is 12% and for the loading is 1% in the partial pressure range of 0.0032 psia. The deviation for the partial pressure is 0.30% and for the loading 1.50% when working in the partial pressure range of 0.730 psia.

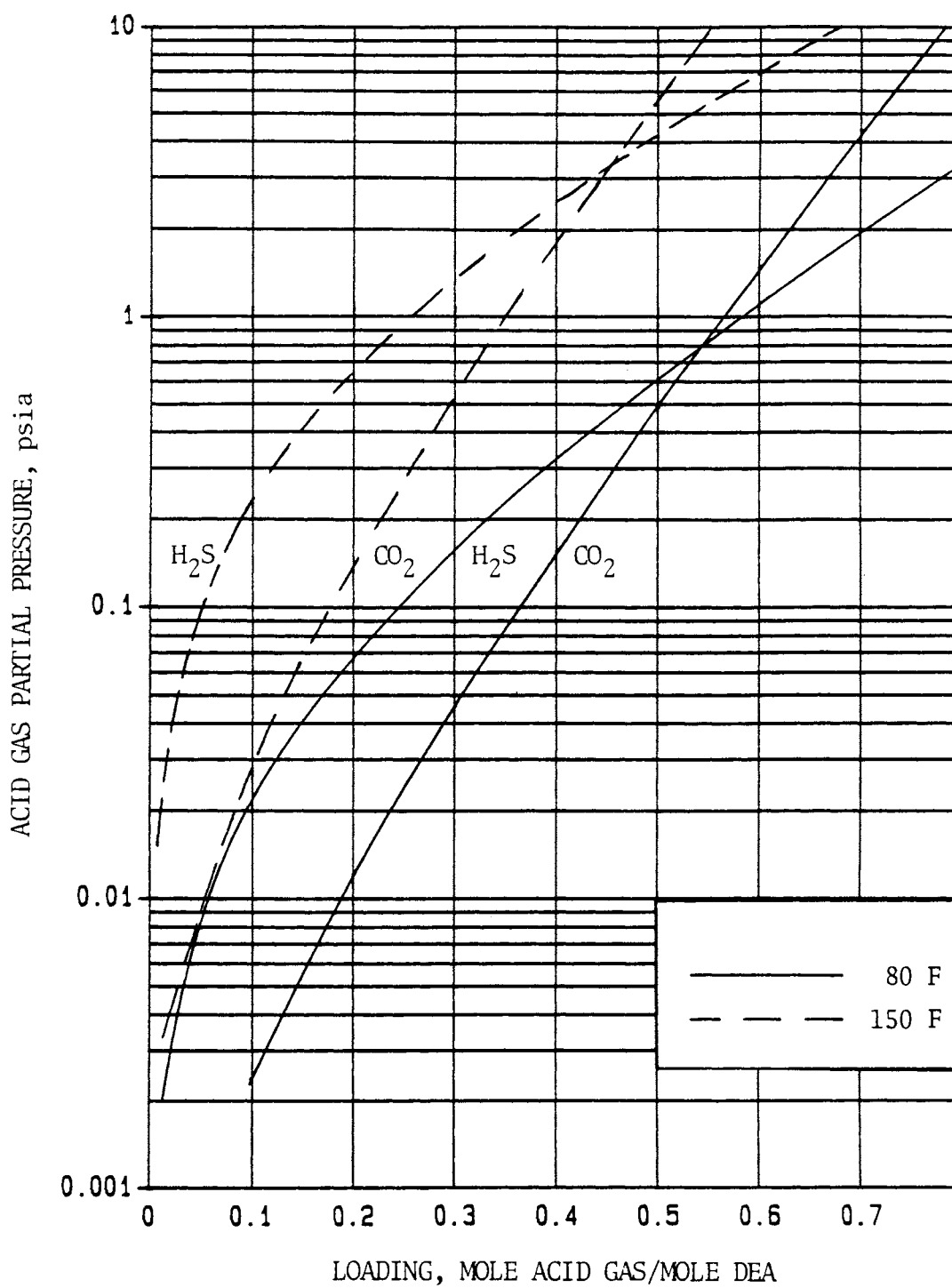


Figure 24. Solubility of Acid Gas in 20% by Weight DEA Aqueous Solution at 80 and 150 F

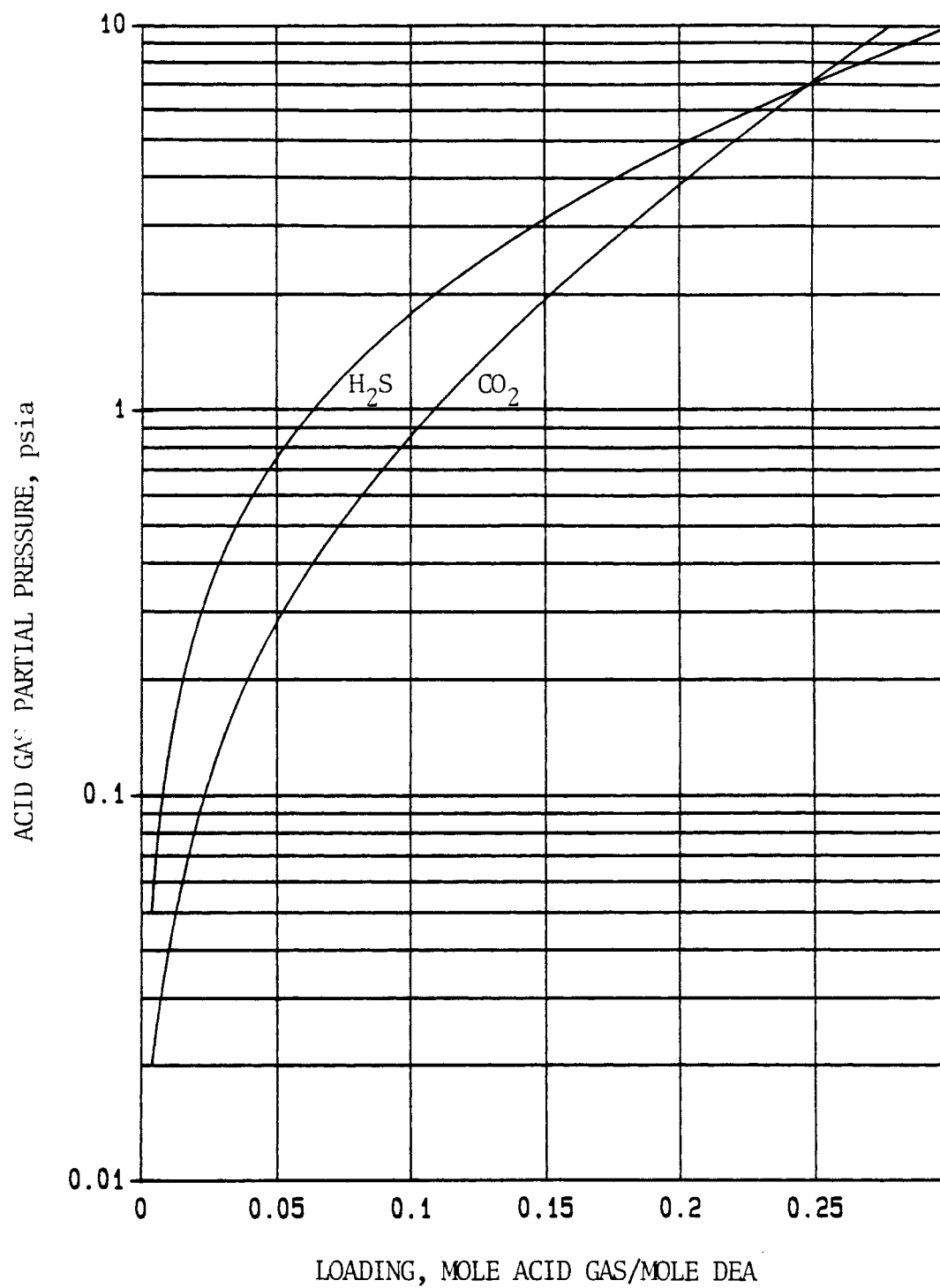


Figure 25. Solubility of Acid Gas in 20% by Weight DEA Aqueous Solution at 240 F

Modeling

Figure 26 shows the plot of $\log(P_A/\beta)$ versus β (loading) for CO_2 in 20% DEA solution at 80°F. CO_2 partial pressures from 0.0032 to 69 psia are included. Data from Bhairi (5), Lee et al. (36), and Mason and Dodge (47) are plotted for comparison. All the data fall along the same straight line. Similar behavior was observed for other DEA concentrations and temperatures for both CO_2 and H_2S .

Coefficients of the straight line equations of $\log(P_A/\beta)$ versus β are presented in Tables XXV and XXVI (Appendix G). These equations were used to calculate equilibrium partial pressures at given loadings from 0.05 to 0.90 mole/mole. The pseudo equilibrium constant $K_{2.10}$ was calculated from the H_2S data and $K_{2.9}$ was calculated from the CO_2 data. The regression program MARQ(12) was used to fit these values of pseudo equilibrium constants to an Arrhenius type equation:

$$K_{2.10} = \exp(-2.0876 - 10491/T) \quad (5.18)$$

$$K_{2.9} = \exp(0.81244 - 1076.7/T) \quad (5.19)$$

The error in calculated partial pressure using these equations was 18.7%. Inspection of the pseudo equilibrium constant values showed that, contrary to the work of Kent and Eisenberg, the psuedo equilibrium constants did not follow an Arrhenius type relationship.

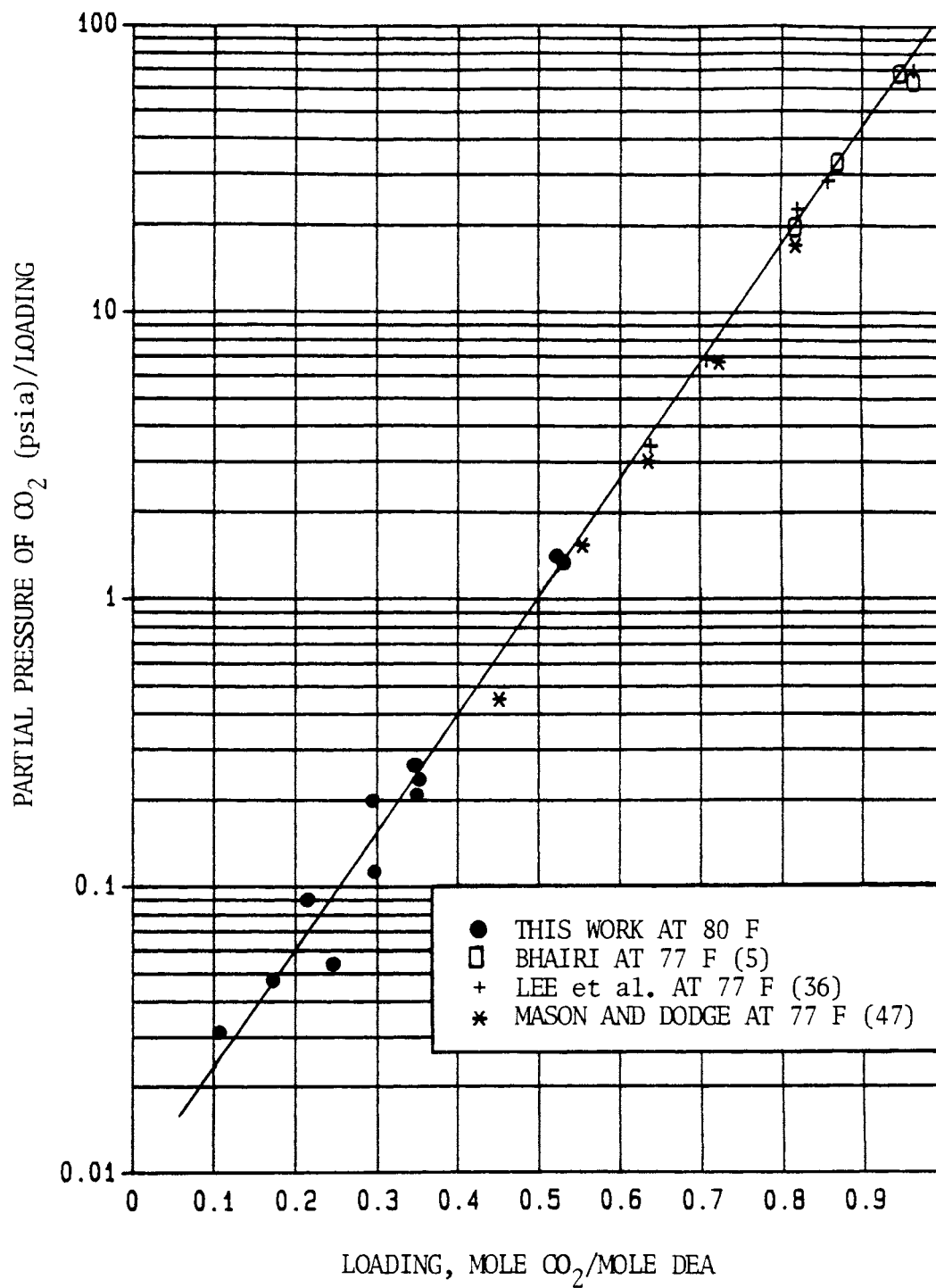


Figure 26. Solubility of CO₂ in 20% by Weight DEA Aqueous Solution at 80°F, Low and High Partial Pressure

The psuedo equilibrium constants were then fitted as a second order function of loading at a given temperature. This reduced the average error in partial pressure to 13%. The equations for $K_{2.10}$ and $K_{2.9}$ are summarized in Tables XXVII - XXIX (Appendix H).

Tables XXXII - XXXIV (Appendix K) show the predictions obtained using the two approaches presented here. The Kent and Eisenberg (29) model predictions are included for comparison. The overall average absolute percentage deviation (OAAPD) indicates that the loading approach is the best. In general, the Arrhenius approach gives an OAAPD twice as large as the loading approach, although improvement with respect to the Kent and Eisenberg model is evident. Similar results were obtained for the other DEA concentrations and for H_2S . The loading approach is better than the Arrhenius because the pseudo equilibrium constants were fitted for a given temperature and DEA weight percentage. This procedure reduces the error that would be passed if all temperatures and weight percentages were fitted at the same time.

The two approaches were made options in an existing computer program (44). For the loading approach, in the contactor where the partial pressure of the acid gases is known, the Newton-Raphson method is used with the respective linear equation for equilibrium to obtain the equilibrium loading to use in $K_{2.10}$ and $K_{2.9}$. In the

regenerator, where the loading of each gas is known, $K_{2.10}$ and $K_{2.9}$ are calculated directly.

The modified program was applied with the loading approach to a DEA contactor for synthesis gas with good results, especially for the predicted H_2S in the outlet gas (see Table XXX, Appendix I). An integrated natural gas plant was simulated also (see Table XXXI, Appendix I). Good agreement with plant data using three equilibrium stages is seen.

In this modeling section, a summary of the two approaches developed has been presented. The use of the loading approach was shown to be the best. Application of this approach to model plant data indicates that good predictions can be obtained.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. An experimental apparatus was developed to measure the equilibrium solubility of acid gas in alkanolamine solution at low acid gas partial pressures. A direct measurement was made of differential pressure between an equilibrium cell and a reference cell. The experimental procedure does not require that vapor or liquid samples be withdrawn for analysis, so equilibrium in the experimental apparatus is never disturbed.

2. A consistency test for evaluation of experimental acid gas-ethanolamine equilibrium data was developed. The test was shown to apply over the full range of partial pressures where chemical reactions dominate.

3. The prediction of acid gas partial pressure was substantially improved by using the smoothed curves from the consistency test to curvefit the pseudo equilibrium constants for the protonation of amine and carbamate formation reactions.

4. The pseudo equilibrium constants were correlated as a second order function of loading at a given temperature. Application of the loading approach to

predict plant data for a contactor in a synthesis gas plant and an integrated high pressure natural gas plant gave good results.

Recommendations

The experimental apparatus and the consistency test should be applied for other amines of industrial interest. Predictions of partial pressures can be improved by using the fitting procedure presented.

Literature data can be checked with the consistency test. The extension to low loadings and partial pressures can be made with more confidence because of the straight line relationship for equilibrium found and few experimental data in the relatively low acid gas partial pressure should be required for cross-checking.

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APPENDIXES

APPENDIX A

EXPERIMENTAL DATA

TABLE III
SOLUBILITY OF CO₂ IN 20% BY WEIGHT DEA
AQUEOUS SOLUTION AT 80°F (26.67°C)

Total Pressure psia (kPa)	CO ₂ Partial Pressure psia (kPa)	CO ₂ Loading moles CO ₂ / mole DEA
0.4479 (3.088)	0.0032 (0.0221)	0.1033
0.4529 (3.123)	0.0082 (0.0565)	0.1724
0.4578 (3.160)	0.0130 (0.0896)	0.2477
0.4646 (3.203)	0.0198 (0.1365)	0.2130
0.4781 (3.296)	0.0333 (0.2296)	0.3005
0.5055 (3.485)	0.0607 (0.4185)	0.2943
0.5168 (3.563)	0.0721 (0.4971)	0.3531
0.5270 (3.634)	0.0822 (0.5667)	0.3534
0.5362 (3.697)	0.0914 (0.6302)	0.3484
1.1602 (7.999)	0.7154 (4.933)	0.5325
1.1764 (8.111)	0.7317 (5.045)	0.5204

TABLE IV
SOLUBILITY OF CO₂ IN 20% BY WEIGHT DEA
AQUEOUS SOLUTION AT 150°F (65.56°C)

Total Pressure psia (kPa)	CO ₂ Partial Pressure psia (kPa)	CO ₂ Loading moles CO ₂ / mole DEA
3.427 (23.63)	0.0047 (0.0324)	0.0521
3.539 (24.40)	0.1167 (0.8046)	0.1862
3.622 (24.97)	0.1996 (1.376)	0.2121
3.704 (25.54)	0.2815 (1.941)	0.2476
3.899 (26.88)	0.4766 (3.286)	0.2926
4.552 (31.38)	1.130 (7.791)	0.3291
5.267 (36.31)	1.845 (12.72)	0.3883
6.456 (44.51)	3.034 (20.92)	0.4397
7.958 (54.87)	4.536 (31.27)	0.5229

TABLE V
SOLUBILITY OF CO₂ IN 20% BY WEIGHT DEA
AQUEOUS SOLUTION AT 240°F (115.56°C)

Total Pressure psia (kPa)	CO ₂ Partial Pressure psia (kPa)	CO ₂ Loading moles CO ₂ / mole DEA
24.26 (167.3)	0.5782 (3.987)	0.1297
24.88 (171.5)	1.202 (8.288)	0.1277
25.87 (178.4)	2.190 (15.10)	0.1449
26.03 (179.5)	2.351 (16.21)	0.1453
26.68 (183.9)	2.995 (20.65)	0.1828
26.98 (186.0)	3.295 (22.72)	0.1542
28.02 (193.2)	4.341 (29.93)	0.1956
28.25 (194.8)	4.565 (31.47)	0.1952
29.24 (201.6)	5.557 (38.31)	0.2242
29.88 (206.0)	6.200 (42.75)	0.2128
30.32 (209.0)	6.636 (45.75)	0.2722
32.50 (224.1)	8.822 (60.83)	0.2758

TABLE VIII
SOLUBILITY OF CO₂ IN 50% BY WEIGHT DEA
AQUEOUS SOLUTION AT 80 AND 150°F

Temperature °F (°C)	Total Pressure psia (kPa)	CO ₂ Partial Pressure psia (kPa)	CO ₂ Loading moles CO ₂ / mole DEA
80 (26.67)	0.3728 (2.570)	0.0145 (0.1000)	0.2386
	0.3955 (2.727)	0.0372 (0.2565)	0.2854
	0.4521 (3.117)	0.0938 (0.6467)	0.3530
	0.6819 (4.702)	0.3236 (2.231)	0.4493
	1.734 (11.96)	1.376 (9.487)	0.5256
	3.623 (24.98)	3.264 (22.50)	0.5062
150 (65.56)	2.935 (20.24)	0.0412 (0.2841)	0.1100
	2.993 (20.64)	0.0990 (0.6826)	0.1463
	3.272 (22.56)	0.3776 (2.604)	0.2312
	3.714 (25.61)	0.8202 (5.655)	0.2786
	4.500 (31.03)	1.606 (11.07)	0.3156
	4.514 (31.12)	1.620 (11.17)	0.3207
	6.377 (43.97)	3.483 (24.01)	0.3888
	9.762 (67.31)	6.868 (47.35)	0.4307

TABLE IX
SOLUBILITY OF CO₂ IN 50% BY WEIGHT DEA
AQUEOUS SOLUTION AT 240°F (115.56°C)

Total Pressure psia (kPa)	CO ₂ Partial Pressure psia (kPa)	CO ₂ Loading moles CO ₂ / mole DEA
20.79 (143.3)	0.1270 (0.8756)	0.0282
21.10 (145.5)	0.4341 (2.993)	0.0370
21.12 (145.6)	0.4515 (3.113)	0.0504
21.45 (147.9)	0.7783 (5.366)	0.0546
21.52 (148.4)	0.8504 (5.863)	0.0692
22.25 (153.4)	1.581 (10.90)	0.0751
22.12 (152.5)	1.452 (10.01)	0.0803
23.29 (160.6)	2.623 (18.08)	0.1017
23.31 (160.7)	2.648 (18.26)	0.1363
23.82 (164.2)	3.155 (21.75)	0.0990
25.45 (175.5)	4.782 (32.97)	0.1316
25.51 (175.9)	4.847 (33.42)	0.1574
29.04 (200.2)	8.368 (57.70)	0.1872

TABLE X
SOLUBILITY OF H₂S IN 20% BY WEIGHT DEA
AQUEOUS SOLUTION AT 80°F (26.67°C)

Total Pressure psia (kPa)	H ₂ S Partial Pressure psia (kPa)	H ₂ S Loading moles H ₂ S/ mole DEA
0.4672 (3.221)	0.0224 (0.1544)	0.1366
0.4714 (3.250)	0.0267 (0.1841)	0.0987
0.4780 (3.296)	0.0338 (0.2330)	0.1133
0.5189 (3.578)	0.0742 (0.5116)	0.2018
0.7977 (5.500)	0.3530 (2.434)	0.4412
1.130 (7.791)	0.6854 (4.726)	0.5181
1.149 (7.922)	0.7040 (4.854)	0.5300
2.743 (18.91)	2.298 (15.84)	0.6642
3.095 (21.34)	2.651 (18.28)	0.7863

TABLE XI
SOLUBILITY OF H₂S IN 20% BY WEIGHT DEA
AQUEOUS SOLUTION AT 150 AND 240°F

Temperature °F (°C)	Total Pressure psia (kPa)		H ₂ S Partial Pressure psia (kPa)		H ₂ S Loading moles H ₂ S/ mole DEA
150 (65.56)	3.824	(26.37)	0.4013	(2.767)	0.1627
	4.104	(28.30)	0.6817	(4.700)	0.2054
	4.340	(29.92)	0.9177	(6.327)	0.2403
	4.556	(31.41)	1.134	(7.819)	0.2799
	4.983	(34.36)	1.560	(10.76)	0.3205
	5.990	(41.30)	2.568	(17.71)	0.3778
	6.776	(46.72)	3.354	(23.12)	0.4580
	8.829	(60.87)	5.407	(37.28)	0.5567
	12.37	(85.29)	8.947	(61.69)	0.6577
240 (115.56)	26.18	(180.5)	2.495	(17.20)	0.1295
	27.25	(187.9)	3.570	(24.61)	0.1643
	29.21	(201.4)	5.525	(38.09)	0.2182
	30.83	(212.6)	7.145	(49.26)	0.2493

TABLE XII
 SOLUBILITY OF H₂S IN 35% BY WEIGHT DEA
 AQUEOUS SOLUTION AT 80°F (26.67°C)

Total Pressure psia (kPa)	H ₂ S Partial Pressure psia (kPa)	H ₂ S Loading moles H ₂ S/ mole DEA
0.4476 (3.086)	0.0519 (0.3578)	0.1263
0.4574 (3.154)	0.0618 (0.4261)	0.1259
0.5589 (3.854)	0.1633 (1.126)	0.2347
0.5623 (3.877)	0.1667 (1.149)	0.2332
0.8908 (6.142)	0.4952 (3.414)	0.3409
0.8945 (6.167)	0.4989 (3.440)	0.3534
0.9992 (6.889)	0.6036 (4.162)	0.3411
1.474 (10.16)	1.079 (7.439)	0.4186
2.619 (18.06)	2.223 (15.33)	0.6166

TABLE XIII
SOLUBILITY OF H₂S IN 35% BY WEIGHT DEA
AQUEOUS SOLUTION AT 150 AND 240°F

Temperature °F (°C)	Total Pressure psia (kPa)	H ₂ S Partial Pressure psia (kPa)	H ₂ S Loading moles H ₂ S/ mole DEA
150 (65.56)	3.320 (22.89)	0.1207 (0.8322)	0.0434
	3.356 (23.14)	0.1567 (1.080)	0.0578
	3.408 (23.50)	0.2085 (1.438)	0.0620
	3.566 (24.59)	0.3664 (2.526)	0.0980
	3.813 (26.29)	0.6139 (4.233)	0.1515
	4.133 (28.50)	0.9336 (6.437)	0.2044
	4.230 (29.16)	1.031 (7.109)	0.1973
	5.200 (35.85)	2.001 (13.80)	0.2788
	8.324 (57.39)	5.124 (35.33)	0.4475
240 (115.56)	24.81 (171.1)	2.491 (17.17)	0.0837
	26.68 (183.9)	4.361 (30.07)	0.1271
	28.26 (194.8)	5.941 (40.96)	0.1580
	31.01 (213.8)	8.695 (59.95)	0.2049
	33.24 (229.2)	10.92 (75.29)	0.2360

TABLE XIV
SOLUBILITY OF H₂S IN 50% BY WEIGHT DEA
AQUEOUS SOLUTION AT 80°F (26.67°C)

Total Pressure psia (kPa)	H ₂ S Partial Pressure psia (kPa)	H ₂ S Loading moles H ₂ S/ mole DEA
0.3943 (2.719)	0.0359 (0.2475)	0.0777
0.4366 (3.010)	0.0783 (0.5399)	0.1500
0.8814 (6.077)	0.5230 (3.606)	0.3423
0.9245 (6.374)	0.5662 (3.904)	0.3362
1.815 (12.51)	1.456 (10.04)	0.4881
3.148 (21.70)	2.790 (19.24)	0.6023
6.336 (43.69)	5.977 (41.21)	0.7244

TABLE XV
SOLUBILITY OF H₂S IN 50% BY WEIGHT DEA
AQUEOUS SOLUTION AT 150 AND 240°F

Temperature °F (°C)	Total Pressure psia (kPa)	H ₂ S Partial Pressure psia (kPa)	H ₂ S Loading moles H ₂ S/ mole DEA
150 (65.56)	3.042 (20.97)	0.1476 (1.018)	0.0404
	3.206 (22.10)	0.3123 (2.153)	0.0728
	3.491 (24.07)	0.5973 (4.118)	0.1179
	3.938 (27.15)	1.044 (7.198)	0.1582
	4.782 (32.97)	1.888 (13.02)	0.2267
	5.714 (39.40)	2.820 (19.44)	0.2874
	6.465 (44.57)	3.571 (24.62)	0.3303
	7.648 (52.73)	4.754 (32.78)	0.3827
240 (115.56)	22.36 (154.2)	1.695 (11.69)	0.0425
	23.76 (163.8)	3.094 (21.33)	0.0751
	25.06 (172.8)	4.393 (30.29)	0.0989
	27.71 (191.0)	7.043 (48.56)	0.1408
	30.12 (207.7)	9.457 (65.20)	0.1760

APPENDIX B

EQUILIBRIUM AND REFERENCE

CELL CALIBRATION

The volume of the equilibrium cell, with thermocouple and glass beads inserted inside, was measured with distilled water at a known temperature using two burettes (100 cc and 50 cc) previously calibrated with mercury. The tolerance for the 100 cc burette is 0.10 cc. The volumes obtained were 973.2, 972.7 and 973.3 cc, respectively, giving an average of 973 cc.

The internal volume of the tubing, valves and fittings connecting the equilibrium cell with the manometers was measured by filling the evacuated connections with distilled water coming from the 50 cc calibrated burette. The experimental volumes were 23.1 cc, 23.3 cc and 23.1 cc, respectively. The average observation is 23.20 cc.

The volumes of the manometers were obtained in a similar way with distilled water. The measurements fit very well those that can be calculated for a glass tube of 0.25" inside diameter. As a result, the volume for the equilibrium cell, V_{EC} , was determined by:

$$V_{EC} = 973 + 23.2 + D_1 + D_2 - V_A \quad (B.1)$$

$$\text{where: } D_1 = d_1 (0.25) (3.1416) (0.635)^2$$

$$D_2 = d_2 (0.25) (3.1416) (0.635)^2$$

d_1 = distance from right side of mercury
meniscus to the 25" mark on top, cm.

d_2 = distance from left side of diethylene
glycol meniscus, in differential

manometer, to the 25" mark on top, cm.

V_A = volume of amine added to the equilibrium cell, cc.

If the mercury manometer is not in use, D_1 is zero. The volume of the reference cell including glass beads, coil after cell plus injection port was measured with distilled water from the 50 cc calibrated burette. The volumes were 39.70, 39.80 and 40.1 cc, with an average of 39.90 cc. The internal volume of the tubing, valve and fittings connecting the reference cell with the differential manometer was experimentally obtained by filling the evacuated connections with distilled water using the 50 cc burette. The volumes were 7.80, 7.60 and 7.60 cc. The average observation is 7.70 cc. Then the volume for the reference cell, V_{RC} , was determined by:

$$V_{RC} = 39.90 + 7.70 + D_3 - V_{A2} \quad (B.2)$$

where: $D_3 = d_3 (0.25) (3.1416) (0.635)^2$

d_3 = distance from the right side of diethylene glycol meniscus, in differential manometer, to the 25" mark on top, cm.

V_{A2} = volume of amine added to the reference cell, cc.

APPENDIX C

CALIBRATION OF THE THERMOCOUPLES

TABLE XVI
EQUILIBRIUM CELL COPPER-CONSTANTAN
THERMOCOUPLE CALIBRATION AGAINST
A PLATINUM RESISTANCE
THERMOMETER FROM THE
NATIONAL BUREAU
OF STANDARDS

Temp. °F Actual	Temp. °F Fitted	Deviation °F	% Deviation
32.00	31.98	-0.02	-0.06
77.54	77.60	+0.04	+0.05
114.40	114.50	+0.10	+0.09
148.80	148.90	+0.10	+0.07
186.50	186.60	+0.10	+0.05
212.10	211.90	-0.20	-0.09
250.60	250.50	-0.10	-0.04
O.A.A.P.D. = 0.06			

$$T = 31.75 + 46.87 \text{ (mv)} - 1.297 \text{ (mv)}^2 + 0.055 \text{ (mv)}^3$$

where: T = Temperature in °F, fitted.

mv = Millivolts read.

O.A.A.P.D. = Overall Average Absolute Percentage
Deviation.

The mv for 80, 150 and 240°F are 1.06, 2.7025 and
4.9875 respectively.

TABLE XVII
OIL BATH COPPER-CONSTANTAN THERMOCOUPLE
CALIBRATION AGAINST A PLATINUM
RESISTANCE THERMOMETER FROM
THE NATIONAL BUREAU
OF STANDARDS

Temp. °F Actual	Temp. °F Fitted	Deviation °F	% Deviation
32.00	32.00	0.00	0.00
76.31	76.38	+0.07	+0.09
114.80	114.80	+0.00	0.00
149.10	149.20	+0.10	+0.07
185.10	185.10	+0.00	0.00
209.80	209.60	-0.20	-0.09
249.60	249.50	-0.10	-0.04
O.A.A.P.D. = 0.04			

$$T = 31.77 + 46.94 \text{ (mv)} - 1.34 \text{ (mv)}^2 + 0.061 \text{ (mv)}^3$$

where: T = Temperature in °F, fitted.

mv = Millivolts read.

O.A.A.P.D. = Overall Average Absolute Percentage
Deviation

The mv for 80, 150 and 240°F are 1.06, 2.7025 and
4.9850 respectively.

APPENDIX D

SYRINGE CALIBRATION

The syringe was filled with distilled water and the water injected in one of the two calibrated burettes, and a reading was taken. As many injections as necessary to fill the burette gave the same amount of readings. Then the average volume for the syringe was obtained. The burettes were previously calibrated with mercury. Syringes of 2 and 5 cc were calibrated using the 50 cc burette. Syringes of 10 and 20 cc were calibrated using the 100 cc burette. The syringe for 50 cc was calibrated using the 100 cc burette, triplicate runs were made. The results of the volumes for the two types of syringes available are shown in next table.

TABLE XVIII
SYRINGE CALIBRATION VOLUMES

Nominal (cc)	Type 1 (cc)	Type 2 (cc)
50	49.80	Φ
20	19.90	Φ
10	9.98	9.96
5	5.05	5.02
2	1.99	2.03

The types 1 and 2 correspond to syringes marketed as Multifit and Micromate, respectively. The reference tem-

perature for the calibrated volumes is 68°F. A small correction for expansion of glass when injecting at room temperature was considered.

APPENDIX E

PHYSICAL PROPERTIES

TABLE XIX
EXPERIMENTAL ACTIVITY COEFFICIENT FOR
WATER IN DEA AQUEOUS SOLUTIONS

T (°F)	20% by Weight DEA	35% by Weight DEA	50% by Weight DEA
80	0.9351	0.8713	0.8462
150	0.9743	0.9540	0.9254
240	0.9958	0.9828	0.9761

TABLE XX
MOLE FRACTION FOR WATER IN DEA
AQUEOUS SOLUTIONS

% by Weight DEA	Mole Fraction H ₂ O
20	0.9589
35	0.9155
50	0.8537

TABLE XXI
VAPOR PRESSURE OF AQUEOUS DEA
SOLUTIONS

% by Weight DEA	T (°F)	This Work (mm Hg)	Dow (22) (mm Hg)	Deviation (%)
20	80	23.00	23.69	-2.91
	150	176.98	180.00	-1.68
	240	1224.70	1258.40	-2.68
35	80	20.46	21.94	-6.75
	150	165.45	164.00	+0.88
	240	1154.00	1234.60	-6.53
50	80	18.53	19.74	-6.13
	150	149.66	150.00	-0.23
	240	1068.8	1117.50	-4.35

TABLE XXII
WATER VAPOR PRESSURE

T (°F)	This Work (mm Hg)	Antoine (54) (mm Hg)	Deviation (%)	Dow (22)
80	25.65	26.26	-2.32	26.04
150	189.43	192.47	-1.58	192.35
240	1282.60	1291.90	-0.72	1291.90

TABLE XXIII
ACTIVITY COEFFICIENT FOR WATER IN DEA
AQUEOUS SOLUTIONS CALCULATED
FROM DOW DATA

T (°F)	20% by Weight DEA	35% by Weight DEA	50% by Weight DEA
80	0.9487	0.9203	0.8880
150	0.9759	0.9313	0.9135
240	1.016	1.044	1.013
Deviations for This Work (%)			
80	-1.44	-5.33	-4.70
150	-0.16	+2.44	+1.31
240	-1.97	-5.85	-3.66

TABLE XXIV
DENSITY OF AQUEOUS DIETHANOLAMINE
SOLUTIONS

% by Weight DEA	T (°F)	Density (g/cc)
20	80	1.0190
	150	1.0020
	240	0.9715
35	80	1.0370
	150	1.0170
	240	0.9865
50	80	1.0540
	150	1.0330
	240	1.0020

The density was obtained from Maddox (45), Figure A 2.18 page 364.

The density of diethylene glycol was taken from Campbell (9), Figure 18.2. A mathematical expression was obtained for the temperature range from 0°C (32°F) to 40°C (104°F)

$$\rho_{\text{DEG}} = 1.1221 - 4.0717 \times 10^{-4} (T-53.6)$$

where: ρ_{DEG} = density of diethylene glycol, gr/cc

T = temperature in °F

This equation was then tested for 60°C (140°F) and gives 1.0869 gr/cc and when compared with the reported value of 1.088 from the same reference, Table 18.1 page 162 gives a deviation of -1.10% which was considered very good.

APPENDIX F

SAMPLE OF CALCULATION

SAMPLE OF CALCULATION

RUN CO₂ - 20% DEA - 80°F

1.- Total number of moles initially in the equilibrium cell.

$$P = 24.775 \text{ in Hg Vacuum} = 629.29 \text{ mm Hg Vacuum}$$

$$P = 742.8 - 629.29 = 113.51 \text{ mm Hg Abs.} = 2.195 \text{ Psia}$$

$$\text{Volume} = 1020.69 \text{ cc}$$

$$\text{moles} = \frac{(113.51/760) \cdot 1020.69}{(82.06) \cdot 299.82} = 6.1965 \times 10^{-3} \text{ gr mol CO}_2$$

2.- Cell of reference.

a) Initial conditions

$$P = 113.51 + \rho_{\text{DEG}} (\text{g/g}_c) h_{\text{DEG}}$$

$$P = 113.51 + 1111.3 \times 6.15 \times (1.8665 \times 10^{-3})$$

$$P = 126.27 \text{ mm Hg Abs.}$$

$$\text{Volume} = 66.511 \text{ cc}$$

b) Final conditions, after injection of 29.949 cc of 20 % DEA to equilibrium cell.

$$\text{Volume} = 78.63 \text{ cc}$$

Assuming ideal gas:

$$P = 126.27 (66.51/78.63) = 106.81 \text{ mm Hg Abs.}$$

3.- Final pressure in the equilibrium cell side

$$P = 106.81 - 1111.3 \times 40.325 (1.8665 \times 10^{-3})$$

$$P = 23.164 \text{ mm Hg Abs.} = 0.4479 \text{ Psia}$$

4.- Loading

a) Final moles in the equilibrium cell

$$\text{Volume} = 974.88 \text{ cc}$$

$$P = 23.164 \text{ mm Hg} = 0.4479 \text{ Psia}$$

$$P^{\circ}_{\text{SOL}} = 23.000 \text{ mm Hg}$$

$$P_{\text{CO}_2} = 0.1640 \text{ mm Hg} = 0.0032 \text{ Psia}$$

$$\text{moles} = \frac{(0.1640/760) 974.88}{(82.06) 299.82}$$

$$\text{moles} = 8.551 \times 10^{-6} \text{ gr mol CO}_2$$

b) Loading, β (mole CO_2 /mole DEA):

$$\text{Amine} = 0.2063 \text{ gr DEA/gr total}$$

$$\text{Density of amine} = 1.0195 \text{ gr/cc}$$

$$\text{Molecular weight of amine} = 105.14$$

$$\text{Injection} = 29.949 \text{ cc of amine}$$

$$\beta = \frac{(6.1965 \times 10^{-3} - 8.551 \times 10^{-6})}{(0.2063) 1.0195 (1.0/105.14) 29.949}$$

$$\beta = 0.1033 \text{ moles of CO}_2/\text{mole DEA}$$

Note: The example presented here is the first data presented in Table III Appendix A.

APPENDIX G

SINGLE ACID GAS VAPOR-LIQUID EQUILIBRIUM EQUATIONS

TABLE XXV
SOLUBILITY OF CO₂ IN DEA AQUEOUS
SOLUTIONS

% by Weight DEA	T (°F)	log (P _A /β)
20	80	-2.0212 + 3.950β
	150	-0.8139 + 3.710β
	240	+0.7259 + 3.100β
35	80	-2.1553 + 4.480β
	150	-0.6021 + 3.804β
	240	+0.7782 + 3.287β
50	80	-2.3973 + 5.320β
	150	-0.8204 + 4.680β
	240	+1.0500 + 3.250β

Note: P_A is the partial pressure of CO₂, psia.
β is the loading, mole CO₂/mole DEA.

TABLE XXVI
SOLUBILITY OF H₂S IN DEA AQUEOUS
SOLUTIONS

% by Weight DEA	T (°F)	log (P _A /β)
20	80	-0.8319 + 1.831β
	150	+0.0514 + 1.736β
	240	+1.1034 + 1.450β
35	80	-0.6653 + 1.903β
	150	+0.3025 + 1.780β
	240	+1.3449 + 1.361β
50	80	-0.5069 + 1.984β
	150	+0.4692 + 1.732β
	240	+1.6136 + 1.147β

Note: P_A is the partial pressure of H₂S, psia.

β is the loading, mole H₂S/mole DEA.

APPENDIX H

PSEUDO EQUILIBRIUM CONSTANTS

$K_{2.10}$ AND $K_{2.9}$

TABLE XXVII
PSEUDO EQUILIBRIUM CONSTANTS $K_{2.10}$
AND $K_{2.9}$ IN 20% BY WEIGHT DEA
AQUEOUS SOLUTION

T (°F)	Type	$K = \frac{a}{a}$	+	$\frac{b\beta}{b}$	+	$\frac{c\beta^2}{c}$
80	$K_{2.10}$	0.8503×10^{-9}		-0.1343×10^{-8}		0.1083×10^{-8}
	$K_{2.9}$	0.3449		-0.5027		0.5219
150	$K_{2.10}$	0.8229×10^{-8}		-0.1697×10^{-7}		0.1544×10^{-7}
	$K_{2.9}$	0.3184		-0.2089		0.08061
240	$K_{2.10}$	0.5086×10^{-7}		-0.8333×10^{-7}		0.1173×10^{-6}
	$K_{2.9}$	0.7791		-1.610		0.8160

Note: β is the loading, mole Acid Gas/mole DEA.

$K_{2.10}$ is the pseudo equilibrium constant for
protonation of amine reaction, (2.10), gm-mole/
liter.

$K_{2.9}$ is the pseudo equilibrium constant for
carbamate formation reaction, (2.9), gm-mole/liter.

TABLE XXVIII
PSEUDO EQUILIBRIUM CONSTANTS $K_{2.10}$
AND $K_{2.9}$ IN 35% BY WEIGHT DEA
AQUEOUS SOLUTION

T (°F)	Type	$K = \frac{a}{a}$	+	$\frac{b\beta}{b}$	+	$\frac{c\beta^2}{c}$
80	$K_{2.10}$	0.7612×10^{-9}		-0.1406×10^{-8}		0.1258×10^{-8}
	$K_{2.9}$	0.2686		-0.1427		0.4051
150	$K_{2.10}$	0.8560×10^{-8}		-0.1844×10^{-7}		0.1761×10^{-7}
	$K_{2.9}$	0.4930		-0.1977		0.0315
240	$K_{2.10}$	0.7036×10^{-7}		-0.1767×10^{-6}		0.1901×10^{-6}
	$K_{2.9}$	0.5935		-0.7676		0.08164

Note: β is the loading, mole Acid Gas/mole DEA.

$K_{2.10}$ is the pseudo equilibrium constant for
protonation of amine reaction, (2.10), gm-mole/
liter.

$K_{2.9}$ is the pseudo equilibrium constant for
carbamate formation reaction, (2.9), gm-mole/liter.

TABLE XXIX
PSEUDO EQUILIBRIUM CONSTANTS $K_{2.10}$
AND $K_{2.9}$ IN 50% BY WEIGHT DEA
AQUEOUS SOLUTION

T (°F)	Type	$K = \frac{a}{a}$	+	$\frac{b\beta}{b}$	+	$\frac{c\beta^2}{c}$
80	$K_{2.10}$	0.7754×10^{-9}		-0.1503×10^{-8}		0.1468×10^{-8}
	$K_{2.9}$	0.1186		0.5116		-0.3602
150	$K_{2.10}$	0.7683×10^{-8}		-0.1338×10^{-7}		0.1177×10^{-7}
	$K_{2.9}$	0.3101		0.5416		-1.062
240	$K_{2.10}$	0.5427×10^{-7}		-0.6210×10^{-7}		0.4709×10^{-7}
	$K_{2.9}$	1.741		-4.931		3.481

Note: β is the loading, mole Acid Gas/mole DEA.

$K_{2.10}$ is the pseudo equilibrium constant for
protonation of amine reaction, (2.10), gm-mole/
liter.

$K_{2.9}$ is the pseudo equilibrium constant for
carbamate formation reaction, (2.9), gm-mole/liter.

APPENDIX I

MODIFIED PROGRAM APPLICATIONS

TABLE XXX
 COMPARISON OF THE MODIFIED PROGRAM
 SIMULATION WITH OPERATING DATA
 OF A DEA CONTACTOR FOR
 SYNTHESIS GAS

Contactor	Reference(32)	Modified Program
Gas Feed, SCF/hr	71900	71900*
CO ₂ , %	19.4	19.4*
H ₂ S, ppm	1196	1196*
Outlet Gas,		
CO ₂ , %	4.2	0.0059
H ₂ S, ppm	33	39
Solution Rate, gpm	41	41*
DEA Solution, wt%	41	41*
Temperature, °F		
Feed Gas	-	100*
Lean Solution	-	100*
Pressure, PSIG	340	340*
No. of Stages	-	2*
Lean Solution Analysis:		
mole CO ₂ /mole DEA	0.0385	0.0385*
mole H ₂ S/mole DEA	0.0047	0.0047*
Rich Solution Analysis:		
mole CO ₂ /mole DEA	0.4008	0.4751
mole H ₂ S/mole DEA	0.0068	0.0073

*Specified

TABLE XXXI
COMPARISON OF THE MODIFIED PROGRAM
SIMULATION WITH A HIGH PRESSURE
NATURAL GAS PLANT USING
DEA AQUEOUS SOLUTION

Plant Variables	Reference(32)	Modified Program
Solution:		
DEA, wt %	20	20*
Flow Rate, gpm	1540	1540*
Contactor:		
Pressure, PSIG	1000	1000*
No. of Stages	30	3*
Feed Gas, MMSCFD	35.5	35.5*
CO ₂ , %	10	10*
H ₂ S, %	15	15*
Sweet Gas,		
CO ₂ , ppm	19.7	0.27
H ₂ S, ppm	4.5	2.00
Regenerator:		
Pressure, PSIG	25	23-27*
No. of Stages	20	4*
Reboiler Temperature, °F	272	272
Steam to Reboiler, lb/hr	92000	92000*
Lean Solution Analysis:		
mole CO ₂ /mole DEA	-	0.0138
mole H ₂ S/mole DEA	-	0.0137
Rich Solution Analysis:		
mole CO ₂ /mole DEA	-	0.2726
mole H ₂ S/mole DEA	-	0.4020

*Specified

APPENDIX J

ERROR ANALYSIS

ERROR ANALYSIS

The traditional error analysis gives an estimate of the errors due to the instruments and technique used, the results of the error analysis provide a range of "acceptable" errors for the experimental determinations. In this analysis an effort is made to determine the maximum error in each experimental value recorded.

The differential manometer could be read to 0.025 in. of diethylene glycol (DEG) using a cathetometer which was carefully aligned in front of the manometer. Mercury manometer was used and could be read to 0.025 in. The accuracy for the temperature is estimated from the potentiometer specifications to be 0.04°F . The error in measuring the volume of the solution was 0.05 cc for every 20 cc injected. The barometric pressure error is 0.05 mm Hg. The volumes for the cells are within ± 0.45 cc and ± 0.20 cc of accuracy. Using these errors, the maximum error was calculated for the lowest partial pressure of CO_2 and the highest, both in 20% DEA solution at 80°F .

Lowest Partial Pressures of CO_2
Measured in 20% DEA - 80°F

Experimental Data (Run 38A)

Initial Mercury Manometer, $P = 24.775$ in Hg Vacuum

Barometric Pressure, $P_b = 742.8$ mm Hg

Temperature, $T = 80^{\circ}\text{F} \pm 0.04$

The pressure corrections will be applied to maximize the CO_2 present.

1. The moles of CO_2 initially in the equilibrium cell are:

$$P = 24.775 - 0.025 = 24.75 \text{ in Hg Vacuum}$$

$$P_b = 742.8 + 0.05 = 742.85 \text{ mm Hg}$$

$$P = 742.85 - 628.65 = 114.2 \text{ mm Hg Abs.}$$

$$T = 80 - 0.04 = 79.96^\circ\text{F} = 299.79^\circ\text{K}$$

$$\text{Equilibrium cell volume} = 1020.69 \text{ cc} \pm 0.45 \text{ cc}$$

$$\text{moles} = \frac{(114.2/760) (1020.69 + 0.45)}{(82.06) 299.79}$$

$$\text{moles} = 6.237 \times 10^{-3} \text{ gr mole } \text{CO}_2.$$

2. Cell of reference.

(a) Initial conditions

$$\Delta h = 6.15 \text{ in DEG} \pm 0.025 \text{ in} = 6.175 \text{ in}$$

$$P = 114.2 + 1111.3 \times 6.175 (1.8665 \times 10^{-3})$$

$$P = 127 \text{ mm Hg Abs.}$$

$$\text{Small Cell volume} = 66.511 \text{ cc} \pm 0.20 \text{ cc}$$

(b) Final conditions, after injection of 29.949 cc of 20% DEA to equilibrium cell

$$\text{Small cell volume} = 78.63 \text{ cc} \pm 0.20 \text{ cc}$$

Assuming ideal gas:

$$P = 127 (66.511 + 0.20) / (78.63 + 0.20)$$

$$P = 107.48 \text{ mm Hg Abs.}$$

3. Final pressure in the equilibrium cell side.

$$\Delta h = 40.325 \text{ in DEG} \pm 0.025 \text{ in}$$

$$P = 107.48 - 1111.3 \times 40.350 (1.866 \times 10^{-3})$$

$$P = 23.782 \text{ mm Hg Abs.}$$

4. Loading

- (a) Final moles in the equilibrium cell.

$$\text{Equilibrium cell volume} = 974.88 \pm 0.45 \pm$$

$$29.949 \left(\frac{0.05}{20} \right)$$

$$\begin{aligned} \text{Equilibrium cell volume} &= 974.88 - 0.45 - \\ 0.075 &= 974.36 \text{ cc} \end{aligned}$$

$$\begin{aligned} \text{Vapor pressure of solution} &= (23.00 \pm 0.635) \\ \text{mm Hg.} \end{aligned}$$

$$P = 23.782 \text{ mm Hg} = 0.4599 \text{ Psia}$$

$$P_{\text{sol}}^{\circ} = 23.635 \text{ mm Hg}$$

$$P_{\text{CO}_2} = 0.147 \text{ mm Hg} = 0.0028 \text{ Psia}$$

$$\begin{aligned} T &= 80 + 0.04 = 80.04^{\circ}\text{F to minimize CO}_2 \\ &\text{present} \end{aligned}$$

$$\text{moles} = \frac{(0.147/760) \quad 974.36}{(82.06) \quad 299.84} = 7.664 \times 10^{-6} \text{ gr mole CO}_2$$

- (b) Loading, β , mole CO₂/mole DEA

$$\text{Amine} = 0.2063 \text{ gr DEA/gr total}$$

$$\text{Density of Amine} = 1.0195 \text{ gr/cc}$$

$$\text{Molecular weight of amine} = 105.14$$

$$\text{Injection} = 29.949 \text{ cc } (1 \pm 0.05/20) = 29.87 \text{ cc}$$

$$\beta = \frac{(6.237 \times 10^{-3} - 7.664 \times 10^{-6})}{(0.2063) (1.0195) 29.87/105.14}$$

$$\beta = 0.1042 \text{ mole of CO}_2/\text{mole DEA}$$

The deviations are calculated based on reported values, $P_{\text{CO}_2} = 0.164 \text{ mm Hg}$, loading = 0.1033 mole/mole:

$$\% \text{ Deviation} = \frac{(0.164 - 0.147)}{0.147} 100$$

$$\% \text{ Deviation} = 11.6\%$$

Loading:

$$\% \text{ Deviation} = \frac{(0.1042 - 0.1033)}{0.1033} 100$$

$$\% \text{ Deviation} = 0.91\%$$

This analysis corresponds to the first data presented in Table III (Appendix A). When the initial amount of CO_2 is minimized and the final maximized the deviations for the partial pressure and the loading are 8.67% and 0.94% respectively.

Largest Partial Pressure of CO₂
Measured in 20% DEA at 80°F

Experimental Data (Run 34A)

Initial Mercury Manometer, P = 23.82 in Hg Vacuum

Barometric Pressure, P_b = 737.50 mm Hg

Temperature, T = 80°F ± 0.04

Maximizing the initial CO₂ present first.

1. Moles of CO₂ initially in the equilibrium cell:

$$P = 23.82 - 0.025 = 23.795 \text{ in Hg Vacuum}$$

$$P_b = 737.5 + 0.05 = 737.55 \text{ mm Hg}$$

$$P = 737.55 - 604.39 = 133.16 \text{ mm Hg Abs.}$$

$$T = 80 - 0.04 = 79.96^\circ\text{F} = 299.79^\circ\text{K}$$

$$\text{Equilibrium cell volume} = 1021.17 \text{ cc} \pm 0.45 \text{ cc}$$

$$\text{moles} = \frac{(133.16/760)(1021.17 + 0.45)}{(82.06) \quad 299.79} = 7.276 \times 10^{-3} \text{ gr mole}$$

$$\text{moles} = 7.276 \times 10^{-3} \text{ gr mole CO}_2.$$

2. Cell of reference.

(a) Initial conditions

$$\Delta h = 4.78 \text{ in DEG} \pm 0.025 \text{ in} = 4.805 \text{ in}$$

$$P = 133.16 + 1111.3 \times 4.805 (1.8665 \times 10^{-3})$$

$$P = 143.12 \text{ mm Hg Abs.}$$

$$\text{Small cell volume} = 67.13 \text{ cc} \pm 0.20 \text{ cc}$$

- (b) Final conditions, after injection of 5 cc of
20% DEA to equilibrium cell

$$\text{Small cell volume} = 76.47 \text{ cc} \pm 0.20 \text{ cc}$$

$$P = 143.12 (67.13 + 0.2) / (76.47 + 0.20)$$

$$P = 125.69 \text{ mm Hg Abs.}$$

3. Final pressure in the equilibrium cell side.

$$\Delta h = 30.875 \text{ in DEG} \pm 0.025 \text{ in}$$

$$P = 125.69 - 1111.3 \times 30.90 (1.866 \times 10^{-3})$$

$$P = 61.57 \text{ mm Hg Abs.}$$

4. Loading

- (a) Final moles in the equilibrium cell.

$$\text{Equilibrium cell volume} = 1003.92 \pm 0.45 \pm$$

$$5 \left(\frac{0.05}{20} \right)$$

$$\begin{aligned} \text{Equilibrium cell volume} &= 1003.92 - 0.45 - \\ &0.013 = 1003.46 \text{ cc} \end{aligned}$$

$$P = 61.57 \text{ mm Hg} = 1.1905 \text{ Psia}$$

$$P_{\text{sol}}^{\circ} = 23.635 \text{ mm Hg}$$

$$P_{\text{CO}_2} = 37.93 \text{ mm Hg} = 0.7335 \text{ Psia}$$

$$T = 80.04^{\circ}\text{F to minimize CO}_2 \text{ present}$$

$$\text{moles} = \frac{(37.93/760) 1003.46}{82.06 \times 299.84} = 2.035 \times 10^{-3} \text{ gr mole CO}_2$$

(b) Loading, β , mole CO₂/mole DEA

gr mole DEA = 0.01005

$$\beta = \frac{(7.276 - 2.035) \times 10^{-3}}{0.01005} = 0.5215$$

The deviations are calculated based on reported values, $P_{\text{CO}_2} = 0.7317$ Psia and $\beta = 0.5204$, then for the partial pressure of CO₂ deviation of 0.25% and for the loading the deviation is 0.22%. When the initial amount of CO₂ is minimized and the final maximized, the deviation for the partial pressure and the loading are 0.21% and 1.42% respectively. This example corresponds to the largest partial pressure of CO₂ presented in Table III, Appendix A.

APPENDIX K

PREDICTIONS FROM THREE MODELS

TABLE XXXII
CALCULATED PARTIAL PRESSURE OF CO₂ IN
35% DEA AQUEOUS SOLUTION AT 80°F

From Straight Line		This Work				Kent and Eisenberg	
Loading	P _A	Loading		Arrhenius		(29)	
β	(psia)	Calc.	% Dev.	Calc.	% Dev.	Calc.	% Dev.
0.05	0.00059	0.0005	-15.3	0.00037	-37.3	0.0003	-49.2
0.15	0.00493	0.0057	+15.6	0.0052	+ 5.48	0.0046	- 6.69
0.25	0.02305	0.0237	+ 2.82	0.0248	+ 7.59	0.0226	- 1.95
0.35	0.09053	0.0850	- 6.11	0.0971	+ 7.26	0.0928	+ 2.51
0.45	0.3265	0.320	- 2.00	0.3791	+16.1	0.400	+22.5
0.55	1.12	1.220	+ 8.93	1.481	+32.2	1.78	+59.0
0.65	3.712	4.13	+11.3	5.168	+39.2	6.78	+82.7
0.75	12.02	12.3	+ 2.33	15.5	+28.6	20.8	+73.0
0.90	67.80	55.4	-18.3	63.9	- 5.75	80.3	+18.4
		O.A.A.P.D.	9.20			19.9	35.1

NOTE: β is in mole CO₂/mole DEA and P_A is partial pressure of CO₂, psia.
 Calc. = Calculated
 Dev. = Deviation
 O.A.A.P.D. is overall average absolute percentage deviation

TABLE XXXIII
CALCULATED PARTIAL PRESSURE OF CO₂ IN
35% DEA AQUEOUS SOLUTION AT 150°F

From Straight Line		This Work				Kent and Eisenberg	
Loading	P _A	Loading		Arrhenius		(29)	
β	(psia)	Calc.	% Dev.	Calc.	% Dev.	Calc.	% Dev.
0.05	0.0194	0.0155	-20.1	0.0069	-64.4	0.0088	-54.6
0.15	0.1395	0.1648	+18.1	0.0956	-31.5	0.1202	-13.6
0.25	0.5583	0.6002	+ 7.50	0.4476	-19.8	0.5501	- 1.47
0.35	1.877	1.797	- 4.26	1.666	-11.2	1.963	+ 4.58
0.45	5.793	5.51	- 4.89	5.91	+ 2.02	6.51	+12.4
0.55	17.0	17.90	+ 5.29	19.9	+17.1	20.3	+19.4
0.65	48.2	56.0	+16.1	57.4	+19.0	55.5	+15.0
0.75	133.6	147.8	+10.6	134.3	+ 0.52	127.4	- 4.64
0.90	596.7	461.0	-22.7	337.7	-43.4	322.3	-46.0
		O.A.A.P.D.	12.2			23.2	19.1

NOTE: β is in mole CO₂/mole DEA and P_A is partial pressure of CO₂, psia.
 Calc. = Calculated
 Dev. = Deviation
 O.A.A.P.D. is overall average absolute percentage deviation

TABLE XXXIV
CALCULATED PARTIAL PRESSURE OF CO₂ IN
35% DEA AQUEOUS SOLUTION AT 240°F

From Straight Line		This Work				Kent and Eisenberg	
Loading	P _A	Loading		Arrhenius		(29)	
β	(psia)	Calc.	% Dev.	Calc.	% Dev.	Calc.	% Dev.
0.05	0.4348	0.3435	-21.6	0.1885	-57.0	0.3281	-25.1
0.15	2.801	3.189	+13.9	2.547	- 9.07	4.179	+49.2
0.25	9.95	10.11	+ 1.61	11.39	+14.5	17.03	+71.2
0.35	29.7	26.9	- 9.43	38.2	+28.6	49.86	+67.9
0.45	81.4	76.2	- 6.39	107.8	+32.4	121.0	+48.6
0.55	212.0	220.5	+ 4.0	250.0	+17.9	249.1	+17.5
0.65	534.1	519.3	- 2.77	470.0	-12.0	442.0	-17.2
0.75	1313.0	965.0	-26.5	752.0	-42.7	692.0	-47.3
		O.A.A.P.D.	10.8			26.8	43.0

NOTE: β is in mole CO₂/mole DEA and P_A is partial pressure of CO₂, psia.
 Calc. = Calculated
 Dev. = Deviation
 O.A.A.P.D. is overall average absolute percentage deviation

VITA

Erardo Mario Elizondo Villarreal

Candidate for the Degree of

Doctor of Philosophy

Thesis: EXPERIMENTAL EQUILIBRIUM AND MODELING FOR THE
ABSORPTION OF ACID GASES IN DIETHANOLAMINE
SOLUTIONS AT LOW AND HIGH PARTIAL PRESSURES

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Monterrey, Nuevo Leon, Mexico,
on April 30, 1953, the son of Dr. Erardo M.
Elizondo Garza (+) and Maria del Refugio
Villarreal; married to Q.I. Maria Martha Elena
Luna on January 27, 1979; has two sons, Erardo
Mario and Roberto Carlos.

Education: Graduated from Preparatoria Number 1 High
School, Monterrey, Nuevo Leon, Mexico, in 1970;
received the Bachelor of Science Degree in
Chemical Engineering from Universidad Autonoma de
Nuevo Leon, Mexico, in 1976; completed coursework
for Master of Science in Chemical Engineering
from Universidad Autonoma de Nuevo Leon, Mexico,
in 1979; completed requirements for the Doctor of
Philosophy Degree in Chemical Engineering at
Oklahoma State University, Stillwater, Oklahoma
in May, 1989.

Professional Experience: Teaching Assistant in
Chemical Engineering Department at the
Universidad Autonoma de Nuevo Leon, Monterrey,
Mexico, from September 1975 to August 1976;
Projects Coordinator in the Industrial Service
Laboratory and Assistant Professor in Chemical
Engineering at the Universidad Autonoma de Nuevo
Leon, Monterrey, Mexico, from September 1975 to
December 1977. Full time Professor in Chemical
Engineering at the Universidad Autonoma de Nuevo
Leon, Monterrey, Mexico, from January 1978 to
June 1979; Engineering Superintendant at Celulosa

y Derivados, S.A. de C.V. in Monterrey, Mexico, from June 1979 to March 1981; Graduate School Secretary at Facultad de Ciencias Quimicas, Universidad Autonoma de Nuevo Leon, Monterrey, Mexico, from March 1981 to August 1981; Independent Chemical Engineer in Monterrey, Mexico, from September 1981 to August 1984.

Professional Membership: Instituto Mexicano de Ingenieros Quimicos (1976-1981); Omega Chi Epsilon.