EXPERIMENTAL EQUILIBRIUM BETWEEN ACID GASES AND ETHANOLAMINE SOLUTIONS

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PREFACE

This research is concerned with the measurement of the equilibrium solubility of acid gases in various alkanolamine solutions. The acid gases considered were carbon dioxide and hydrogen sulfide. Amines investigated were monoethanolamine, diglycolamine, diethanolamine and methyldiethanolamine. Measurements of the solubility were made at acid gas partial pressures to 1000 psia and temperatures from 77 to 240°F.

I wish to express my sincere gratitude and deep appreciation to my major advisor throughout my graduate work, Dr. Robert N. Maddox. His concern, help and intelligent guidance are invaluable.

I am also indebted to Dr. Gilbert J. Mains for his interest and valuable discussions. Thanks are also due to the committee members, Dr. Jan Wagner, Dr. Anthony L. Hines, and the late Dr. John H. Erbar for their advisement in the course of this work.

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CHAPTER I

INTRODUCTION

Acid gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2), when dissolved in an aqueous medium, dissociate to form a weak acid. The removal of such gases from the parent gas is designated as "gas sweetening".

Hydrogen sulfide and carbon dioxide are frequently present in natural gas, refinery gas, and synthesis gas. Their presence is of great concern economically and environmentally. Acid gases are a source of severe corrosion in pipelines and process equipment. Environmentally, hydrogen sulfide is extremely toxic; its combustion products sulfur dioxide and trioxide, when combined with particulates and moisture, produce the most damaging effects attributed to atmospheric air pollution. Acid rain is also attributed to sulfur oxides (1).

There are several techniques available for the removal of acid gases from the parent gas. However, alkanolamines are the most widely used of the many available solvents. The first alkanolamine used as an absorbent for acid gases is credited to Bottoms (2, 3), who in the early 30's used Triethanolamine (TEA) in sweetening sour natural gas. Monoethanolamine (MEA) and diethanolamine (DEA) have displaced TEA largely because of its low capacity, low reactivity and its relatively poor stability (4). Blohm and Reisenfeld (5) introduced in 1955 a somewhat different type of alkanolamine, β, β'-hydroxyaminoethylether, commercially known as Diglycolamine (DGA). This amine couples the reactivity and stability of MEA, but has a vapor pressure several fold lower than that of MEA. This has the advantage of reducing the vaporization losses and avoiding degradation reactions which frequently occur with primary amines, such as MEA.

Methyldiethanolamine (MDEA) was introduced as a potential acid gas absorbent in the early 1950's (6, 7). MDEA has been described as a selective absorbent for H_2S in the presence of CO_2. Although its use has been limited, an increasing role for MDEA is expected in connection with enriching the H_2S content of the acid gas feed to Claus sulfur recovery plants and the feed to processes used for the synthesis of sulfur derivatives (8).

This study was undertaken to generate experimental data measurements on the solubility (physically dissolved and chemically reacted) of CO_2 and H_2S in alkanolamine aqueous solutions. The following systems were studied:

1 - MEA - CO_2
2 - MEA - H_2S
3 - DEA - CO_2
4 - DGA - CO_2
5 - DGA - H_2S
6 - MDEA - CO_2
7 - MDEA - H_2S

The experimental measurements were made at acid gas partial pressures to 1000 psia and temperatures from 77° to 240°F.

The apparatus used is a modification of those used by Akashah (9) and Adeyiga (10) based on a concept originally introduced by Woertz (11). The method used to calculate the acid gas loadings is different from those used by all other researchers in the field. The development described here is much simpler and safer to operate. No gas chromatograph analysis nor liquid chemical analysis is required, reducing time and cost needed to generate a set of data. Accurate and consistent data are obtained.

CHAPTER II

LITERATURE SURVEY

The information on the solubility of acid gases in MEA, DEA, DGA and MDEA aqueous solutions is presented in this chapter. Experimental techniques used to measure the solubilities are also briefly stated.

MEA Data

Several workers have investigated the solubility of CO_2 and H_2S in MEA aqueous solutions. The first published data were reported by Mason and Dodge (12) who studied the solubility of CO_2 in MEA aqueous solutions ranging from 0.5 to 12.5 N in the temperature range 32° to 167°F, with CO_2 partial pressures ranging from about 0.2 to 14.5 psia. Muhlbauer and Monaghan (13), Murzin and Leites (14), Nasir and Mather (15) and Isaacs et al. (16) all investigated the solubility of CO_2 in MEA solutions at low CO_2 partial pressures. Reed and Wood (17), Lyudkovskaya and Leibush (18), and Lee et al. (19, 20) investigated the solubility of CO_2 in MEA at high partial pressures.

Rieger et al. (21), Leibush and Schneerson (22) Muhlbauer and Monaghan (13), Jones et al. (23), Nasir and Mather (15) and Isaacs et al. (16) studied the solubility of H_2S in MEA solutions at low H_2S partial pressure. Lawson and Garst (24) Lee et al. (19, 25) investigated the solubility at high partial pressure.

Data on the solubility of mixtures of CO_2 and H_2S are less available both as to the range of acid gas partial pressure and the concentration of the amine solution. Leibush and Schneerson (22), Muhlbauer and Monaghan (13), Jones et al. (23) and Lawson and Garst (24) studied the simultaneous solubilities of CO_2 and H_2S in 2.5 N MEA. Only limited data are reported on the solubility of acid gases in 5.0 N MEA solution (15, 24).

Table I summarizes the conditions of the measurements found in the literature.

DEA Data

The first published data on the solubility of CO_2 in DEA aqueous solutions was reported by Bottoms (3). He presented a small-scale plot showing the solubility of CO_2 in 50% DEA aqueous solution at temperatures ranging from 77 to 131°F with CO_2 partial pressure up to 14.7 psia. The most usable data are those of Mason and Dodge (12), Reed and Wood (17), Murzin and Leites (14) and Isaacs and co-workers (35) for partial pressures of CO_2 less than atmospheric. And those of Lee and co-workers (28, 29) and Lawson and Garst (24) for high CO_2 partial pressure.

H_2S solubilities in DEA solutions are best represented by Leibush and Schneerson (22), Lee et al. (28, 30, 31) and Lawson and Garst (24).

Data on the solubility of mixtures of CO_2 and H_2S in DEA solutions are limited. However, of the available data, those of Lee and co-workers (19, 28, 32, 33, 34), and Isaacs and co-workers (35) cover the high and low acid gas partial pressure ranges. Table II summarizes the conditions of the measurements found in the literature.

TABLE I

LITERATURE SURVEY OF PUBLISHED DATA
MEA AQUEOUS SOLUTION-ACID GAS(ES)

Acid Gas(es)	Normality	Temperature °F	Partial Pressure psia	Reference
CO_2	0.5, 2.0, 5.0, 9.5, 12.5	32, 77, 122, 167	0.19 - 14.5	12
"	2.5	212, 248, 284	20.0 - 250.	17
"	0.5, 2.0, 5.0	77, 122, 167	37 - 588	18
"	2.5, 5.0, 7.5, 10.0	86, 122, 157	15 - 500	26
"	2.5	77, 212	1.9×10^{-2} - 21.0	13
"	2.5	104, 140, 176, 212, 248, 284	0.01 - 135	23
"	0.5, 1.0, 2.0, 2.5, 3.4	86, 104, 122, 140, 158, 176	< 13.5	14
"	2.5	104, 212	0.3 - 850	19
"	2.5	104, 284	0.2 - 390	24
"	5.0	200	3.3 - 65.7	24
"	1.0, 2.5, 3.75, 5.0	77, 104, 140, 176, 212, 248	0.03 - 960	20
"	2.5	176, 212	1.5×10^{-4} - 0.15	15
"	2.5	176, 212	1.3×10^{-3} - 0.25	16
H_2S	0.6, 1.5, 2.0, 3.0, 5.0	77, 113, 140	0.5 - 13.5	21
"	0.93 - 2.5	59, 77, 122	< 6.7	22
"	0.86, 2.9, 4.1, 7.0	80, 100, 120, 140	1.22×10^{-5} - 5.6	27
"	2.5	77, 212	1.9×10^{-2} - 18.4	13
"	2.5	104, 140, 176, 212, 248, 284	1.9×10^{-2} - 16.4	23
"	2.5, 5.0	104, 212	0.3 - 600	19
"	2.5, 5.0	77, 104, 140, 176, 212, 248	0.02 - 320	25
"	2.5	104, 140, 176, 212, 248, 284	1.7×10^{-4} - 560	24
"	5.0	80, 100, 200	1.9×10^{-4} - 24.1	24
"	2.5	77, 212	1.9×10^{-2} - 18.4	13

TABLE I (Continued)

Acid Gas(es)	Normality	Temperature °F	Partial Pressure psia	Reference
H_2S	2.5	176, 212	$5.8 \times 10^{-4} - 0.3$	15
"	2.5	212	$1.3 \times 10^{-3} - 0.23$	16
$CO_2 - H_2S$	2.5	77	$CO_2 < 1.5$ $H_2S < 1.4$	22
"	2.5	77, 212	$CO_2 < 2.50$ $H_2S < 18.6$	13
"	2.5	104, 140, 212, 248	$CO_2 < 67.8$ $H_2S < 30.0$	23
"	2.5	77, 104, 140, 212, 248	$CO_2 < 28.8$ $H_2S < 23.1$	24
"	5.0	100, 150, 200	$CO_2 < 33.3$ $H_2S < 41.9$	24
"	5.0	212	$CO_2 < 0.43$ $H_2S < 1.35$	15

TABLE II

LITERATURE SURVEY OF PUBLISHED DATA DEA AQUEOUS SOLUTION-ACID GAS(ES)

Acid Gas(es)	Normality	Temperature °F	Partial Pressure psia	Reference
CO_2	(50)	77,95,113,131	< 14.7	3
"	0.5, 2.0, 5.0, 8.0	32, 77, 122, 167	0.19 - 14.6	12
"	2.5	212, 284	35.0 - 230.0	17
"	0.5, 1.0, 2.0, 5.0, 8.0	86, 104, 122, 140, 158, 176	13.5	14
"	(50)	104, 122, 167, 212, 248	0.5 - 826.0	28
"	0.5, 2.0, 3.5, 5.0	77, 122, 167, 212, 248	0.1 - 827.0	29
"	(25)	100, 150, 175, 200, 225, 250	0.29 - 634.0	24
"	2.0	104, 212	$1.8 \times 10^{-2} - 0.48$	35
H_2S	(50)	77, 95, 113, 131	< 14.7	3
"	0.97, 2.0	59, 77, 122	$9.3 \times 10^{-5} - 4.23$	22
"	(10, 25, 50)	80, 140	< 13.8	27
"	(25)	77, 122	0.2 - 87.5	28
"	0.5, 2.0, 3.5, 5.0	77, 122, 167, 212, 248	0.1 - 306	30, 31
"	(25)	100, 125, 150, 175, 200, 225, 250, 275, 300	$1.3 \times 10^{-4} - 537.4$	24
"	2.0	104, 212	$1.0 \times 10^{-3} - 0.46$	35
CO_2-H_2S	2.0	77	$CO_2 < 1.55$ $H_2S < 4.65$	22
"	(40)	167	$CO_2 < 100$ $H_2S < 180$	28
"	2.0, 3.5	122, 212	$CO_2 < 837$ $H_2S < 240$	19, 32-34
"	(25)	100, 125, 150, 175, 200, 225, 250	$0.33 < CO_2 < 332.5$ $0.12 < H_2S < 319.0$	24
"	2.0	104, 212	$8.3 \times 10^{-4} < CO_2 < 0.77$ $2.2 \times 10^{-3} < H_2S < 0.83$	25

DGA Data

Very little acid gas solubility data in DGA solutions are reported in the literature. Most of the articles on DGA are qualitative in nature (36, 37, 38, 39). Physical properties of DGA and its aqueous solutions are given by Maddox (40) and Kohl and Riesenfeld (4).

The first extensive study on the acid gas solubility of DGA aqueous solutions was conducted by Martin et al. (41). They reported the solubility of CO_2 and H_2S in a 60 weight % DGA aqueous solution at 122 and 212°F. Partial pressures of CO_2 ranged from 0.23 to 867.3 psia while H_2S partial pressures ranged from 0.37 to 274.1 psia. Dingman et al. (42) investigated acid gas levels down to low loadings and low acid gas partial pressures in 65 weight % DGA solution. Simultaneous solubilities of CO_2 and H_2S are reported at 100 and 180°F. CO_2 partial pressure ranged from 2.9×10^{-5} to 27.0 psia, and H_2S partial pressures ranged from 4.3×10^{-5} to 27.1 psia.

MDEA Data

The determination to find an agent for the selective removal of one acid gas has led to methyldiethanolamine (MDEA). It was first mentioned as a sweetening agent in the early 1950's by Frazier and Kohl (6) and Miller and Kohl (7). They published pilot plant and commerical plant studies on the qualitative solubility of MDEA aqueous solutions. Recently other qualitative studies on comparative selectivity were conducted by Vidaurri and Kahre (39) and Goar (43). However, data on the equilibrium solubility of CO_2 and H_2S in MDEA aqueous solutions was not published until 1982, when Jou and co-workers (8) investigated the solubility of CO_2 and H_2S in 1.0, 2.0 and 4.28 N MDEA solutions at temperatures of 77, 104, 158, 212 and 248°F. The CO_2 partial pressure ranged from 1.5×10^{-4} to 960 psia; H_2S partial pressure ranged from 3.0×10^{-4} up to 854 psia.

Experimental Techniques For Solubility Studies

The experimental devices used to measure the solubility of acid gases in alkanolamine solutions are basically two kinds. The open system, and the closed system. The open "flow" system (12, 13, 16, 27) consists of a series of small absorbers placed in a constant temperature bath. The amine solution of a desired concentration is placed in the absorbers. One, or a mixture of acid gases, and an inert gas carrier - such as nitrogen - are bubbled in the amine solution. Equilibrium is reached when no change in the exit gas composition is observed. Gas and liquid samples are then taken for analysis.

This method is used for low acid gas partial pressures and low temperature. This system requires constant attention to maintain constant gas flow and pressure. Variation in the amine concentration can be a problem especially at high equilibrium temperatures.

The closed system (23, 29, 31) consists of an equilibrium cell, 0.5 - 2.0 liters in size, placed in a constant temperature bath. The cell is purged with an inert gas and then charged with the desired amine solution, usually 10 to 20% of its volume, CO_2 and/or H_2S are then added in an amount determined by observation of the pressure. If necessary, an inert gas is added so that the total pressure is always greater than atmospheric. Observation of the pressure determines the equilibrium. Liquid and vapor samples are then taken.

In both techniques, the composition of the vapor phase samples is usually determined by gas chromotagraphy. The acid gas content of the liquid samples is determined by evolving the acid gas by the addition of an excess of a strong acid and by heating. The amount of gas evolved is measured volumetrically. If H_2S is present, it is oxidized using excess of an oxidizing agent such as iodine solution then titrating the excess iodine with standard salt solution such as sodium thiosulfate solution.

Other information needed in order to calculate acid gas loadings, are the solution vapor pressure at the equilibrium temperature, P-V-T data to calculate the amount of the acid gas evolved and the amine concentration which is calculated using acid titration. The amount of amine is determined from the weight of the liquid sample.

Both types of analysis require careful and long procedures. Gas chromatographic analysis requires frequent calibration with standard gas mixtures. Measurements of small acid gas concentrations are subject to substantial deviations (23). Considerable difficulty is encountered in determining the vapor-liquid equilibrium in this region (42).

The Chemistry of Acid Gas Reactions

All alkanolamines have at least one hydroxyl group and one amino group which provide the necessary alkalinity for their reactions with acid gases in water solution. The effectiveness of any amine for absorption of both acid gases is due primarily to its alkalinity (4).

H_2S and CO_2 are acid gases which react to form weak acids in aqueous solution. When the acid is in contact with the weak base amine solution, they combine chemically to form an acid-base complex called a salt, thus removing the acid gas from the main stream.

Alkanolamines can be categorized chemically according to their molecular structure as being primary, secondary, or tertiary, depending upon the degree of substitution of the central nitrogen by organic groups (see Figure 1). Primary amines such as MEA and DGA show single substitution of the central nitrogen. Secondary amines such as DEA show double substitution of the central nitrogen. MDEA, a tertiary amine, shows a triple substitution. Table III (40) summarizes important physical properties of the amines illustrated in Figure 1.

There is considerable disagreement as to the mechanism of the absorption of acid gases in amine solutions. This is due to the complexity of the reactions which can not be said to be understood (4, 40).

Two types of mechanisms are thought to be responsible for the reactions. The direct reaction between the acid gases and the amine in the aqueous amine solution. The other mechanism assumes that the acid gas constituents must be absorbed in the amine solution before they can react. The two types are considerably different and would call for different interpretations of data (40).

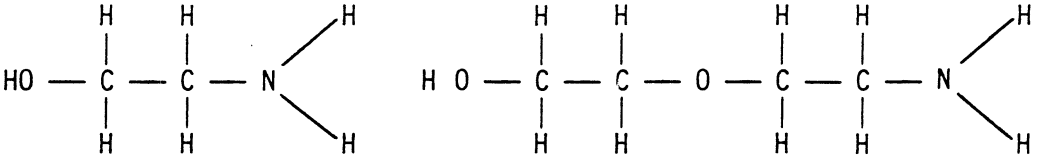
The principal reactions occuring between amines and acid gases may be represented by the following overall reactions (47)

H_2S:

$$2\ RNH_2 + H_2S \rightarrow (RNH_3)_2S \qquad (1)$$

$$(RNH_3)_2S \rightarrow 2\ RNH_3HS \qquad (2)$$

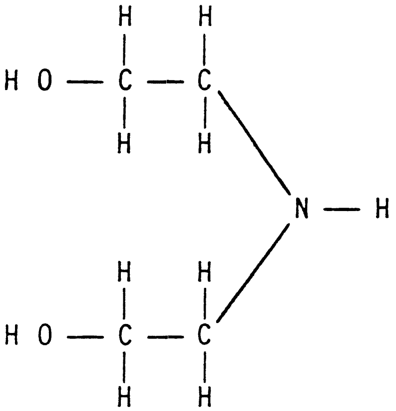
Primary Amines:



Monoethanolamine

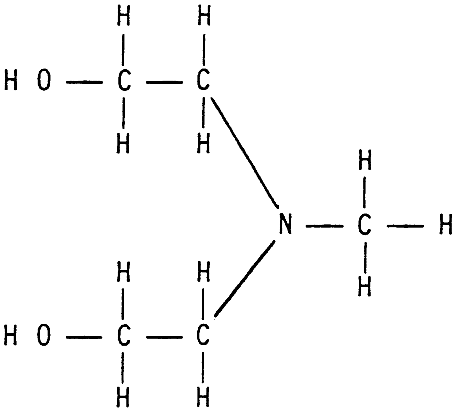
Diglycolamine®

Secondary Amine:



Diethanolamine

Tertiary Amine:



Methyldiethanolamine

Figure 1. Chemical Structure of Formulas for Alkanolamines of Interest in This Study

TABLE III

PHYSICAL PROPERTIES FOR ETHANOLAMINES

	Primary Amines		Secondary Amine	Tertiary Amine
	Monoethanolamine	Diglycolamine	Diethanolamine	Methyldiethanolamine
Formula	$HOC_2H_4NH_2$	$H(OC_2H_4)_2NH_2$	$(HOC_2H_4)_2NH$	$(HOC_2H_4)_2NCH_3$
Molecular Weight	61.08	105.14	105.14	119.17
Boiling point at 760 mm Hg, °F	338.9	430	516.2	477
Freezing point, °F	50.9	9.5	82.4	-5.8
Critical constants				
Pressure, psia	868	547.11	474.7	5623[5]
Temperature, °F	662	756.6	827.8	611.6[5]
Density at 20°C, gm/cc	1.018	1.058 at 60°C	1.095	1.0426
Weight, lb/gal.	8.48 at 60°F	8.82 at 60°F	9.09 at 60°F	8.69
Specific gravity, 20°C/20°C	1.0179	1.0572	1.0919 (30°C/20°C)	1.0418
Specific heat at 60°F, BTU/lb/°F	0.608 at 68°F	0.571	0.600	-
Thermal conductivity at 68°F, BTU/hr, FT', °F/ft	0.148	0.121	0.127	-

TABLE III (Continued)

	Primary Amines		Secondary Amine	Tertiary Amine
	Monoethanolamine	Diglycolamine	Diethanolamine	Methyldiethanolamine
Heat of vaporization, BTU/lb	335 at 760 mm Hg	219.14 at 760 mm Hg	288 at 73 mm Hg	223
Heat of reaction, BTU/lb of Acid Gas				
H_2S	-	-674	-	-
CO_2	-	-850	-	-
Viscosity, cp	24.1 at 68°F	40 at 60°F	350 at 68°F (at 90% wt. solution)	101 at 20°C
Constants for Antoine Equation				
A	8.02401	8.6211	8.12303	16.23
B	1921.6	2721.1	2315.46	7456.8
C	203.3	249.54	173.3	311.71

1. Data for MEA, DEA, and DGA (except for Antoine constants) from GPA Engineering Data Book (45).
2. Data from MDEA (excpet for Antoine constants) from Kohl and Riesenfeld (4).
3. Antoine constants for MEA and DEA from Dow (46).
4. Antoine constants for DGA, and MDEA fitted by Maddox (40).

CO_2:

$$2\ RNH_2 + CO_2 + H_2O \rightarrow (RNH_3)_2\ CO_3 \quad (3)$$

$$(RNH_3)_2\ CO_3 + CO_2 + H_2O \rightarrow 2\ RNH_3HCO_3 \quad (4)$$

$$2RNH_2 + CO_2 \rightarrow RNHCOONH_3R \quad (5)$$

where R is the organic group.

A better understanding of the reaction phenomena can be attained by considering the reactions in aqueous solutions between the existing ionic species.

Amine - H_2S Reactions

H_2S, being a Bronstead acid (proton donor), reacts rapidly by the following direct proton-transfer reaction (4, 40, 48)

$$H_2S + RNH \rightarrow RNH_2^{+} + HS^{-} \quad (6)$$

The reaction is exactly the same for primary, secondary and tertiary amines. Other reaction equilibria which describe the system in the aqueous solution are:

$$H_2O \rightarrow H^{+} + OH^{-} \quad (7)$$

$$H_2S \rightarrow H^{+} + HS^{-} \quad (8)$$

$$HS^{-} \rightarrow H^{+} + S^{=} \quad (9)$$

$$RNH_2^+ \leftrightarrow H^+ + RNH \qquad (10)$$

The HS^- ion does not dissociate into the $S^=$ ion except at a high pH with an equilibrium constant of about 10^{-14} (48).

Amine - CO_2 Reactions

The chemistry of CO_2-amine reactions is much more complex than that of H_2S. CO_2 being an anhydride (also called electron acceptor Lewis acid) needs to hydrate to become a Bronstead acid. Primary amines such as MEA and DGA, and secondary amines such as DEA all show limited tendency to absorb CO_2 beyond 0.5 mole CO_2/mole of amine. This reluctance can be attributed to stable carbamates formed with amines in which the amino nitrogen is attached to a primary alkyl group (49, 50, 51). The reactions can be written as follows

$$CO_2 + RNH_2 \leftrightarrow RNHCOO^- + H^+ \qquad (11)$$

$$RNH_2 + H^+ \leftrightarrow RNH_3^+ \qquad (12)$$

From these reactions, an overall reaction can be expressed as

$$CO_2 + 2\ RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (13)$$

where $RNHCOO^-$ is the carbamate and RNH_3^+ is the protonated amine.

If the carbamate formation was the only reaction, the maximum loading would be limited by stoichiometry to 0.5 mole CO_2/mole amine. In general amines can have loadings higher than 0.5 especially at high acid gas partial pressure. This can be attributed to the carbamate hydrolysis or (carbamate reversion to bicarbonate) via the following reactions (52, 53)

$$H_2O \leftrightarrow H^+ + OH^- \tag{14}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{15}$$

$$RNHCOO^- + H^+ \leftrightarrow RNH_2 + CO_2 \tag{16}$$

The overall reaction can be written as

$$RNHCOOO^- + H_2O \leftrightarrow HCO_3^- + RNH_2 \tag{17}$$

Carbamate hydrolysis provides free amine which can react with additional CO_2. This will allow the loading to exceed 0.5.

Another reaction path is confirmed by solution chemistry studies (48) in which bicarbonate ion is formed instead of the carbonate ion as a CO_2 sink

$$CO_2 + RNH_2 + H_2O \leftrightarrow HCO_3^- + RNH_3^+ \tag{18}$$

This reaction occurs at all loadings.

Maddox and Mains (53) used a reaction model and predicted the change in ionic species in 2.0 N MEA solution at 100°F as a function of loading. Figures 2 and 3 clearly indicate the agreement with the mechanisms discussed above.

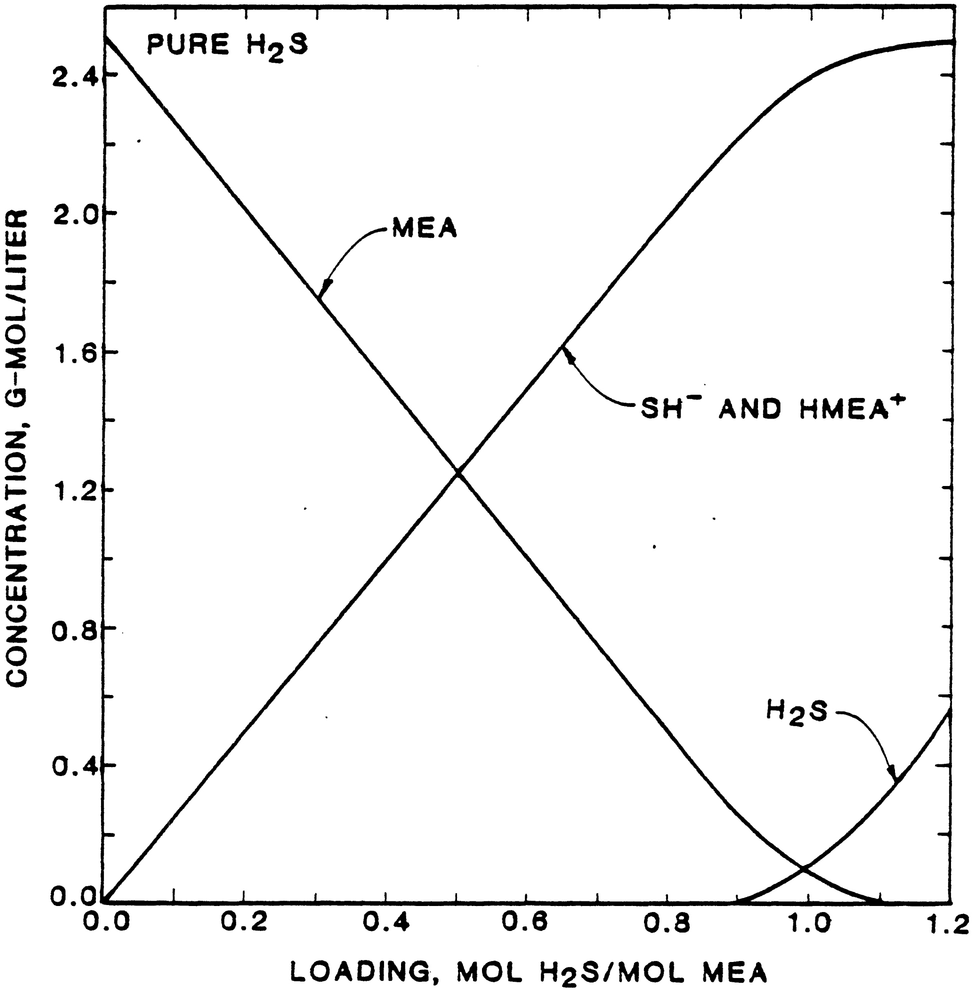


Figure 2. Concentration of Major Species When 2.0 N MEA Reacts With Pure H_2S

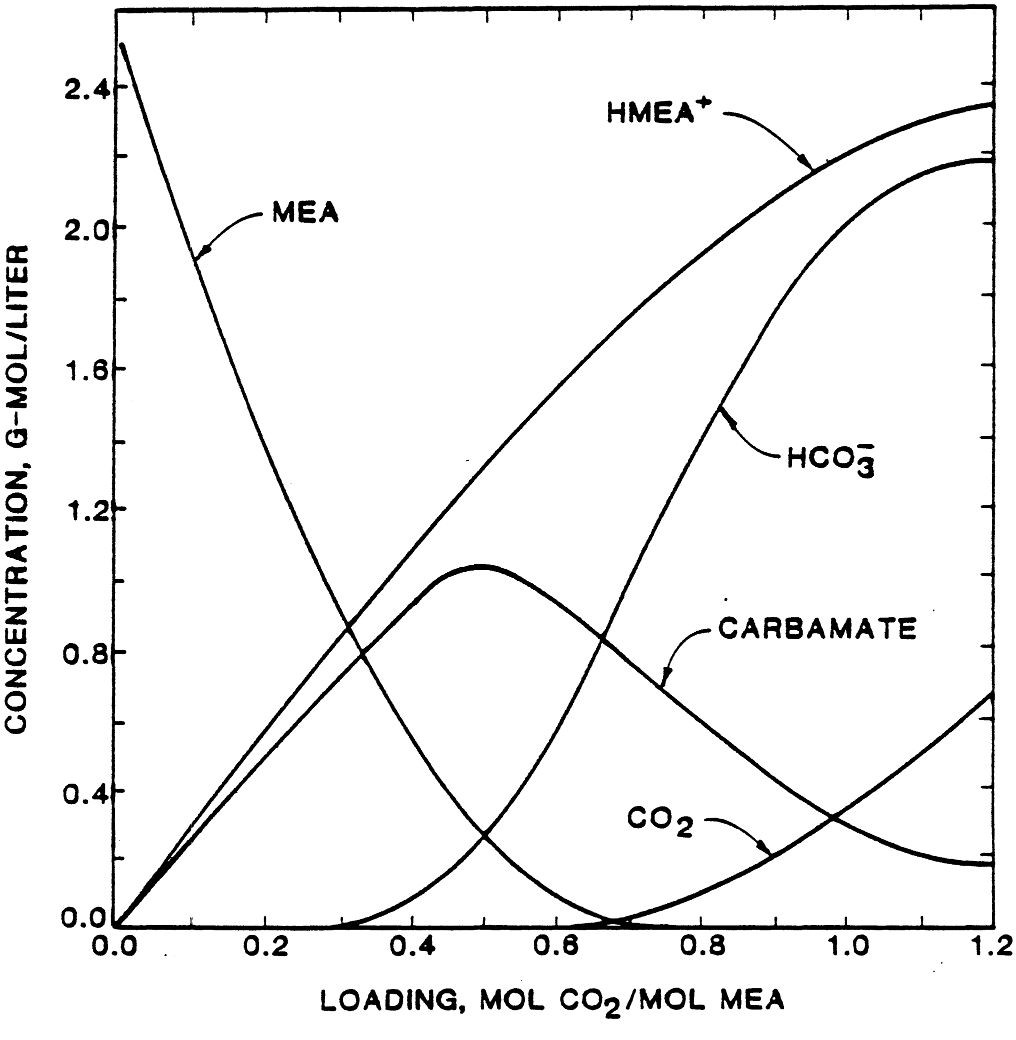


Figure 3. Concentration of Major Species When 2.0 N MEA Reacts With Pure CO_2

Tertiary amines show a different limiting behavior. They are unable to form the stable carbamate. Aqueous tertiary amines react with CO_2 to form the bicarbonate ion

$$CO_2 + RR'R''N \overset{H_2O}{\rightleftharpoons} HCO_3^- + RR'R''N\,H^+ \tag{19}$$

The stoichiometric absorption of CO_2 can reach 1.0 mole of CO_2/mole of amine. This is well supported by available experimental data. Figure 4 shows that the shape of the curve for CO_2 and MDEA is exactly the same as that for H_2S and MEA and H_2S and DEA. This agrees with the findings that no stable carbamates are formed when aqueous tertiary amines react with CO_2.

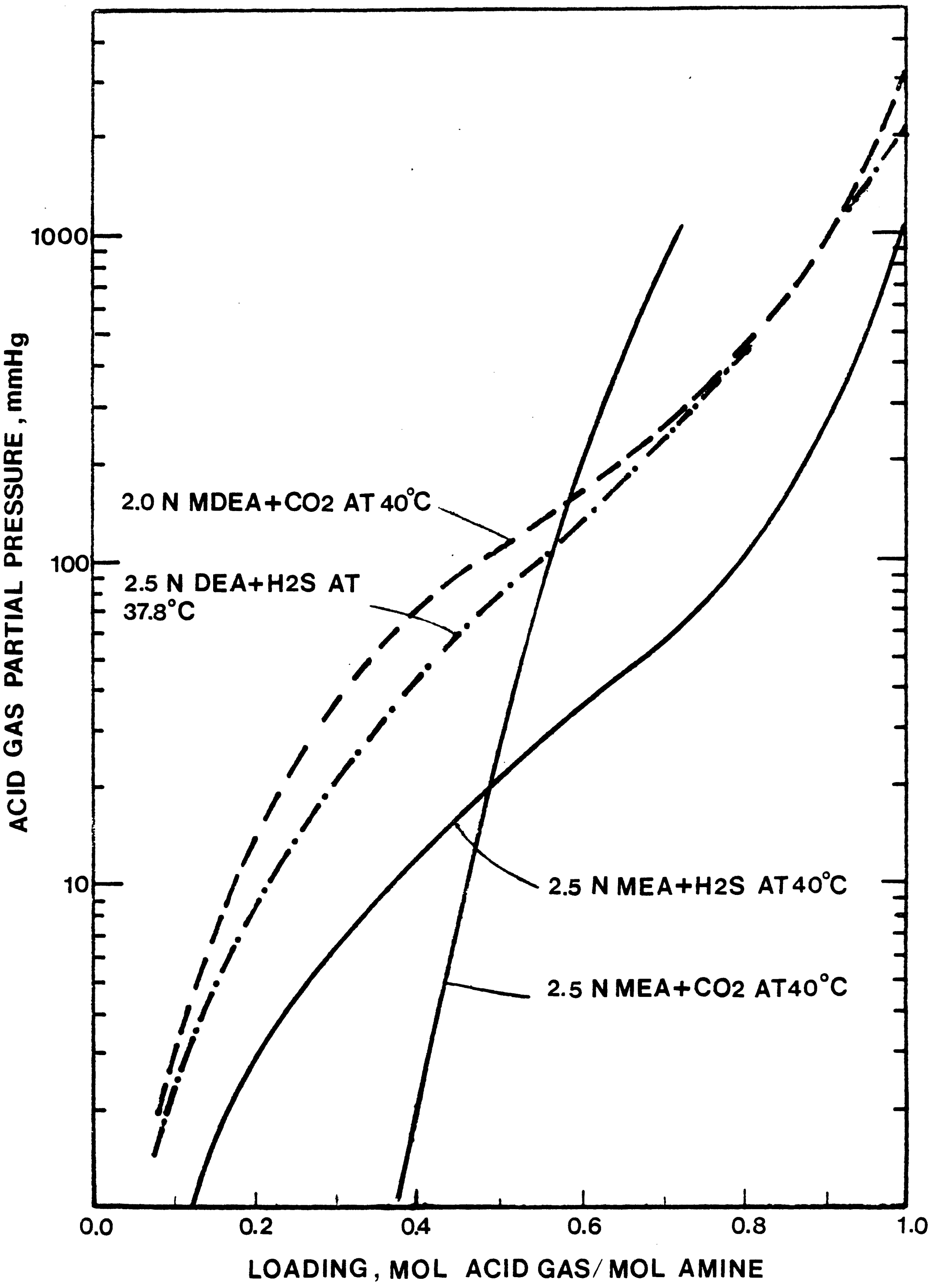


Figure 4. Equilibrium Loading of MEA, DEA and MDEA ot Different Acid Gas Partial Pressures

CHAPTER III

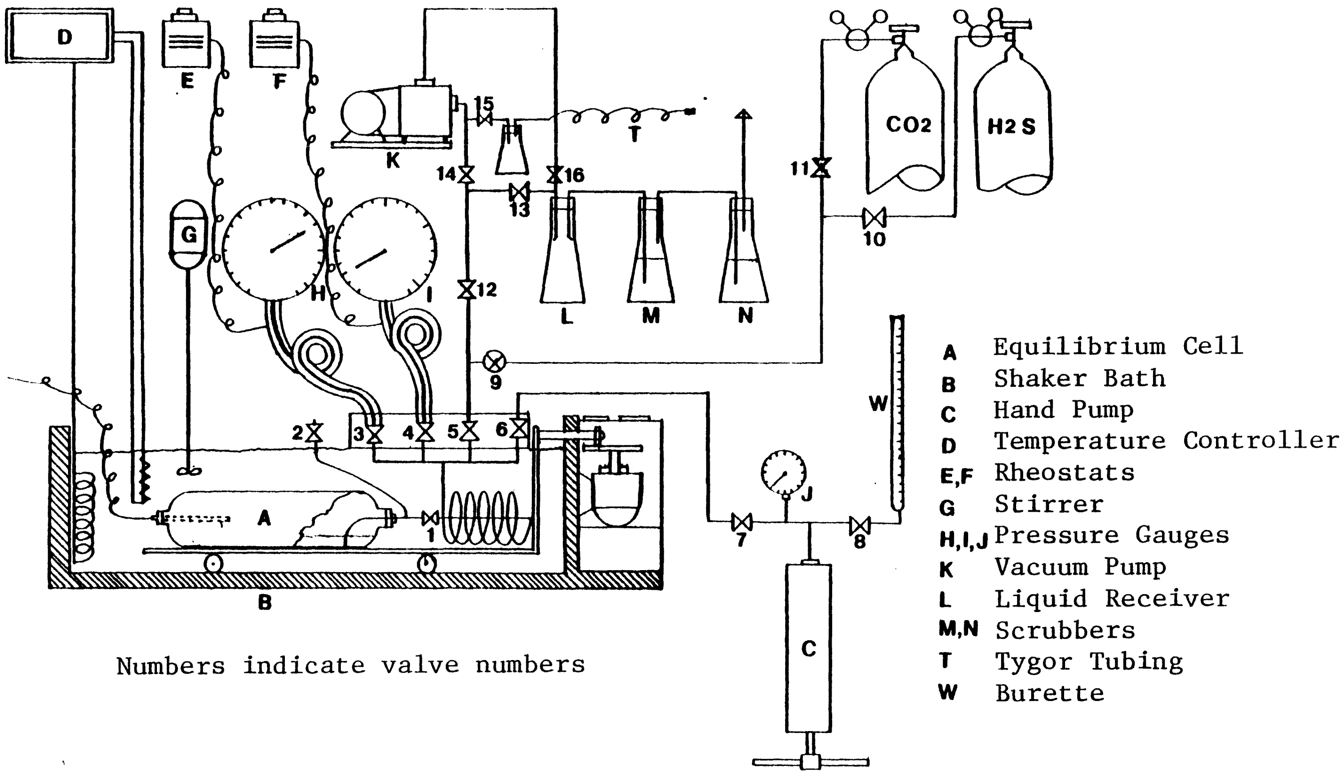
EXPERIMENTAL APPARATUS

The apparatus used here is an improvement of a similar one used by Akashah (9) and Adeyiga (10). Both reported CO_2 and H_2S solubilities in physical solvents.

It consists of an equilibrium cell placed in a constant temperature shaker bath. Pressure gauges, gas and liquid feed lines are attached to one of the two ports of the cell. A thermocouple is attached to the second port and extends inside the cell. A schematic diagram of the apparatus is shown in Figure 5. The major parts are:

Constant Temperature Shaker Bath

The bath is rectangular shaped with a capacity of 9 gallons (Model 50 Cat. #66802), made by Precision Scientific, GCA Corporation. It is equipped with a built-in reciprocal motion which shakes the shaker tray. A built-in variable speed tachometer allows variation from 20 to 200 oscillations per minute. Stroke length of the shaker tray can be adjusted from 0.5 to 1.5 inch per cycle. It is also equipped with a built-in temperature controller with a sensitivity of ± 0.07 to ± 0.20°F at 100 and 150°F, respectively. The temperature uniformity is ± 0.2 to ± 0.8°F at 100 and 150°F, respectively. The controller range is from room temperature to 212°F.



A	Equilibrium Cell
B	Shaker Bath
C	Hand Pump
D	Temperature Controller
E,F	Rheostats
G	Stirrer
H,I,J	Pressure Gauges
K	Vacuum Pump
L	Liquid Receiver
M,N	Scrubbers
T	Tygor Tubing
W	Burette

Numbers indicate valve numbers

Figure 5. Schematic Diagram of the Apparatus Used

To improve the temperature control and expand the temperature range, the bath is supplied with a Fisher temperature controller (Model 44, Catalog No. 15-177) with a temperature range of -40 to 300°F. The unit responded to a temperature change of ± 0.005°F. An electric stirrer was also installed to insure temperature uniformity throughout the bath. Polyalkylene glycol, supplied by Union Carbide, was used as bath fluid.

Equilibrium Cell

The equilibrium cell is a stainless steel cylinder (304-HDF4) made by Whitey. It has a volume of 1010 cc determined by displacement of distilled water at a known temperature (see Appendix B). There are two 1/4" ports. One is used for gas and solution charging. The feed line extends inside the cell and bends until it touches the internal wall of the cell. This is found useful when discharging the used solution at the end of a run. The second port was used to install 1/8" stainless steel closed end tubing supplied by Omega. It extends 6" inside the cell. A copper-constantan thermocouple is inserted inside the tubing to protect the thermocouple wire from corrosion. Another copper-constantan thermocouple is placed in the glycol bath near the cell. The calibration data for the thermocouples are presented in Appendix C.

Pressure Gauges

Three pressure gauges were used depending on the system pressure. High pressure measurements were taken using a 0 - 3000 psi Heise gauge (Solid Front -C- 51054). The diameter of the dial is 12" with 5 psi subdivisions. The accuracy is reported to be 0.1% of full scale reading throughout the entire range. The internal volume of the bourden tube is 12 cc.

For medium pressure measurements, a 0 - 300 psi Heise gauge (Solid Front-B-47141R) was used. The diameter of the dial is 16" with 0.2 psi subdivisions. The accuracy is also 0.1% of full scale reading throughout the entire range. The internal volume of the bourden tube is 27 cc. Both gauges are designed to tolerate full vacuum.

Low pressure measurements were made with a 30" vac-0-60 psi gauge made by Roylyn, 3D instruments (Model Serial No. 786600). The dial is 9" in diameter with 0.2 psi subdivision in the 0-60 psi range, and 1" Hg subdivision in the range of 0-30" Hg vacuum. The accuracy is reported to be 1/4 of 1% of full scale reading. The internal volume of the bourden tube is 5 cc.

The calibration of the pressure gauges was carried out using a Ruska Model 2400 HL dead weight tester. The subatmospheric dial of the low pressure gauge was calibrated against a mercury manometer. The calibration data are presented in Appendix D. All gauges were tested periodically to check the accuracy.

Gas Feed System

The gas feed system consists of CO_2 and H_2S cylinders. Each cylinder is equipped with a pressure regulator and 1/8" valve leading to the equilibrium cell assembly. The desired pressure in the cell was attained by regulating a needle metering valve.

The system is connected to a 1/3 Hp Welch Dow-Seal vacuum pump (serial no. 57893). The guaranteed pressure by the manufacturer is 2×10^{-4} Torr. Oil is changed approximately every two months.

Liquid Feed System

The liquid feed system consists of a high pressure displacement pump made by High Pressure Equipment Company (Model 87-6-S), with a capacity of 60 cc. It is connected to a 3-way junction. A 50 ml burette, in which the amine solution under study is placed, is connected to one side of the junction, the other side is connected to the equilibrium cell.

The amount of solution transferred from the burette through the pump and into the equilibrium cell is determined by taking the difference between the initial and final readings of the graduated burette.

The cell is connected to the gas and liquid feed systems by a 60" long coil of 1/16" stainless steel tubing. This allows the equilibrium cell to be rocked while connected to the fixed pressure gauges, gas and liquid feed systems.

Auxiliary Equipment

The auxiliary equipment consists of:

1 - Potentiometer: made by Leeds and Northrup Company (Model No. 8686). It has a range of -10.0 to 100.1 millivolts with the smallest division being 0.005 millivolts. Its limits of error are ± 0.03% of reading +6 μV.

2 - Heating Tapes: made by Sargent Welch (Briskheat 3/4"). Three 24" long tapes were used to heat the connecting lines leading to the pressure gauges.

3 - Rheostats: made by Aloe Scientific, 110 V, used with the heating tapes to control the temperature of lines above the bath leading to the pressure gauges.

4 - Digital Thermometer: made by Omega, type T, (Model No. 2160A). It is used as a quick check when controlling the bath temperature and also to check the temperature of the lines leading to the pressure gauges.

5 - Sodium Hydroxide Scrubbers: two 1 liter plastic Erlenmeyer flasks in series. The gas to be vented is bubbled in 4 N NaOH solution, Another flask is placed prior to the scrubbers to receive the used amine solution at the end of a run. This is done using the acid gas pressure. The flashed gas will then pass through the scrubbers.

6 - Other auxiliary equipment is: electronic balance made by Mettler (Model No. P1210) used to make the amine aqueous solution. It is capable of weighing to 0.001 gram. Magnetic Stirrer made by Sargent (Model S-76490).

Fittings and valves are all 1/8" stainless steel made by Parker C.P.I.

Materials

MEA and DGA were obtained from Alfa Products and were 96% and 98% purity, respectively. Aldrich Chemical Company provided DEA and MDEA both of 97% purity.

Carbon dioxide and hydrogen sulfide gases were supplied by Matheson with 99.5% purity. The materials were used as received without further purification.

CHAPTER IV

EXPERIMENTAL PROCEDURES

In this chapter, the procedure used in measuring experimental data and calculating the acid cas solubility is described.

Operational Procedure

The equilibrium cell was washed clean. A few glass beads 1/4" in diameter were placed inside the cell for liquid mixing. The cell was then attached to the system. The bath was filled with glycol and brought to the equilibrium temperature by setting the temperature controller to the desired temperature. The temperatures of the tubing above the bath and leading to the pressure gauges were controlled approximately 5°F above the equilibrium temperature using heating tapes and rheostats. This was done to prevent condensate formation in the pressure gauge assembly. Steps are then taken as follows:

1 - Using the acid gas under study purge with valves 9, 10 or 11, 12 and 13 open and valves 5, 14 and 16 closed.

2 - Using the vacuum pump evacuate the equilibrium cell with valves 1, 3 or 4, 5, 12, 14 and 16 open. Valves 2, 6, 9, 13 and 15 were kept closed.

3 - With valves 2, 6 and 12 closed admit CO_2 or H_2S into the cell to a pressure of about 40 psi, then vent the system through

the scrubbers with valves 5, 12 and 13 open and valve 9 closed.

4 - Repeat steps 2 and 3. This will insure an air free system.

5 - Admit the acid gas into the cell. The desired pressure can be attained using the metering valve #9. Wait until temperature and pressure stabilize. Record the temperature and pressure.

6 - Prepare the liquid feed system. Place the amine solution in the clean burette. Open valve 8 to fill the tubing connecting the burette to valve 8 then close valve 8. Disconnect the line between valves 5 and 7. Evacuate the clean hand pump by connecting the tygon tubing to valve 7. Keeping valves 7, 15 and 16 open and 8, 13 and 14 closed, evacuate the liquid feed system including the pump and the solution pressure gauge. Close valve 7 and open valve 8 and allow the solution to fill the voids of the system. Connect the line between valves 6 and 7 without tightening the nut at valve 6. Open valves 7 and 8 and allow the solution to flow by gravity to displace the air and fill the line. Tighten the nut at valve 6. Fill the burette with the amine solution. The system is now ready for solution injection.

7 - The pressure gauges should be isolated by closing valves 3 and 4 to prevent any of the solution entering the pressure gauges. The shaker should now be on with a proper speed. Introduce the predetermined amount of solution into the equilibrium cell.

8 - Wait a few minutes then open the pressure gauge valve. The higher pressure of the pressure gauge assembly will force the

small amount of solution out of the coil into the cell. Record the pressure as it drops on a regular basis.

9 - When equilibrium is reached, no change in pressure will be observed. The temperature and pressure are recorded.

10 - Another injection can now be introduced to get another equilibrium measurement. In this case steps 7, 8 and 9 are repeated. This procedure can be repeated to obtain several data points until the solution occupies about 70% of the equilibrium cell volume.

11 - Discharge the used solution into the solution trap using the gas pressure by opening valves 5, 12 and 13. If the final pressure in the cell is subatmospheric introduce some gas into the cell to raise the pressure and drive the solution out of the cell.

If H_2S is in use, the cell is evaculated as in step 2. Air is introduced into the cell by opening valve 2 when the level of H_2S is considered safe, the cell is removed from the bath and cleaned. The lines are rinsed. Steps 1-11 can now be repeated.

Determination of Experimental Solubility

The solubility of an acid gas in an amine solution was determined by mass balance. Knowing the cell volume, gas temperature and pressure before and after the injection of the solution, the amount of acid gas dissolved in the amine can be calculated. The SRK equation of state (44) is used to calculate the density of the vapor phase.

Other necessary data to determine the solubility were:

1 - the barometric pressure,

2 - solution vapor pressure at the equilibrium temperature,

3 - weight percent of amine in solution, and

4 - density of the amine solution at room temperature and at the equilibrium temperature.

Three assumptions were made in the calculations:

1 - the liquid was assumed incompressible,

2 - liquid volume does not change due to acid gas solubility, and

3 - although the experimental vapor pressure of the amine solution is used, only water vapor was assumed to be present with the acid gas above the liquid. This is a reasonable assumption since the vapor pressure of the amines are very small compared to that of water. Physical properties of the amine solutions used in the calculations are presented in Appendix E.

A sample calculation is presented in Appendix F. Error analysis is given in Appendix G.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

MEA Data

Experimental measurements of the solubility of CO_2 in 2.5 N MEA solution have been made. Partial pressures of CO_2 ranged from 0.8 to 990 psia at temperatures of 25, 60 and 80°C. The experimental data are shown in Tables IV, V and VI of Appendix A and illustrated in Figure 6. The data show not only a small amount of experimental scatter in each set of data, but also show good agreement internally and with each other. Data from Muhlbauer and Monaghan (13), Jones, et al. (23) and Lee et al. (20) are also shown for comparison. The data from Muhlbauer and Monoghan cover only a limited temperature-partial pressure range but show good agreement with this work. The Jones et al. data also show reasonable agreement at both 60 and 80°C. However, there appears to be some departure between the data of this work and the data reported by Lee, et al. in the 10 to 150 psia CO_2 partial pressure range, particularly for 60°C.

Experimental determinations of the equilibrium solubility between H_2S and 2.5 N MEA solution were taken at 25°C. H_2S partial pressure ranged from 1.9 to 200 psia. The data are presented in Table VII of Appendix A. Figure 7 illustrates the data which appear to be highly consistent. Data from Muhlbauer and Monaghan (13) and Lee et al. (25)

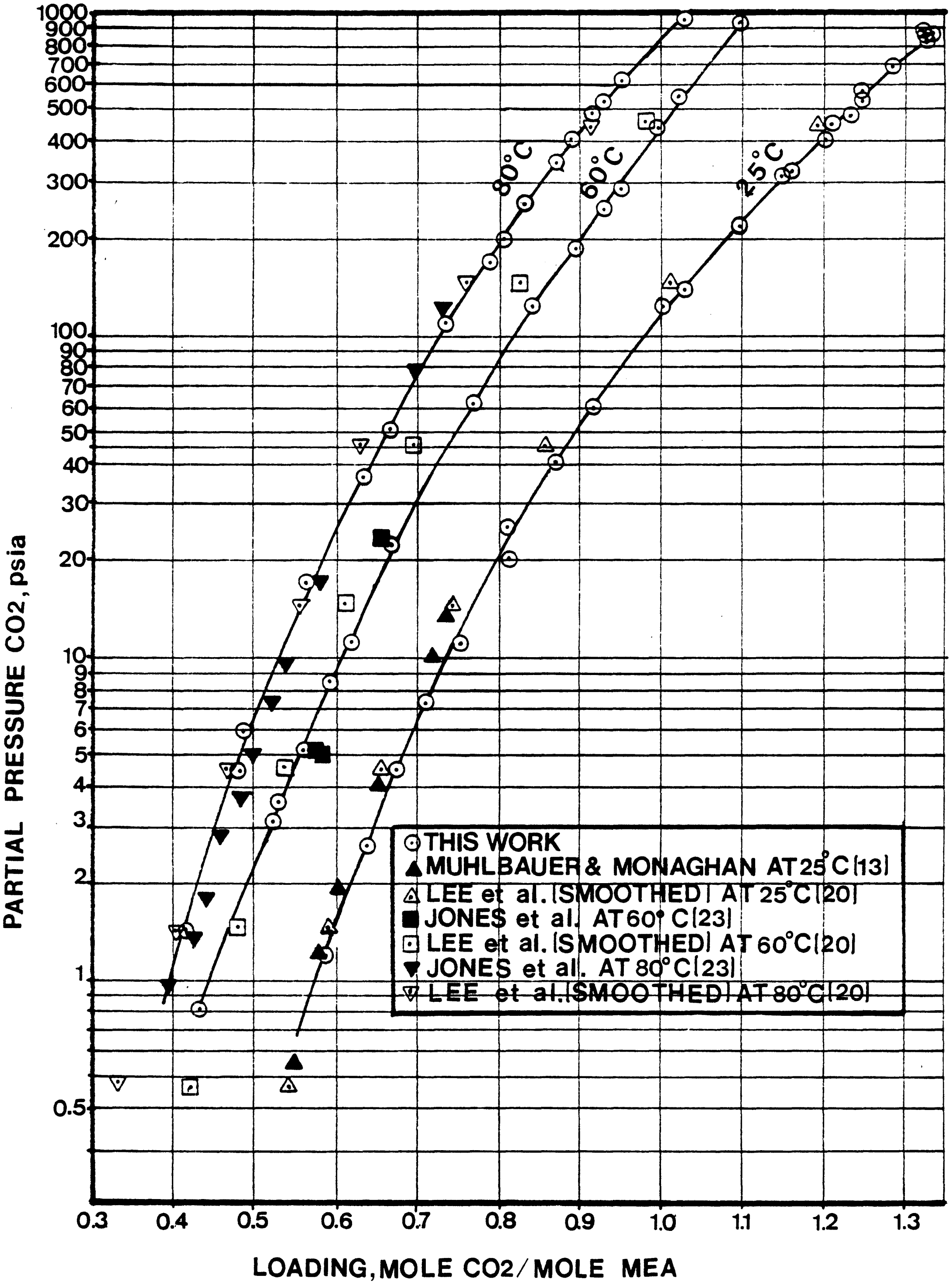


Figure 6. Solubility of CO_2 in 2.5 N MEA Solution at 25, 60 and 80°C

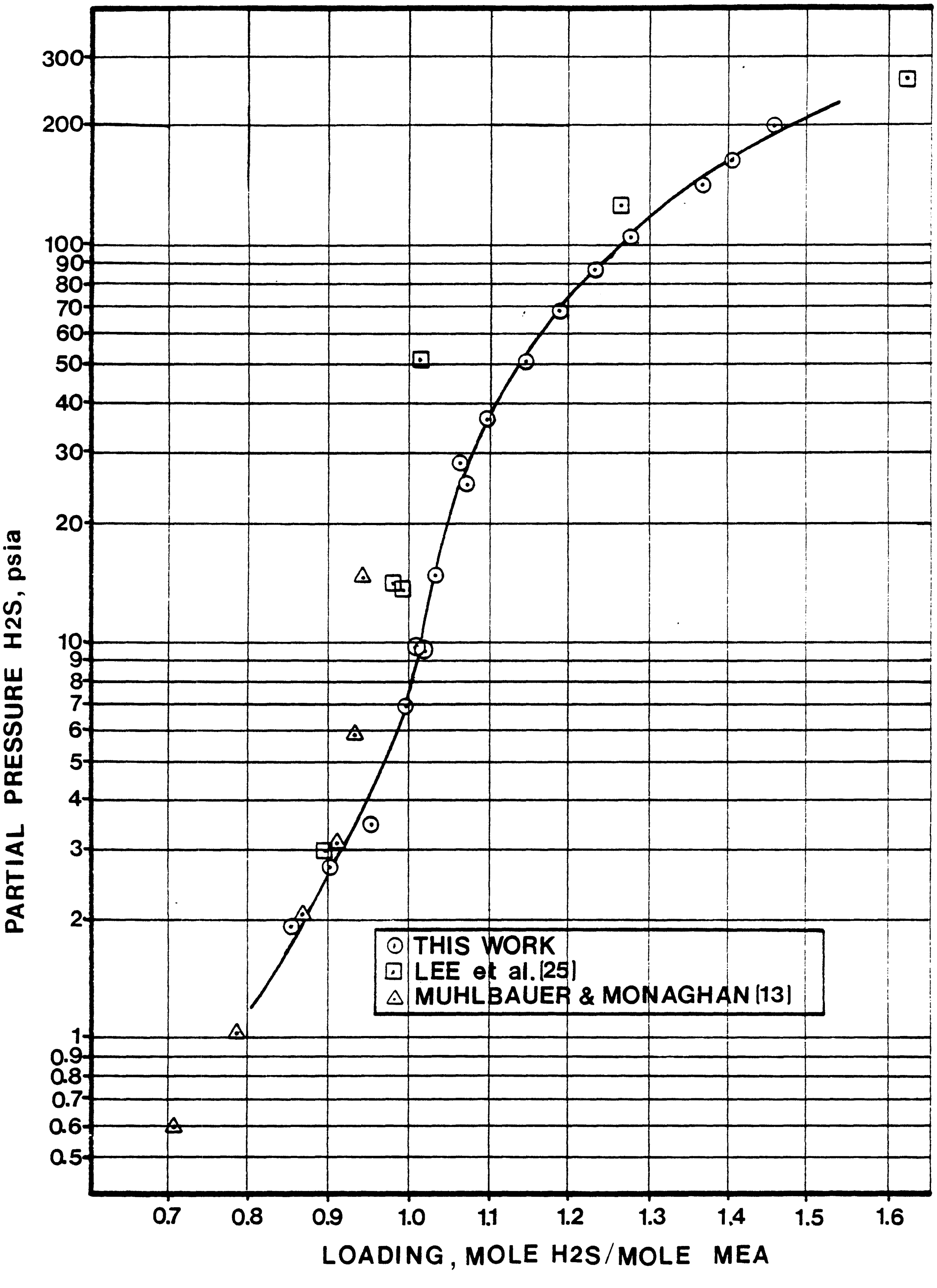


Figure 7. Solubility of H_2S in 2.5 N MEA Solution at 25°C

are also shown for comparison. Both references show lower H_2S solubility. However, the data appear to be in reasonable agreement below 5 psia and higher than 100 psia partial pressure of H_2S.

Figure 8 represents the equilibrium solubility of CO_2 and H_2S in 2.5 N MEA at 25°C. The equilibrium partial pressure of CO_2 is many fold higher than that of H_2S at any acid gas loading. Also note the difference in the shapes of the equilibrium curves. In the vicinity of 1.0 mole H_2S/mole MEA loading the H_2S curve passes through an inflection point where it changes its slope. This is probably due to the dominance of physical solubility of H_2S in the solution beyond a loading of 1.0.

DGA Data

The experimental equilibrium solubility of CO_2 in 20% by weight DGA aqueous solution at 25°C is plotted in Figure 9, and tabulated in Table VIII of Appendix A. The data cover the range of 1.4 to 820 psia CO_2 partial pressure. The data seem to be consistent describing a smooth curve. No literature data are available for comparison.

Experimental measurements of CO_2 solubility in 40% by weight DGA aqueous solution were also made. The partial pressure of CO_2 ranged from approximately 1 to 620 psia at temperatures of 40 and 60°C. The data are plotted in Figure 10 and tabulated in Table IX of Appendix A. Here also the data appear to be internally consistent and with a curve similar in shape to those expected for a CO_2-secondary amine system.

The equilibrium solubility of H_2S in 40% by weight DGA aqueous solution was also measured at both 40 and 60°C. The data are plotted in Figure 11 and presented in Table X and XI of Appendix A. The two sets of data appear to be consistent with similar shape lines through the

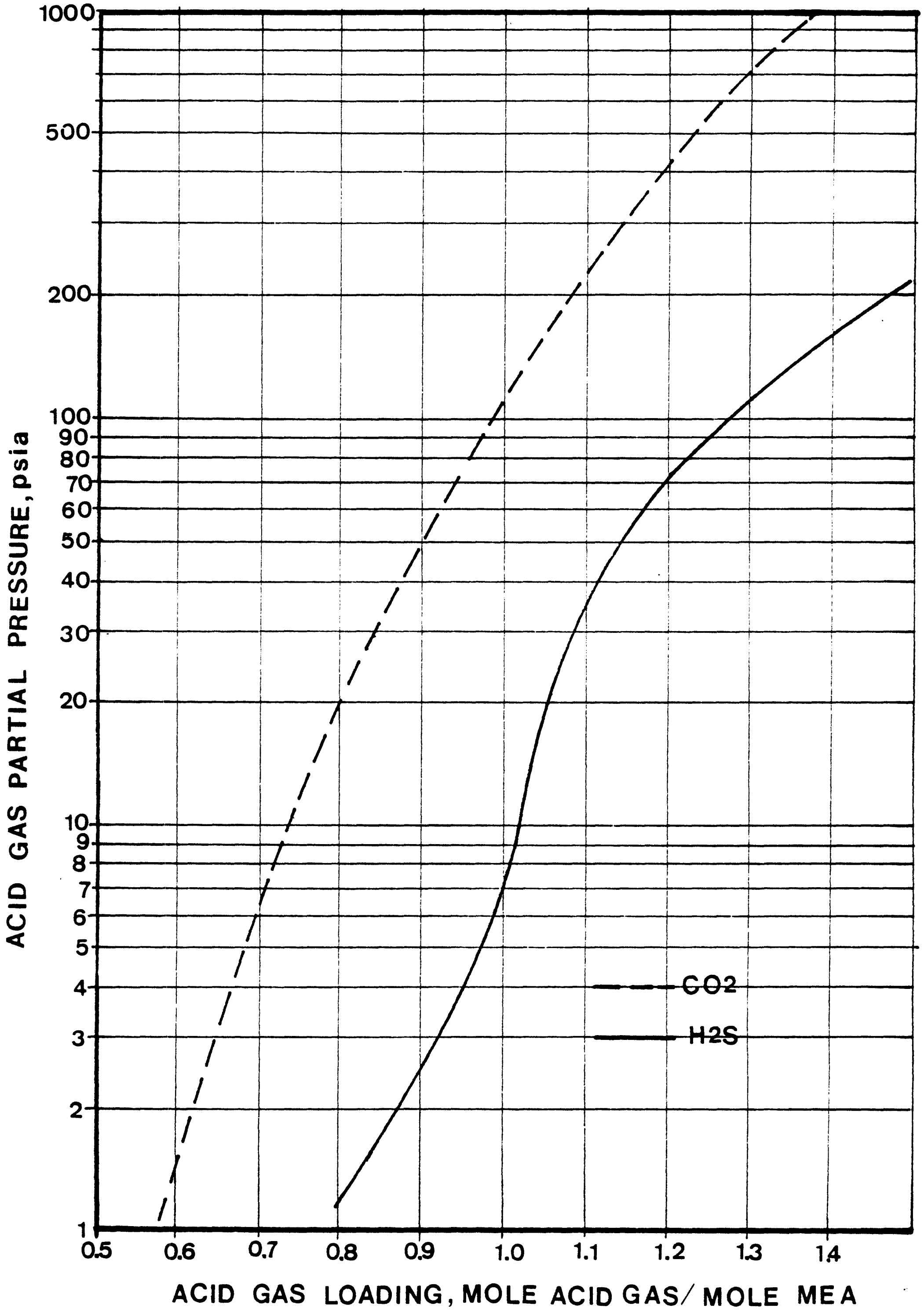


Figure 8. Solubility of CO_2 and H_2S in 2.5 N MEA Solution at 25°C

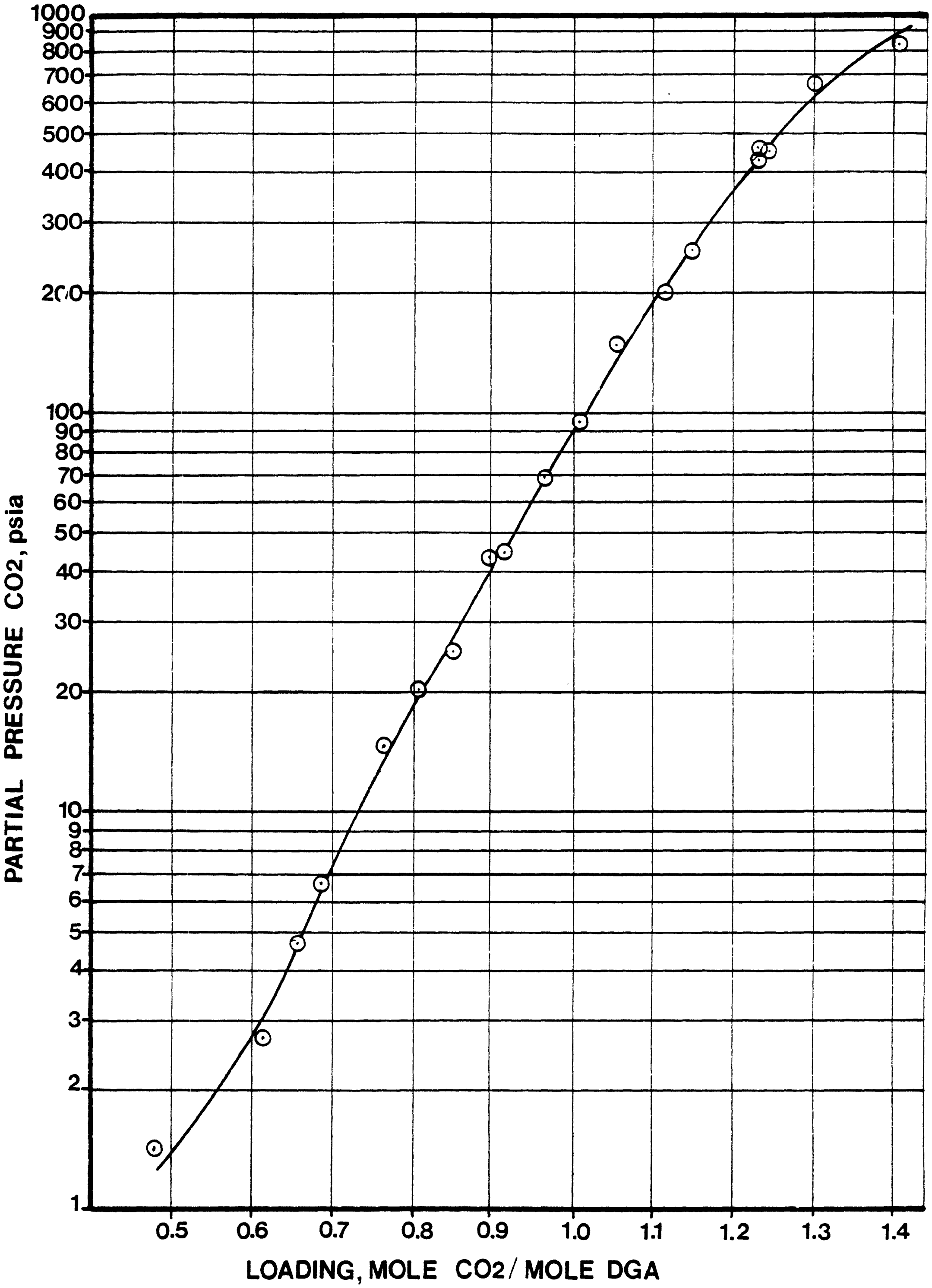


Figure 9. Solubility of CO_2 in 20% by Weight DGA Aqueous Solution at 25°C

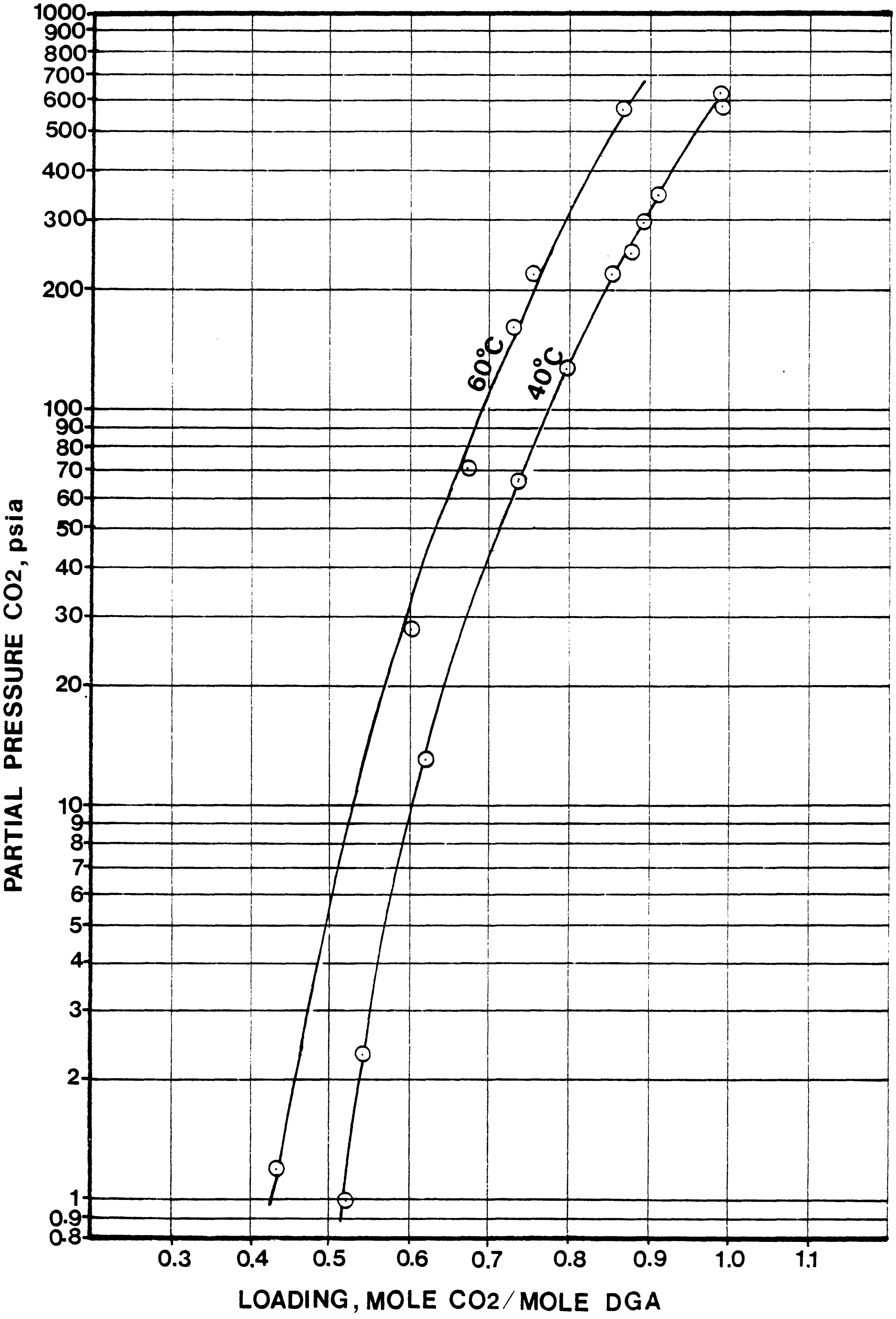


Figure 10. Solubility of CO_2 in 40% by Weight DGA Aqueous Solution at 40 and 60°C

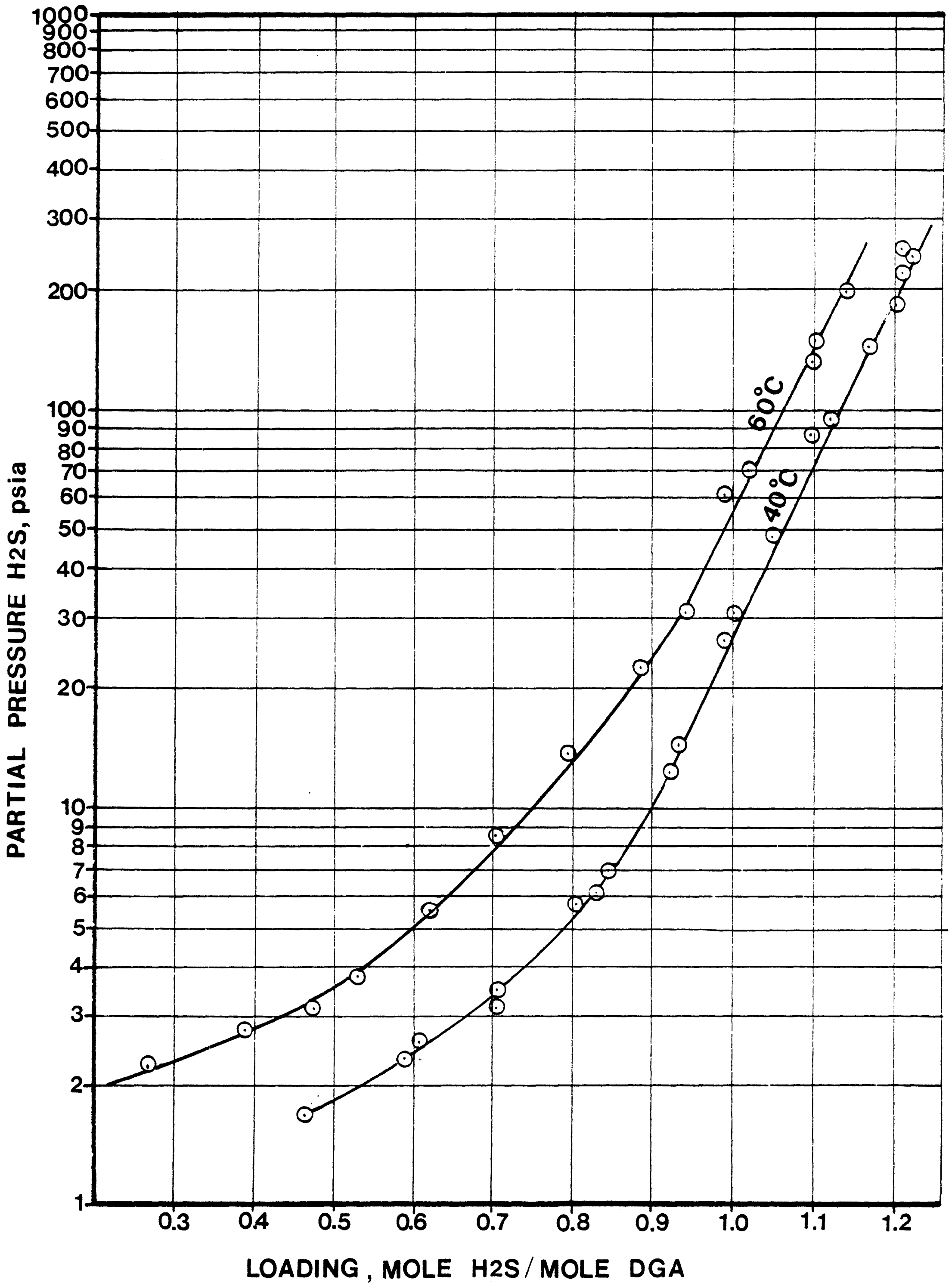


Figure 11. Solubility of H_2S in 40% by Weight DGA Aqueous Solution at 40 and 60°C

experimental points. No literature data are available for solubility of CO_2 or H_2S in 40 weight % DGA aqueous solution.

Figure 12 shows the solubility of CO_2 and H_2S at 40 and 60°C for comparison. At 40°C, H_2S loadings are approximately 40% higher than those of CO_2 at acid gas partial pressures higher than 30 psia. Below 30 psia the H_2S loading decreases rapidly with decreasing H_2S partial pressure. Under 2 psia acid gas partial pressure CO_2 loading becomes higher. This is due to the formatin of the stable carbamate in this region. Similar behavior is also observed at 60°C.

Equilibrium solubility data of CO_2 in 60% by weight DGA aqueous solution were obtained at 50°C covering the range from 1 to 960 psia CO_2 partial pressure. The data are presented in Figure 13 and tabulated in Table XII of Appendix A. Data from Martin et al. (41) are also shown for comparison. The data collected in this work show higher loadings at corresponding CO_2 partial pressures. Dingman et al. (42) used an equilibrium model accounting for the nonideality of the system using activity coefficients and adjusting the value of Henry's constant with changing solvent composition. They reported the predicted solubility of CO_2 in 60% DGA-water system. Their results are also plotted in Figure 13 showing better agreement with the data collected in this work.

Solubility of H_2S in 60% by weight DGA aqueous solution at 50 and 80°C are tabulated in Tables XIII and XIV of Appendix A. The H_2S partial pressure ranged from about 1.5 to 250 psia. The data are plotted in Figure 14 and seem to exhibit a high degree of consistency. The two sets of data show similar shape lines through the experimental points. Data from Martin et al. (41) at 50°C are also plotted but show substantial deviation from the present data especially between 7 and 200

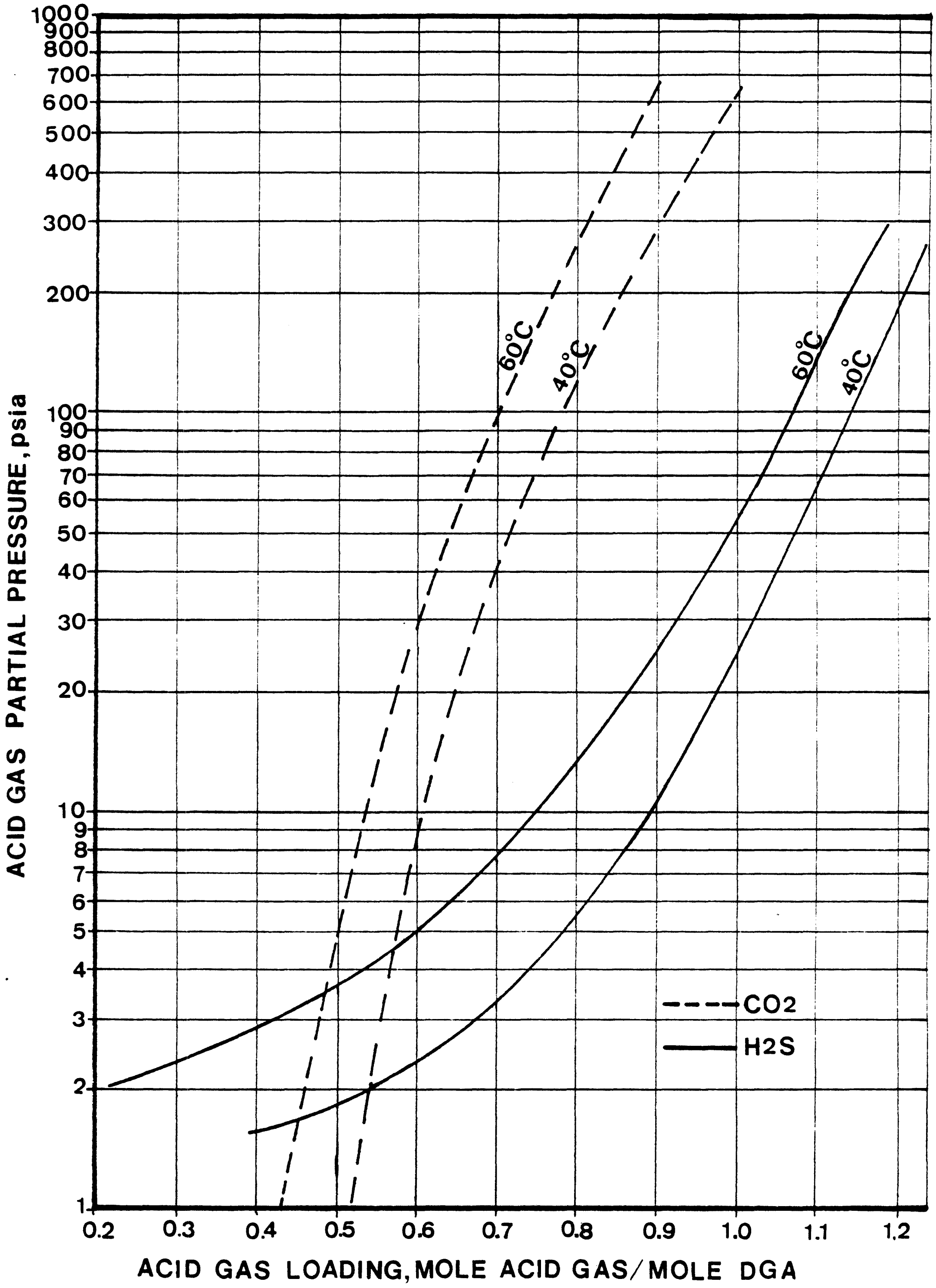


Figure 12. Solubility of CO_2 and H_2S in 40% by Weight DGA Aqueous Solution at 40 and 60°C

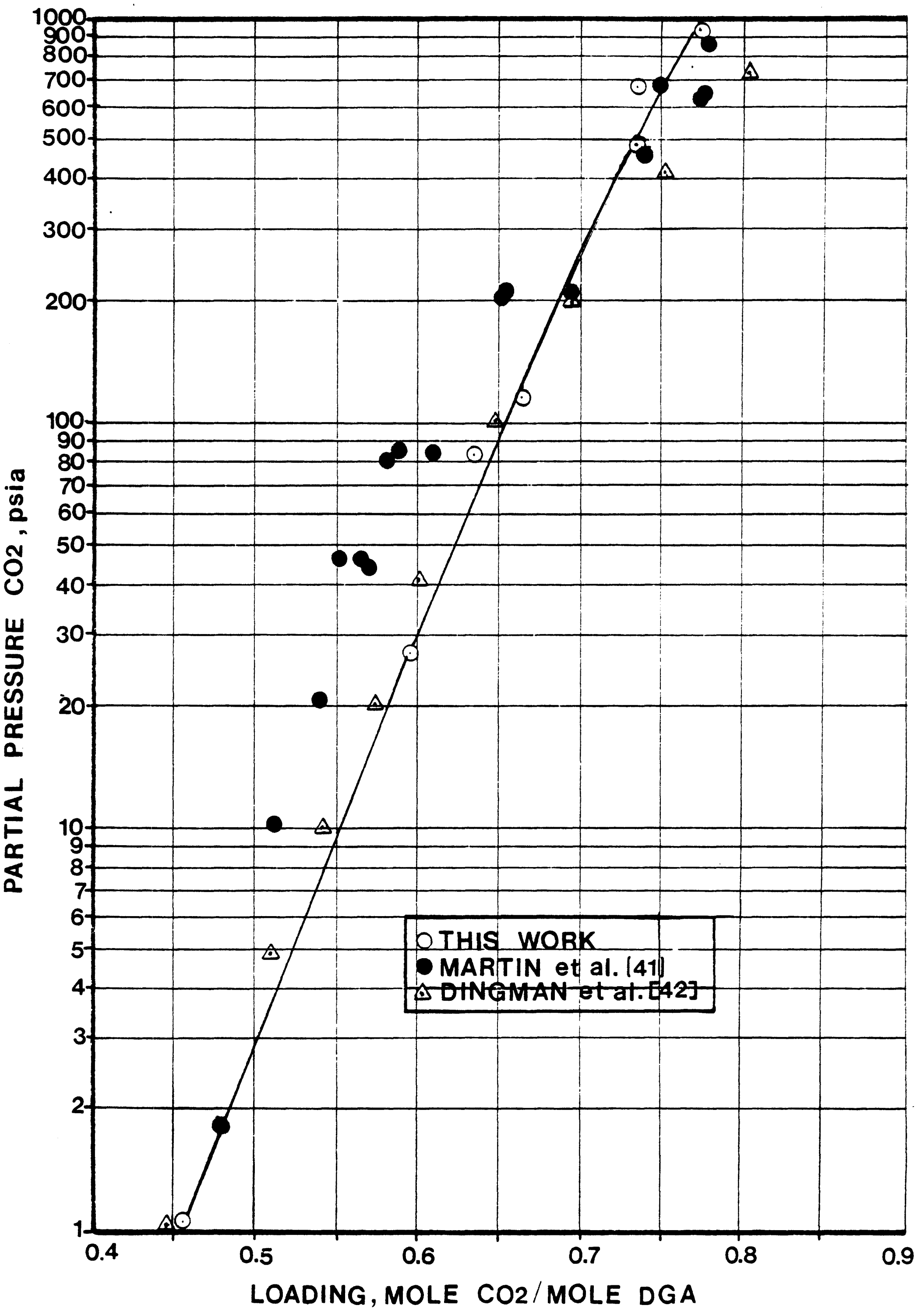


Figure 13. Solubility of CO_2 in 60% by Weight DGA Aqueous Solution at 50°C

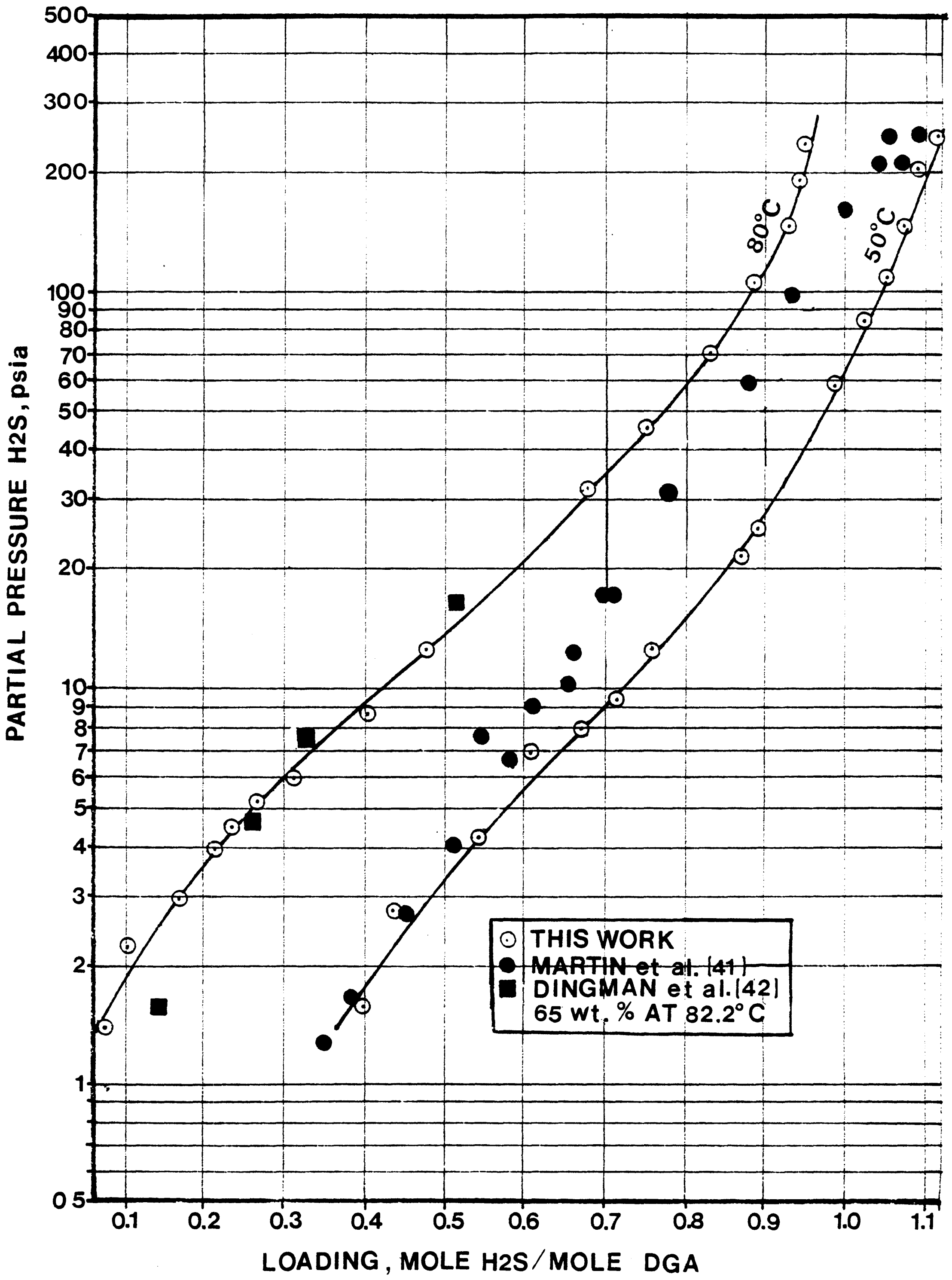


Figure 14. Solubility of H_2S in 60% by Weight DGA Aqueous Solution at 50 and 80°C

psia H_2S partial pressure. The data of Martin et al. describe a straight line which is not believed to be consistent with H_2S-amine-water system at such temperature. Data from Dingman et al (42) for the solubility of H_2S in 65 weight % DGA aqueous solution at 180°F (82.2°C) are also shown for comparison. Their data describe a curve closely resembling that of this work.

DEA Data

The equilibrium solubility of CO_2 in 0.5 and 2.0 N DEA solutions was measured at 25°C. Partial pressure of CO_2 ranged from 1 to 300 psia. The data are presented in Tables XV and XVI of Appendix A and plotted in Figure 15 along with data taken from previous work. The data of this work show high internal consistency and good agreement with the limited data reported by Mason and Dodge (14) for both DEA concentrations. They are in excellent agreement with the smoothed data published by Lee et al. (29).

The figure shows that the solubility decreases with increasing solution strength.

MDEA Data

Experimental measurements of CO_2 solubility in 1.0 N MDEA solution at 25°C were made. The partial pressure of CO_2 ranged from 2 up to 300 psia. The results are presented in Figure 16 and tabulated in Table XVII of Appendix A. The data points appear to be consistent. No literature data are available for comparison.

Figure 17 shows the equilibrium solubility of H_2S in 1.0 N MDEA at 25°C. The raw data are presented in Table XVIII of Appendix A. Also

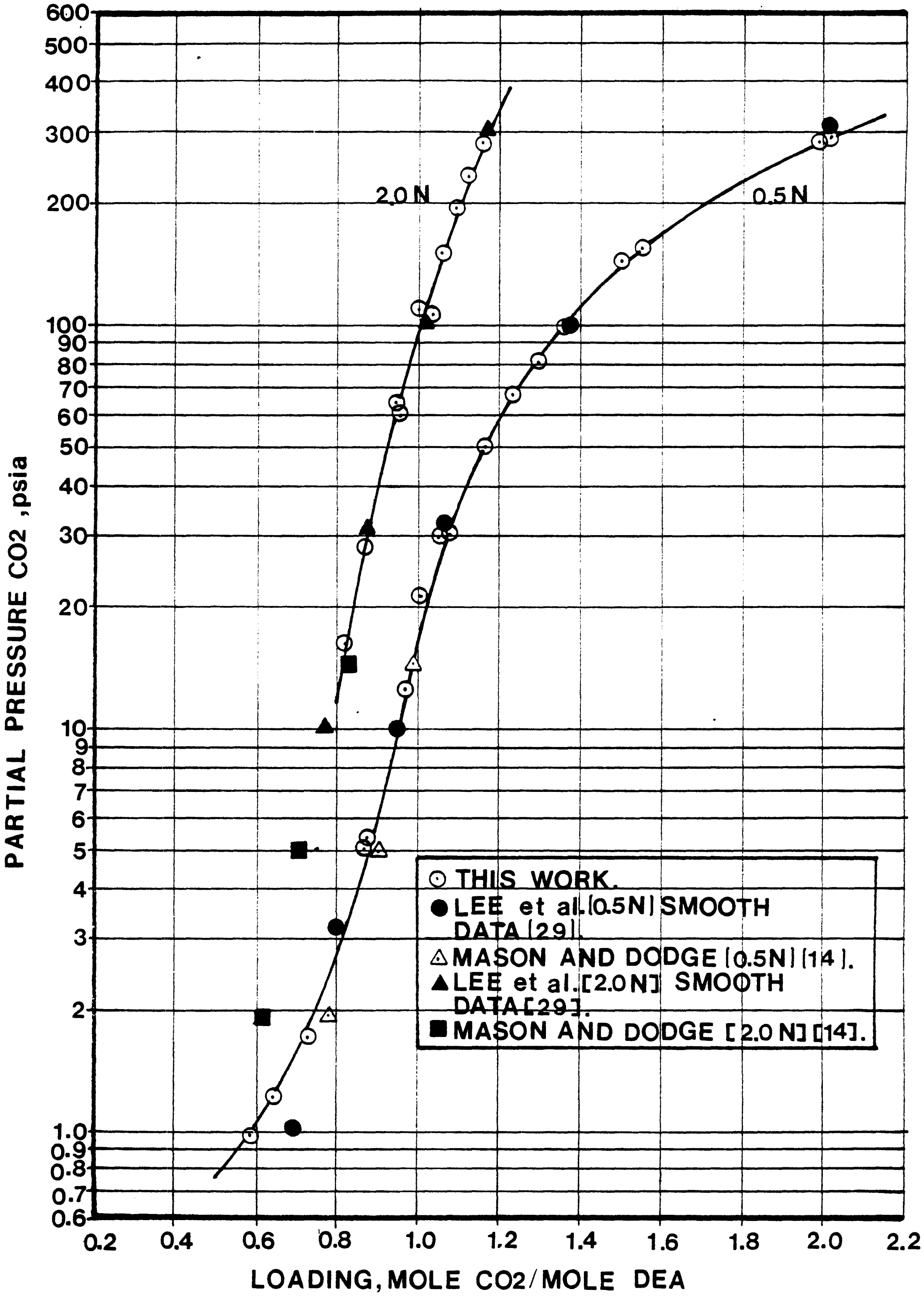


Figure 15. Solubility of CO_2 in 0.5 and 2.0 N DEA Solution at 25°C

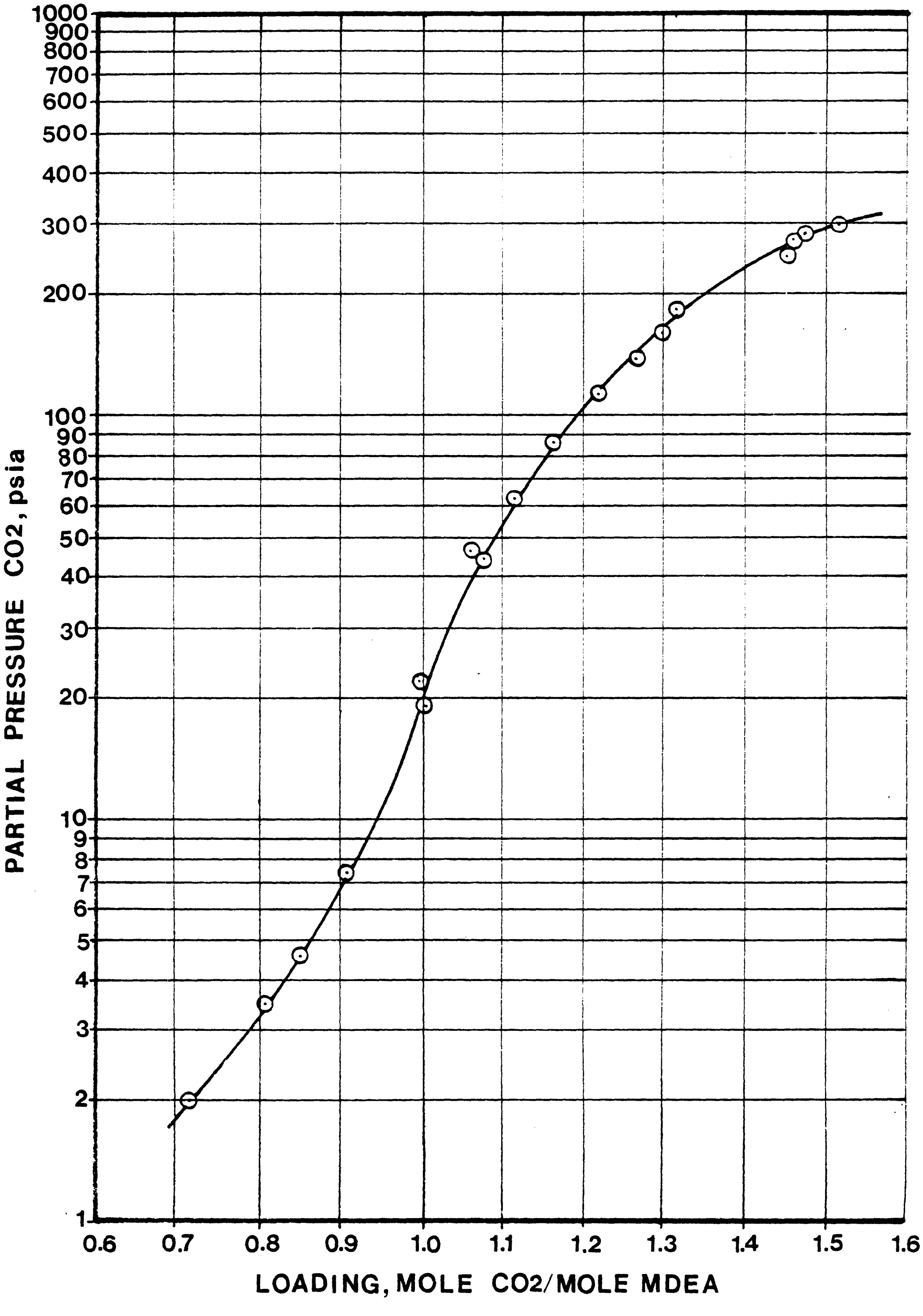


Figure 16. Solubility of CO_2 in 1.0 N MDEA Solution at 25°C

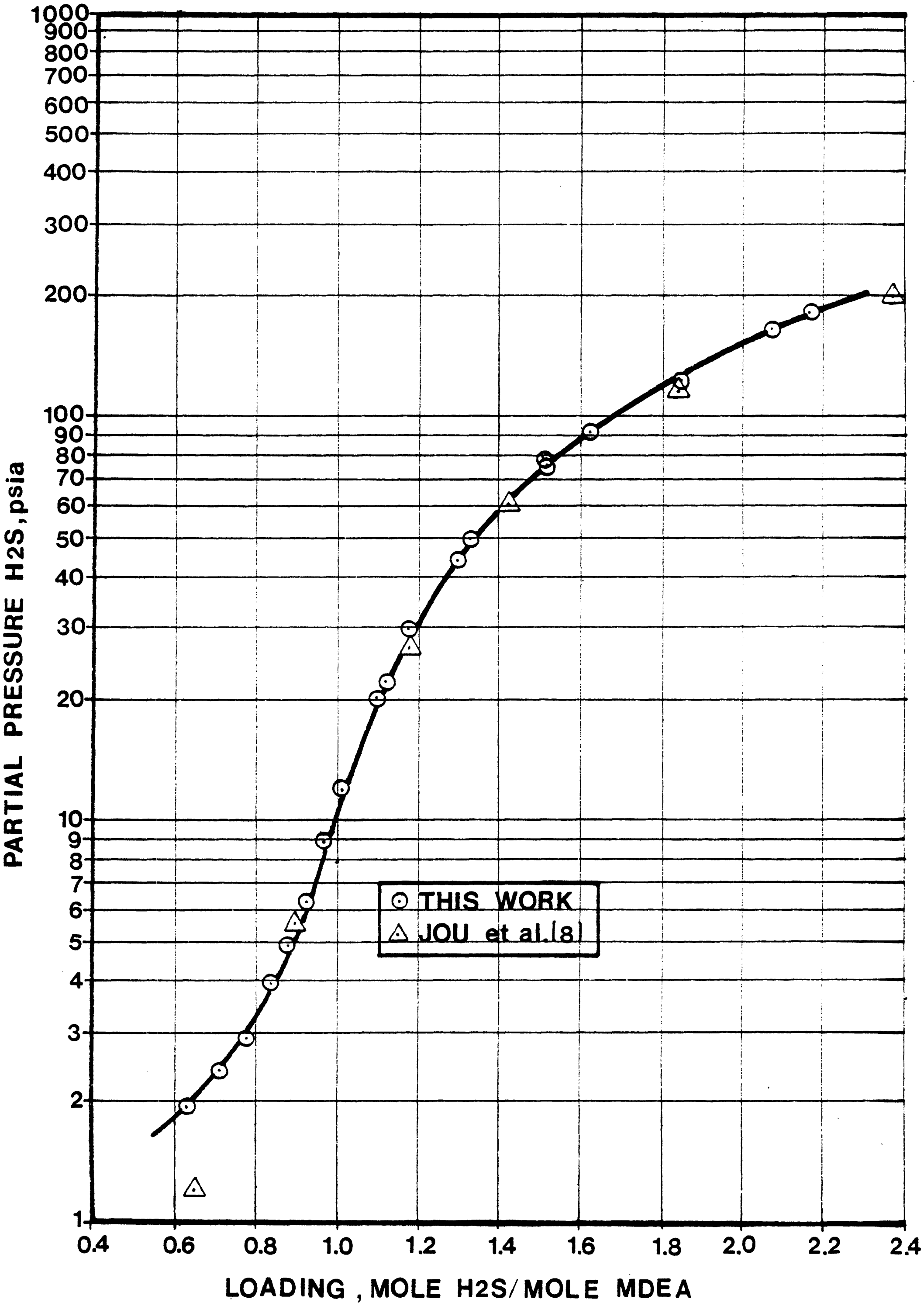


Figure 17. Solubility of H_2S in 1.0 N MDEA Solution at 25°C

shown on the figure are data from Jou et al. (8) which show good agreement with the results of this work except for H_2S solubility corresponding to equilibrium partial pressures of less than 2 psia. The shape of the CO_2 equilibrium curve is exactly the same as that of H_2S. This is in agreement with the findings discussed in Chapter II which verify the similar reaction mechanisms between CO_2 or H_2S with tertiary amines such as MDEA.

Equilibrium solubility data of CO_2 in 2.0 N MDEA solution at 25 and 50°C are plotted in Figure 18 and tabulated in Tables XIX and XX of Appendix A. The two data sets describe two similar curves. The curves are particularly similar for CO_2 loadings greater than 1.0 mole CO_2/mole MDEA where the mechanism of physical solubility dominates.

Data from Jou et al. (8) on the solubility of CO_2 in 2.0 N MDEA solution at 25°C are also shown on the figure for comparison. Their data is substantially higher than those reported in this work except near the region of 1.0 mole CO_2/mole MDEA loading.

Figure 19 represents the solubility of CO_2 in 1.0 and 2.0 N MDEA solutions at 25°C. The CO_2 solubility decreases with increasing amine concentration. The equilibrium curves also show that the physical solubility decreases with increasing amine concentration. This is due to the "salting out" effect (48).

Equilibrium solubility data of CO_2 in 20% by weight MDEA aqueous solution were taken at 100, 150 and 240°F. CO_2 partial pressure ranged from 2.7 up to 900 psia. The raw data are tabulated in Tables XXI, XXII and XXIII of Appendix A and plotted in Figure 20.

Figure 21 represents data taken for the solubility of H_2S in 20% by weight MDEA aqueous solution at 100, 150 and 240°F. H_2S partial

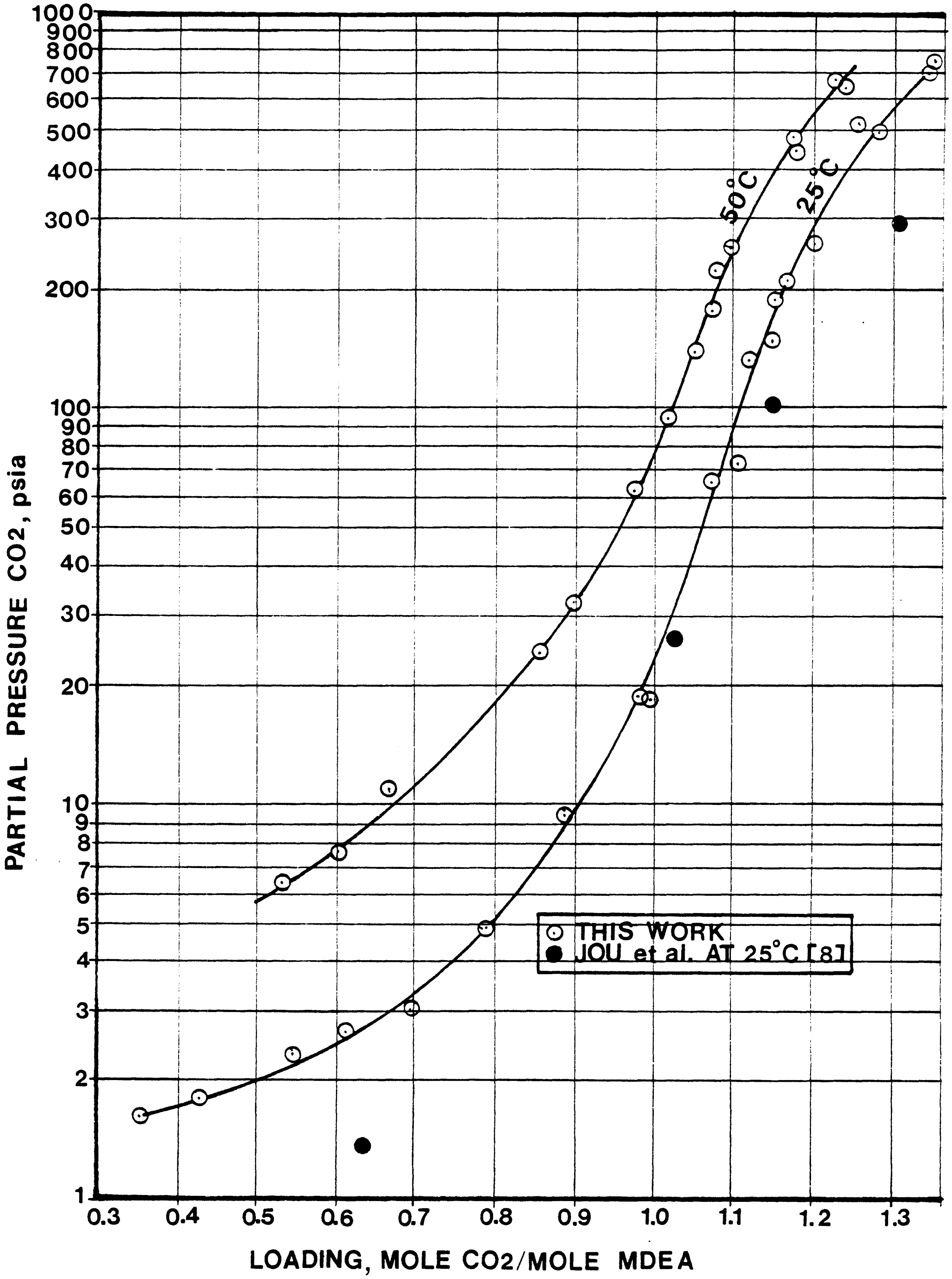


Figure 18. Solubility of CO_2 in 2.0 N MDEA Solution at 25 and 50°C

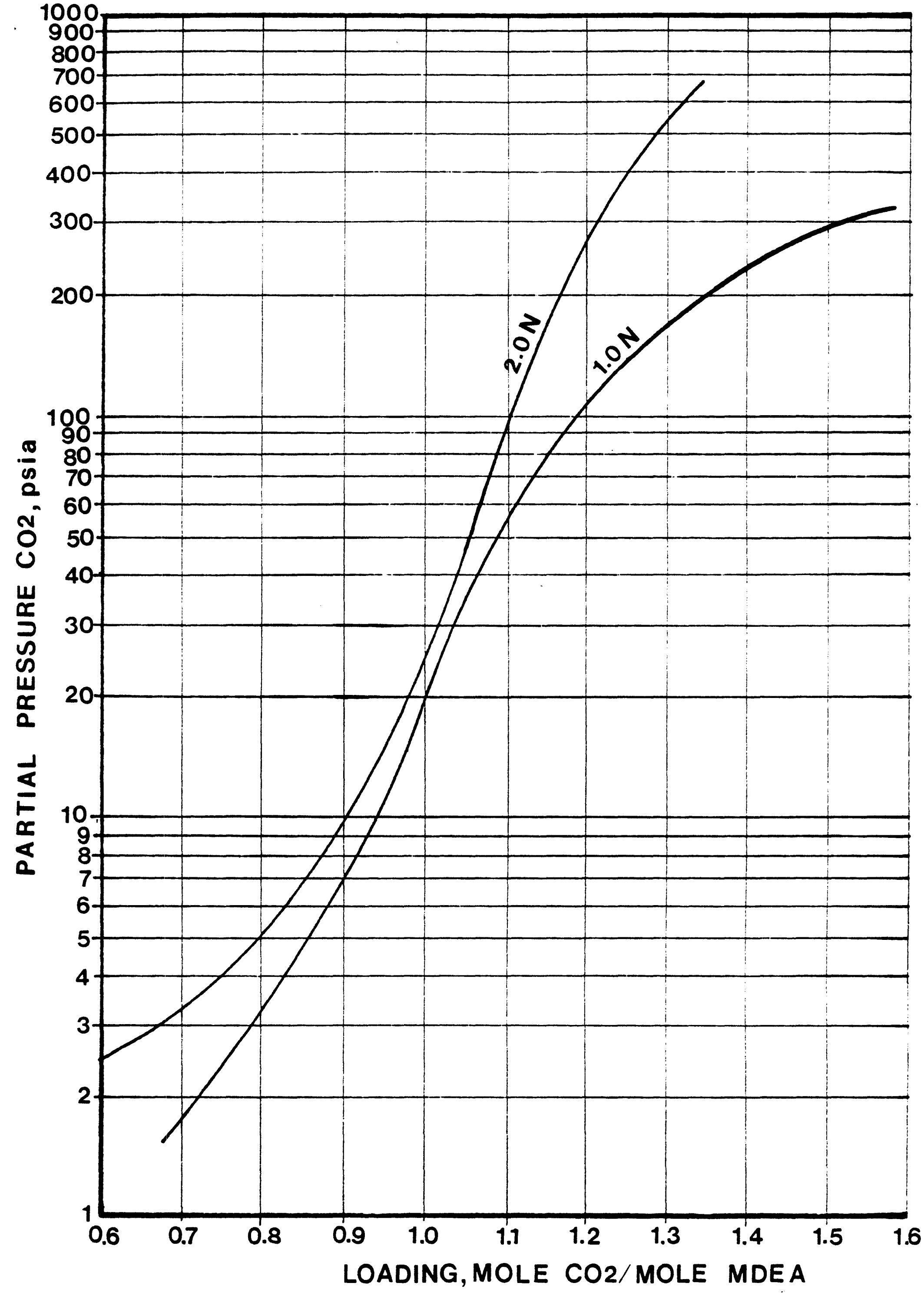


Figure 19. Solubility of CO_2 in 1.0 and 2.0 N MDEA Solution at 25°C

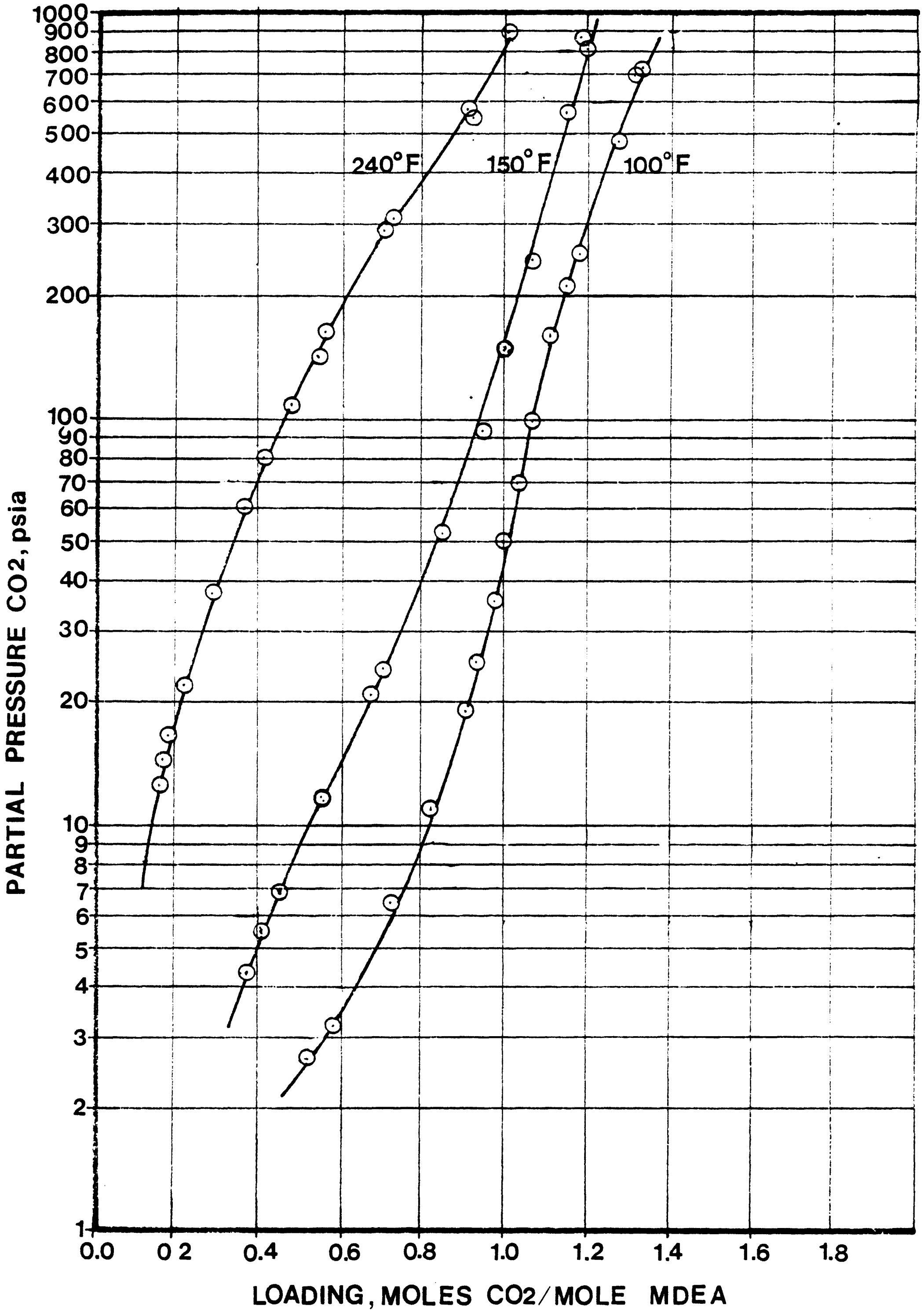


Figure 20. Solubility of CO_2 in 20% by Weight MDEA Aqueous Solution at 100, 150 and 240°F

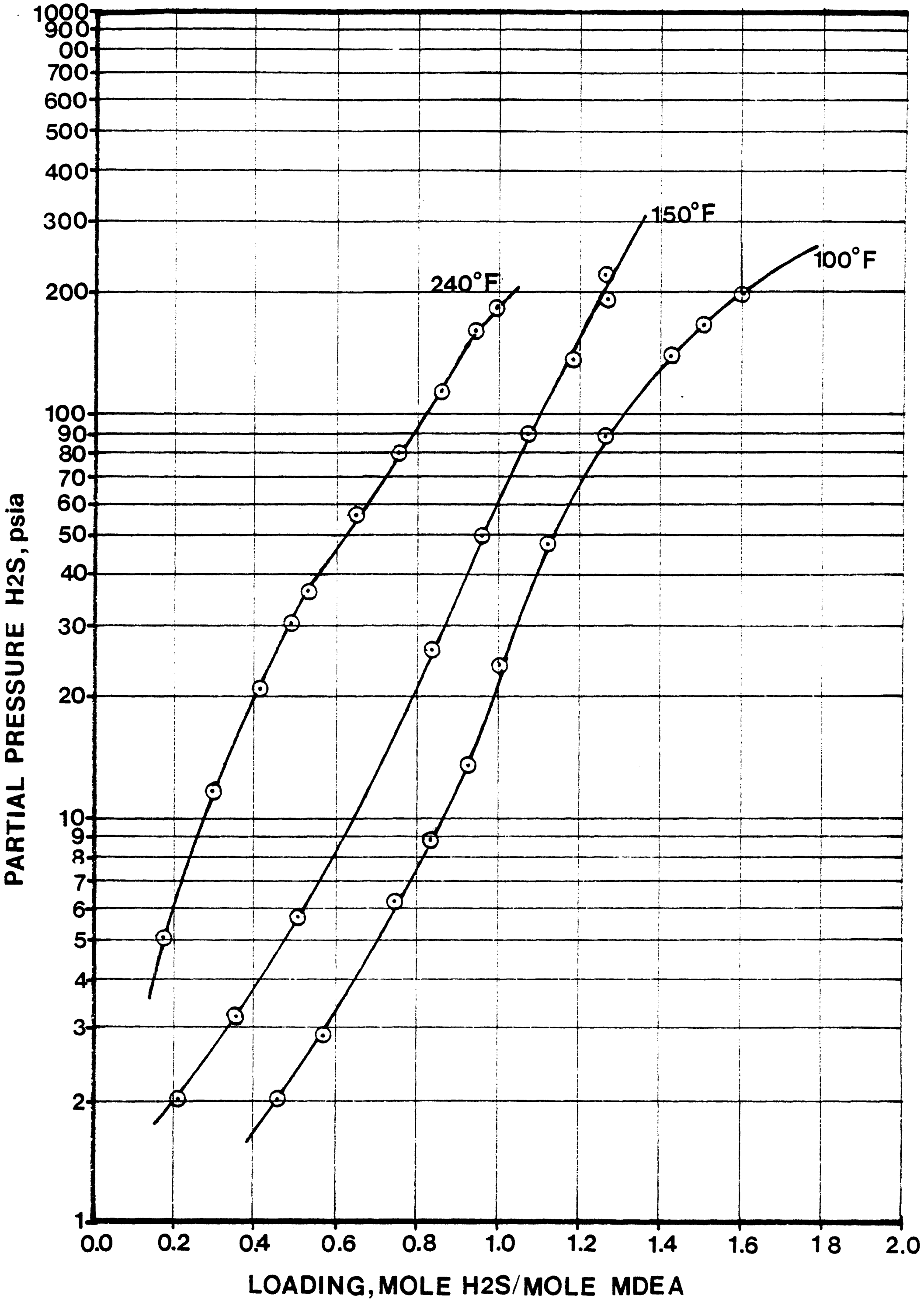


Figure 21. Solubility of H_2S in 20% by Weight MDEA Aqueous Solution at 100, 150 and 240°F

pressure ranged from 2 to 220 psia. The data are tabulated in Tables XXIV, XXV and XXVI of Appendix A. No literature data are available on these systems.

Figure 22 represents the solubility of both CO_2 and H_2S for comparison.

All sets of data have almost no data scatter and appear to be very consistent. The shape of the curves describing the CO_2 solubility change with temperature in the same manner as was observed in the CO_2-2.0 N MDEA system (see Figure 18). The H_2S data also follow the same pattern.

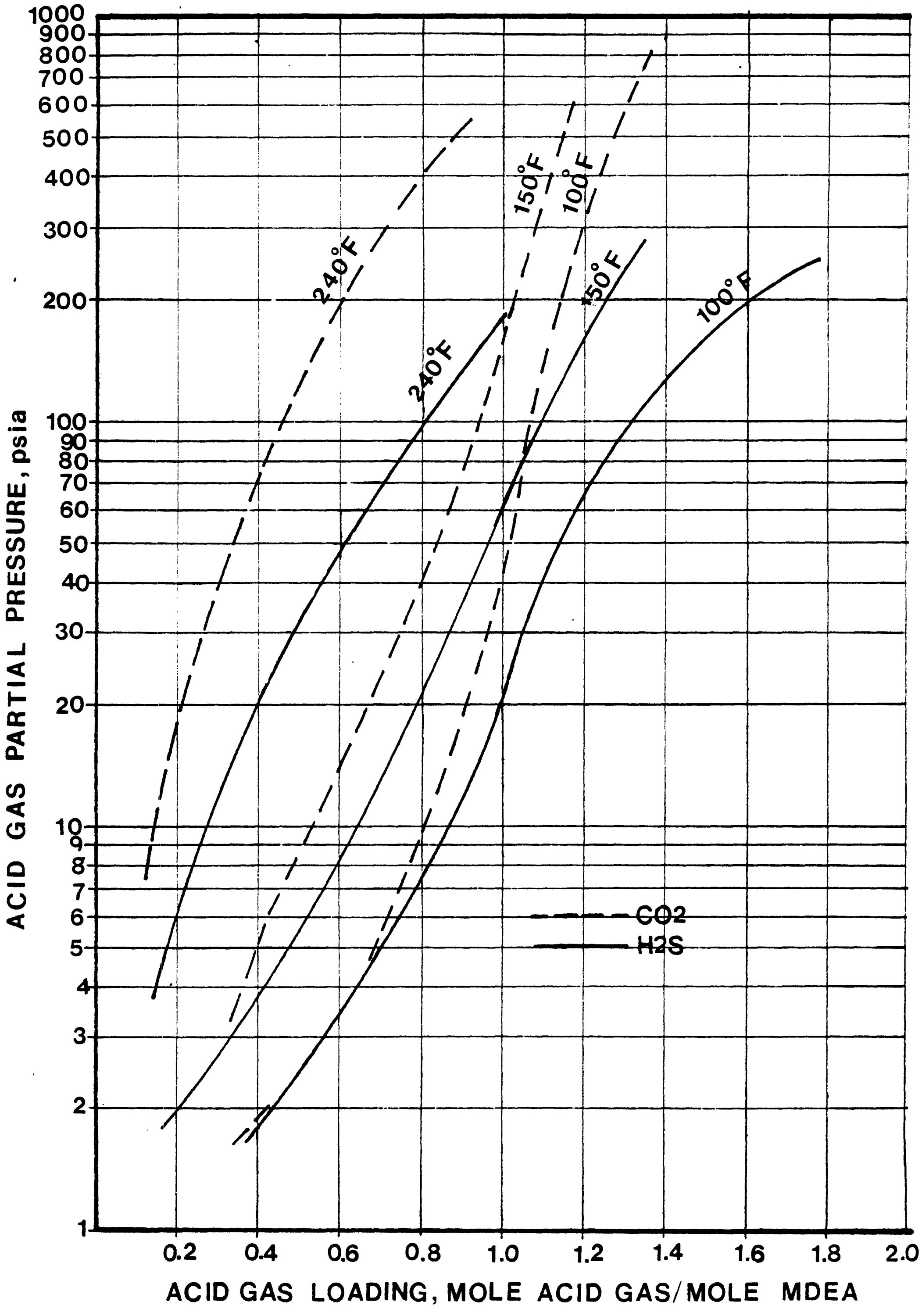


Figure 22. Solubility of CO_2 and H_2S in 20% by Weight MDEA Aqueous Solution at 100, 150 and 240°F

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A single equilibrium cell was used to measure the solubility of carbon dioxide and hydrogen sulfide in alkanolamine solutions. A simple procedure was used where no chromatograph nor chemical analysis is required.

The following conclusions may be drawn from the results of this study.

1 - The apparatus used and the technique developed were sound as demonstrated by the consistent data collected.

2 - Within the conditions of the experiment, the solubility of either CO_2 or H_2S per mole amine decreases with increasing temperature and with increasing solution strength.

3 - The H_2S solubility in primary amine solutions is substantially higher than that of CO_2 at high acid gas partial pressures. However, at low acid gas partial pressure in the vicinity of CO_2 loading of 0.5 mole CO_2/mole amine the H_2S solubility becomes lower.

4 - In a specified MDEA solution strength and temperature the H_2S solubility is higher than that of CO_2 especially at high acid gas partial pressure. However, the two solubilities approach each other at lower acid gas partial pressure.

5 - The physically dissolved acid gas in an amine solution can be substantial as compared to the chemically reacted acid gas, especially at high acid gas partial pressure and low temperature.

Recommendations

The following recommendations can be useful for further investigations in this area of research.

1 - A modification in the apparatus should be introduced to measure solubilities corresponding to acid gas partial pressures down to 1 mm Hg.

2 - Measurements of the physical solubility of acid gases in amine solutions should be performed.

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APPENDIX A

EXPERIMENTAL DATA

TABLE IV

SOLUBILITY OF CO_2 IN 2.5 N MEA SOLUTION AT 25°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole MEA
883.42	883.00	1.322
865.96	865.54	1.325
847.45	847.02	1.325
834.31	833.88	1.322
687.12	686.69	1.283
569.38	568.96	1.247
541.81	541.38	1.251
486.01	485.58	1.235
453.48	453.08	1.213
400.27	399.85	1.204
324.35	323.92	1.164
311.43	311.00	1.153
220.46	220.04	1.098
137.72	137.29	1.031
125.49	125.07	1.006
60.41	59.99	0.917
40.50	40.08	0.871
25.56	25.14	0.813
20.50	20.07	0.815
11.52	11.09	0.755
7.68	7.26	0.714
4.90	4.47	0.675
3.06	2.64	0.639
1.06	1.18	0.586

TABLE V

SOLUBILITY OF CO_2 IN 2.5 N MEA SOLUTION AT 60°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/moles MEA
944.08	941.29	1.096
927.45	924.66	1.100
555.37	552.58	1.021
448.37	445.58	0.991
289.10	286.31	0.948
250.19	247.40	0.929
189.63	186.84	0.896
125.80	123.01	0.842
64.76	61.96	0.770
25.25	22.44	0.673
14.15	11.35	0.618
11.22	8.43	0.595
7.99	5.20	0.563
6.37	3.57	0.528
5.87	3.08	0.524
5.70	2.91	0.499
3.60	0.81	0.436

TABLE VI

SOLUBILITY OF CO_2 IN 2.5 N MEA
SOLUTION AT 80°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole MEA
991.89	985.15	1.033
628.66	621.92	0.953
534.11	527.37	0.927
500.89	494.15	0.917
409.39	402.65	0.893
348.59	341.85	0.872
260.95	254.21	0.832
203.95	197.21	0.807
176.88	170.14	0.787
114.76	108.02	0.737
58.97	52.23	0.668
42.65	35.91	0.636
32.31	28.57	0.591
26.57	19.83	0.593
23.79	17.05	0.567
12.67	5.93	0.489
11.09	4.35	0.484
8.16	1.41	0.424
7.68	0.94	0.413

TABLE VII

SOLUBILITY OF H_2S IN 2.5 N MEA AQUEOUS SOLUTION AT 25°C

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole MEA
202.38	201.96	1.454
162.36	161.94	1.403
142.44	142.02	1.366
104.42	104.00	1.276
86.10	85.68	1.233
67.80	67.38	1.187
50.80	50.38	1.144
36.62	36.20	1.094
28.45	28.03	1.081
25.50	25.08	1.074
15.16	14.74	1.036
10.17	9.75	1.014
9.94	9.52	1.018
7.29	6.87	0.995
3.90	3.48	0.947
3.12	2.70	0.897
2.32	1.90	0.849
1.38	0.96	0.717

TABLE VIII

SOLUBILITY OF CO_2 IN 20% BY WEIGHT DGA SOLUTION AT 25°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole DGA
828.84	828.47	1.405
667.57	667.20	1.302
455.01	454.64	1.235
444.31	443.94	1.241
420.11	419.74	1.230
255.31	254.94	1.152
200.25	199.88	1.118
149.29	148.93	1.054
95.71	95.34	1.010
69.29	68.92	0.966
44.94	44.57	0.915
44.12	43.75	0.894
25.64	25.27	0.851
20.50	20.13	0.805
15.25	14.88	0.765
7.01	6.64	0.684
5.07	4.70	0.657
3.11	2.74	0.613
1.78	1.41	0.479

TABLE IX

SOLUBILITY OF CO_2 IN 40% BY WEIGHT DGA AQUEOUS SOLUTION AT 40 AND 60°C

Temperature °C	Total Pressure psia	CO_2 Partial Press. psia	Loading moles CO_2/mole DGA
40	618.70	617.78	0.9858
	585.19	584.26	0.9872
	350.69	349.77	0.9109
	297.19	296.27	0.8926
	248.19	247.27	0.8744
	220.77	219.84	0.8535
	129.10	128.17	0.7968
	67.91	66.98	0.7384
	14.11	13.18	0.6181
	3.27	2.34	0.5432
	1.91	0.986	0.5196
60	565.69	563.18	0.8660
	224.97	222.46	0.7537
	163.17	160.66	0.7305
	72.85	70.34	0.6748
	30.47	27.96	0.6023
	3.68	1.17	0.4326

TABLE X

SOLUBILITY OF H_2S IN 40% BY WEIGHT DGA AQUEOUS SOLUTION AT 40°C

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole DGA
256.64	255.72	1.2088
246.28	245.36	1.2242
222.04	221.12	1.2041
184.00	183.08	1.2017
145.41	144.48	1.1759
95.41	94.49	1.1194
87.59	86.49	1.0957
48.82	47.90	1.0502
32.12	31.19	1.0056
27.42	26.50	0.9895
15.32	14.40	0.9362
13.27	12.34	0.9231
7.93	7.00	0.8463
7.10	6.17	0.8304
6.703	5.78	0.8036
4.43	3.50	0.7014
4.23	3.31	0.7056
3.52	2.60	0.6056
3.22	2.30	0.5912
2.60	1.69	0.4645

TABLE XI

SOLUBILITY OF H_2S IN 40% BY WEIGHT DGA AQUEOUS SOLUTION AT 60°C

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole DGA
201.88	199.37	1.1437
152.26	149.75	1.1006
135.64	133.13	1.1024
73.94	71.43	1.0208
64.08	61.57	0.9870
35.46	32.95	0.9406
25.06	22.55	0.8822
16.36	13.85	0.7959
11.12	8.61	0.7024
8.00	5.49	0.6157
6.29	3.78	0.5329
5.67	3.16	0.4766
5.29	2.78	0.3929
4.76	2.25	0.2723

TABLE XII

SOLUBILITY OF CO_2 IN 60% BY WEIGHT DGA AQUEOUS SOLUTION AT 50°C

Total Pressure psia	CO_2 Partial Press. psia	Loading moles CO_2/mole DGA
947.69	946.43	0.7757
672.24	670.99	0.7648
485.22	483.97	0.7730
116.26	115.01	0.6682
85.44	84.19	0.6350
27.86	26.60	0.5984
2.29	1.04	0.4580

TABLE XIII

SOLUBILITY OF H_2S IN 60% BY WEIGHT DGA AQUEOUS SOLUTION AT 50°C

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole DGA
248.19	246.93	1.1072
205.21	203.95	1.0842
147.55	146.55	1.0753
109.54	108.29	1.0529
87.43	86.17	1.0223
60.00	58.75	0.9864
26.81	25.55	0.8914
23.63	22.37	0.8708
14.10	12.85	0.7558
10.77	9.52	0.7104
9.30	8.05	0.6707
7.24	5.99	0.6073
5.58	4.32	0.5376
4.08	2.82	0.4354
2.87	1.61	0.3985

TABLE XIV

SOLUBILITY OF H_2S IN 60% BY WEIGHT DGA AQUEOUS SOLUTION AT 80°C

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole DGA
243.10	238.28	0.9503
198.86	193.86	0.9404
152.64	147.82	0.9291
110.84	106.02	0.8864
76.54	71.72	0.8258
51.71	46.88	0.7542
37.67	32.84	0.6781
24.67	19.84	0.5747
17.52	12.69	0.4761
13.66	8.83	0.4048
10.96	6.14	0.3095
10.13	5.31	0.2618
9.35	4.53	0.2284
8.91	4.08	0.2129
7.78	2.96	0.1636
7.10	2.28	0.1029
6.73	1.91	0.0677

TABLE XV

SOLUBILITY OF CO_2 IN 0.5 N DEA SOLUTION AT 25°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole DEA
292.34	291.89	2.012
289.59	280.14	1.999
155.54	155.09	1.542
144.77	144.33	1.501
98.83	98.38	1.359
82.72	82.28	1.294
67.34	66.89	1.231
50.92	50.48	1.165
31.01	30.57	1.074
30.91	30.46	1.059
21.92	21.47	1.012
12.94	12.50	0.970
5.83	5.38	0.875
5.57	5.13	0.866
2.15	1.703	0.724
1.66	1.214	0.655
1.44	0.993	0.598

TABLE XVI

SOLUBILITY OF CO_2 IN 2.0 N DEA SOLUTION AT 25°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole DEA
281.41	280.99	1.157
236.19	235.77	1.127
195.78	195.36	1.097
150.01	149.59	1.060
109.41	108.99	1.002
105.61	105.19	1.017
64.57	64.16	0.945
61.31	60.89	0.962
28.97	28.55	0.868
16.66	16.24	0.817

TABLE XVII

SOLUBILITY OF CO_2 IN 1.0 N MDEA
AT 25°C

Total Pressure psia	CO_2 Partial Press. psia	Loading moles CO_2/mole MDEA
298.38	297.96	1.5068
287.66	287.20	1.4751
275.11	274.68	1.4619
263.17	262.74	1.4534
182.31	181.88	1.3147
161.71	161.28	1.2999
139.15	138.72	1.2656
114.99	114.56	1.2202
89.25	88.83	1.1662
64.36	63.95	1.1187
44.92	47.46	1.0806
19.72	21.99	1.0094
12.87	21.45	0.9756
47.89	47.46	1.0627
22.42	21.99	1.0056
7.58	7.16	0.9119
5.03	4.60	0.8555
3.95	3.52	0.8105
2.42	1.99	0.7193

TABLE XVIII

SOLUBILITY OF H_2S IN 1.0 N MDEA SOLUTION AT 25°C

Total Pressure psia	H_2S Partial Press. psia	H_2S Loading moles H_2S/mole MDEA
186.00	185.58	2.1703
164.88	164.46	2.0728
125.37	124.95	1.8458
91.44	91.02	1.6236
80.42	79.99	1.5170
76.74	76.32	1.5196
50.24	49.82	1.3367
45.07	44.65	1.2948
30.64	30.22	1.1922
22.37	21.95	1.1234
20.66	20.24	1.1032
12.41	11.99	1.0109
9.34	8.92	0.9684
6.69	6.27	0.9258
5.35	4.93	0.8804
4.42	4.00	0.8378
3.29	2.87	0.7798
2.80	2.38	0.7101
2.40	1.97	0.6380

TABLE XIX

SOLUBILITY OF CO_2 IN 2.0 N MDEA SOLUTION AT 25°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole MDEA
706.33	705.98	1.3458
702.79	702.44	1.3411
512.33	511.98	1.2559
500.33	500.00	1.2822
263.75	263.40	1.1888
213.45	213.10	1.1648
192.45	192.10	1.1492
149.38	149.03	1.1446
134.14	133.79	1.1192
74.20	73.85	1.1010
66.50	66.15	1.0710
19.10	18.75	0.9866
18.67	18.32	0.9909
9.71	9.36	0.8878
5.24	4.89	0.7895
3.43	3.08	0.6941
3.00	2.65	0.6117
2.67	2.32	0.5459
2.15	1.80	0.4305
1.96	1.61	0.3549

TABLE XX

SOLUBILITY OF CO_2 IN 2.0 N MDEA SOLUTION AT 50°C

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole MDEA
676.23	674.69	1.2222
669.21	667.67	1.2284
659.21	657.67	1.2350
478.21	476.67	1.1715
442.71	441.17	1.1743
260.66	259.12	1.0963
224.71	222.52	1.0790
180.43	178.89	1.0697
131.19	130.40	1.0499
96.76	95.22	1.0194
63.93	62.39	0.9799
33.43	31.89	0.8969
25.93	24.39	0.8568
12.52	10.98	0.6668
9.16	7.62	0.6011
7.94	6.40	0.5351

TABLE XXI

SOLUBILITY OF CO_2 IN 20% BY WEIGHT MDEA AQUEOUS SOLUTION AT 100°F

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole MDEA
721.28	720.59	1.3359
710.29	709.60	1.3198
486.32	485.63	1.2734
225.05	254.35	1.1766
211.35	210.65	1.1453
159.75	159.05	1.1070
99.93	99.23	1.0581
69.06	68.36	1.0253
49.56	48.86	0.9963
37.56	36.86	0.9723
25.75	25.05	0.9332
19.55	18.85	0.9015
11.89	11.19	0.8184
7.24	6.54	0.7250
3.90	3.20	0.5716
3.44	2.74	0.5112

TABLE XXII

SOLUBILITY OF CO_2 IN 20% BY WEIGHT MDEA AQUEOUS SOLUTION AT 150°F

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/mole MDEA
854.28	851.00	1.1938
834.78	831.50	1.1992
575.80	572.52	1.1448
251.70	248.42	1.0634
152.12	148.84	0.9991
97.82	94.54	0.9390
56.12	52.84	0.8505
27.54	24.26	0.7057
24.54	21.26	0.6741
14.99	11.71	0.5455
10.20	6.92	0.4433
8.78	5.50	0.4029
7.55	4.27	0.3692

TABLE XXIII

SOLUBILITY OF CO_2 IN 20% BY WEIGHT MDEA AQUEOUS SOLUTION AT 240°F

Total Pressure psia	CO_2 Partial Press. psia	CO_2 Loading moles CO_2/moles Amine
918.30	894.04	1.005
592.00	567.74	0.896
586.80	562.54	0.897
336.08	311.82	0.722
313.80	289.54	0.709
184.72	160.47	0.559
166.67	142.41	0.543
133.00	108.74	0.480
106.51	82.25	0.413
86.91	62.65	0.358
61.85	37.59	0.294
46.65	22.39	0.220
41.05	16.79	0.184
38.94	14.68	0.170
36.84	12.58	0.157

TABLE XXIV

SOLUBILITY OF H_2S IN 20% BY WEIGHT MDEA AQUEOUS SOLUTION AT 100°F

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole MDEA
197.37	196.68	1.587
168.79	168.10	1.508
140.91	140.22	1.426
88.75	88.06	1.264
48.78	48.09	1.121
24.78	24.09	1.003
14.30	13.61	0.926
9.59	8.89	0.833
6.94	6.24	0.743
3.60	2.91	0.568
2.77	2.07	0.456

TABLE XXV

SOLUBILITY OF H_2S IN 20% BY WEIGHT MDEA AQUEOUS SOLUTION AT 150°F

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole MDEA
226.24	222.96	1.255
197.42	194.14	1.259
141.42	138.14	1.178
85.94	89.22	1.070
53.50	50.22	0.958
29.58	26.30	0.828
8.98	5.70	0.504
6.53	3.24	0.347
5.20	1.92	0.212

TABLE XXVI

SOLUBILITY OF H_2S IN 20% BY WEIGHT MDEA AQUEOUS SOLUTION AT 240°F

Total Pressure psia	H_2S Partial Press. psia	Loading moles H_2S/mole MDEA
208.14	183.88	0.988
185.34	161.08	0.937
139.16	114.90	0.854
104.36	80.10	0.747
80.58	56.32	0.646
60.18	35.92	0.522
54.27	30.01	0.483
45.08	20.82	0.406
35.88	11.62	0.292
29.28	5.02	0.180

APPENDIX B

EQUILIBRIUM CELL CALIBRATION

The volume of the equilibrium cell - with thermocouple and glass beads inserted inside - was determined with distilled water as a reference. Three determinations of the volume were obtained using a 1000 ml volumetric flask (with a tolerance of ± 0.3 ml) and a 50 ml burette (with a tolerance of ± 0.1 ml). The volumes obtained were 1009.5, 1010.0 and 1010.5 ml, respectively, with an average of 1010.0 ml.

The internal volume of the tubing and fittings connecting the cell to the 300 psi pressure gauge was determined by filling the evacuated tubes and fittings with distilled water. The determinations were 7.7, 7.5 and 7.6 ml, respectively. The average of the observations is 7.6 ml.

The internal volume of the bourdon tube of the 3000 psi pressure gauge is 12 ml. Therefore the volume of this system (cell + fittings + gauge) is 1029.6 ml.

The tubing and fittings connecting the cell to the 3000 psi gauge were calibrated as mentioned above. The three observations were 7.5, 7.4 and 7.6 ml, respectively, with an average of 7.5 ml. The volume of the bourdon tube of this gauge is 27.0 ml. The total volume of this system is 1044.5 ml.

The 60 psi gauge has an internal volume of 5.0 ml. The volume of the tubing and fittings connecting the cell to the gauge were determined as before with three observations of 7.6 ml each. The total volume of this system is 1022.6 ml.

The internals volume of the bourdon tubes of the pressure gauges were supplied by the manufacturers.

APPENDIX C

CALIBRATION OF THE THERMOCOUPLES

TABLE XXVII

CALIBRATION OF COPPER-CONTANTAN (CELL) THERMOCOUPLE AGAINST A THERMOCOUPLE CALIBRATED BY THE NATIONAL BUREAU OF STANDARDS

Temp. °F Actual (T_a)	Temp. °F Indicated (T_i)	Temp. °F Fitted (T_f)	Dev. °F	% Dev.
32.0 (ice)	32.0	32.024	0.024	0.08
75.169	75.130	75.121	-0.048	-0.06
125.721	125.750	125.732	0.011	0.01
172.192	172.22	172.221	0.029	0.02
222.627	222.56	222.611	-0.016	-0.01

A.A.P.D. = 0.04

$T_f = 0.062496 + 0.998594 * T_i + 6.0873 \times 10^{-6} * T_i^2$

TABLE XXVIII

CALIBRATION OF COPPER-CONTANTAN (BATH) THERMOCOUPLE AGAINST A THERMOCOUPLE CALIBRATED BY THE NATIONAL BUREAU OF STANDARDS

Temp. °F Actual (T_a)	Temp. °F Indicated (T_i)	Temp. °F Fitted (T_f)	Dev. °F	% Dev.
32.0 (ice)	32.0	32.006	0.006	0.020
75.169	75.217	75.170	0.001	0.001
125.721	125.750	125.684	-0.037	-0.029
172.192	172.28	172.239	0.047	0.027
222.627	222.58	222.611	-0.016	-0.007
			A.A.P.D. =	0.02

$T_f = 0.067516 + 0.997778 * T_i + 9.236 \times 10^{-7} * T_i^2$

APPENDIX D

CALIBRATION OF PRESSURE GAUGES

TABLE XXIX

CALIBRATION OF (30" HG VAC-0-60 PSIG) 3D SERIAL # 786600 PRESSURE GAUGE

Test Pressure	Gauge Pressure
5.5 in Hg Vac.	5.5 In Hg Vac.
15.0 in Hg Vac.	15.0 in Hg Vac.
21.0 in Hg Vac	21.0 in Hg Vac.
24.0 in Hg Vac.	24.0 in Hg Vac.
30.00 psi	29.90 psi
40.00 psi	39.96 psi
50.00 psi	49.96 psi
60.00 psi	59.95 psi

TABLE XXX

CALIBRATION of (0-3000 PSI) HEISE GAUGE MODEL SOLID FRONT-C-51054

Test Pressure psi	Gauge Pressure psi
130.0	129.9
230.0	229.8
330.0	329.9
455.0	455.0
554.0	554.0
655.0	655.0
760.0	760.0
850.0	850.0
900.0	900.0
1000.0	1000.0
1200.0	1200.0

TABLE XXXI

CALIBRATION OF (0-300 PSI) HEISE GAUGE MODEL SOLID FRONT-B-4714R

Test Pressure psi	Gauge Pressure psi
30.00	30.10
40.00	40.00
60.00	60.00
80.00	80.00
130.00	130.00
180.00	180.00
230.00	230.00
280.00	280.00

APPENDIX E

PHYSICAL PROPERTIES OF AMINE SOLUTIONS

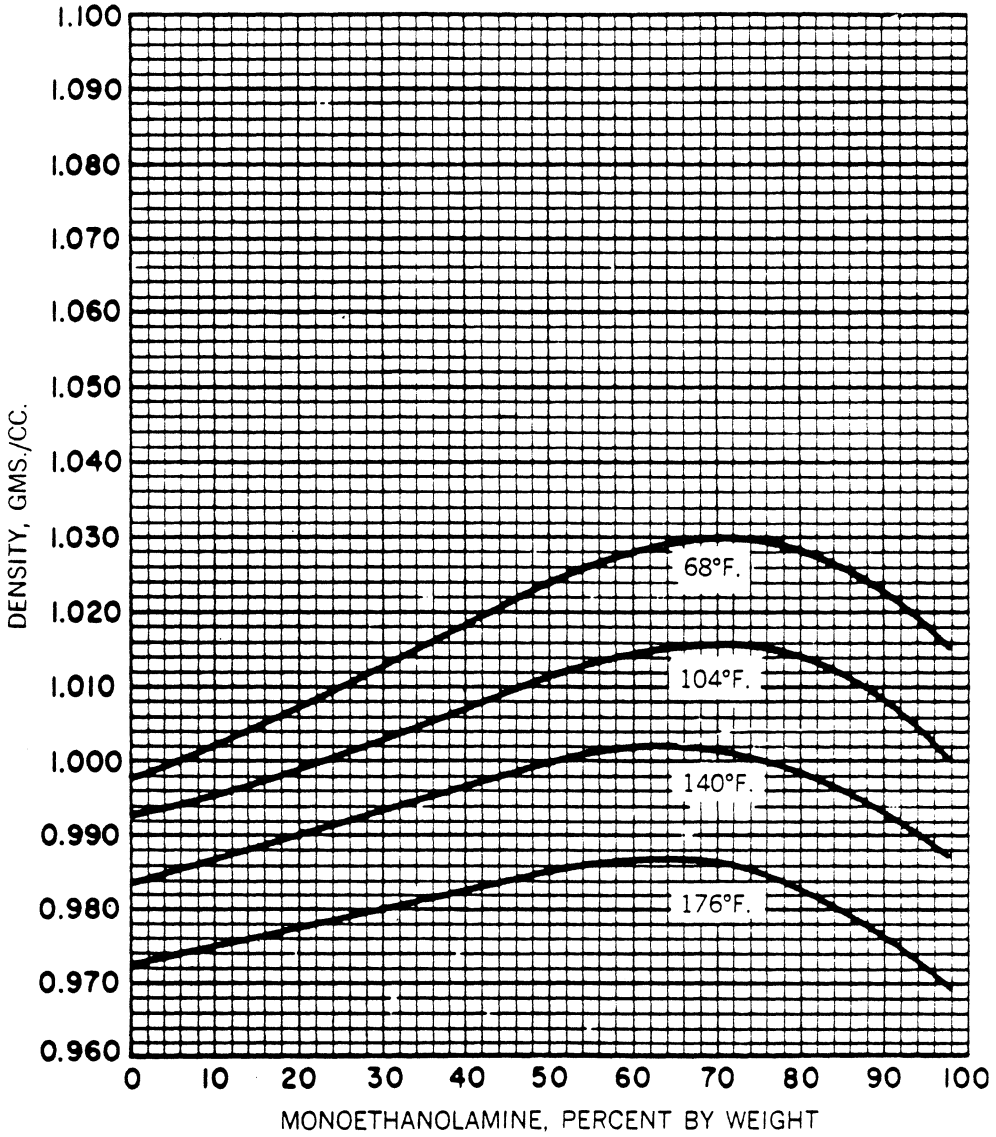

Figure 23. Density of MEA Aqueous Solutions (46)

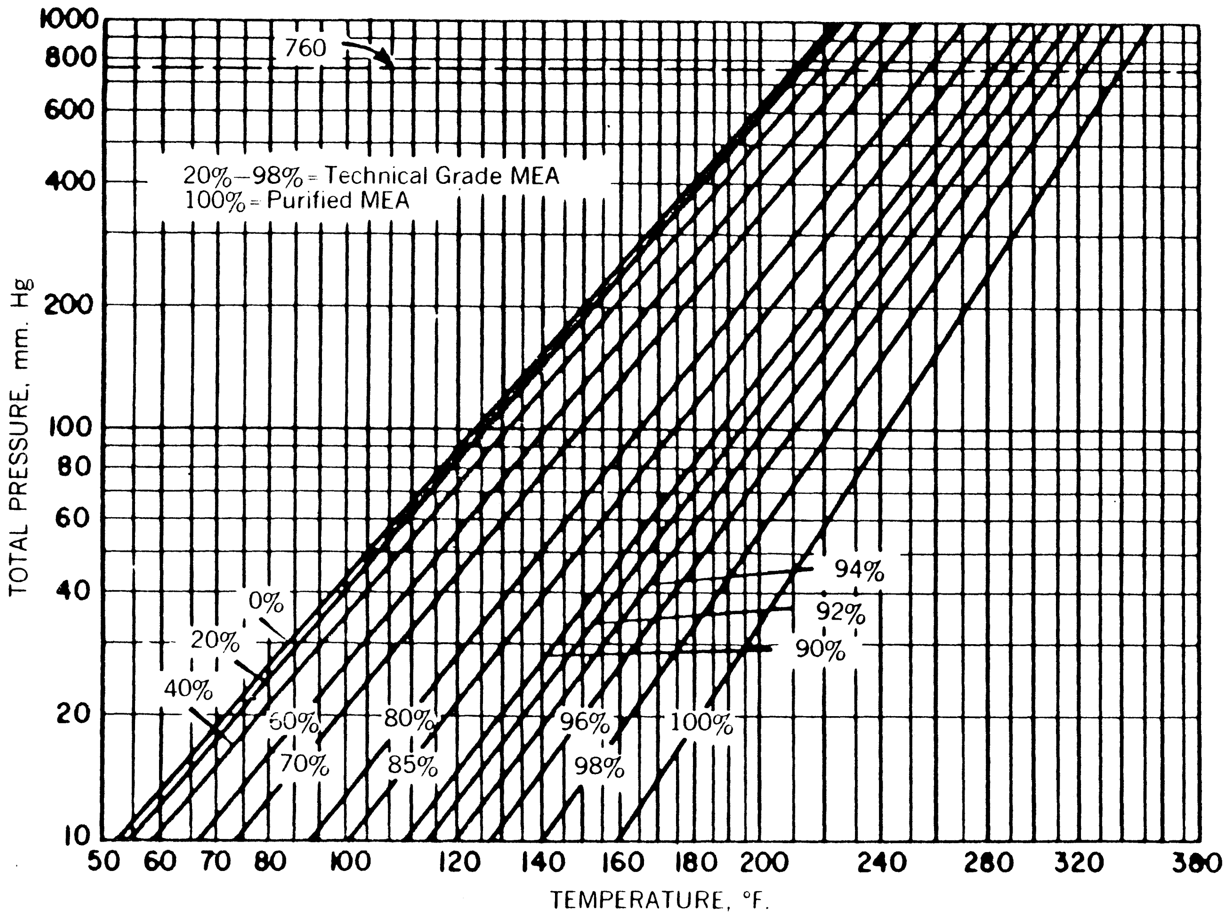

Figure 24. Vapor Pressure of Aqueous MEA Solutions (46)

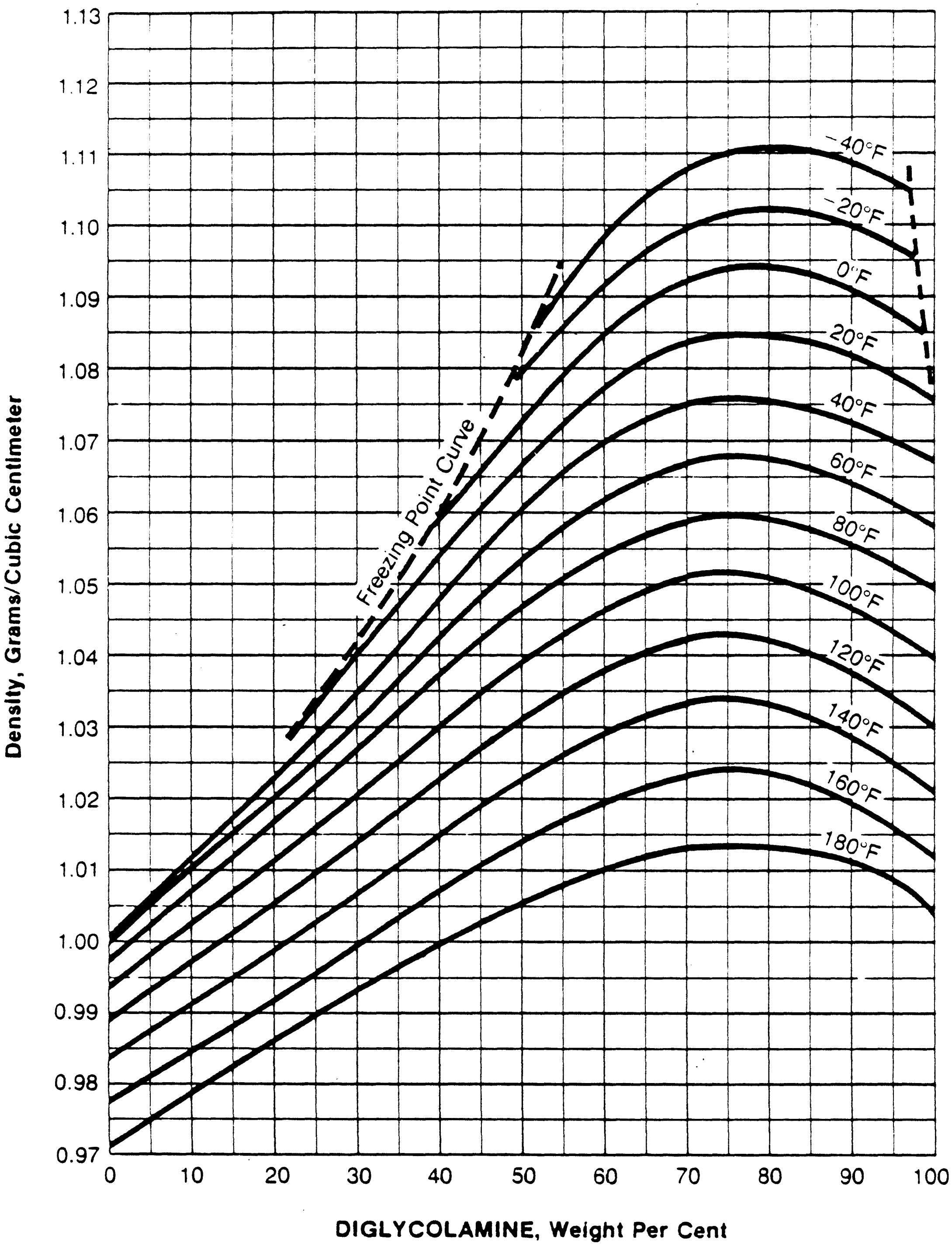

Figure 25. Density of DGA Aqueous Solutions (54)

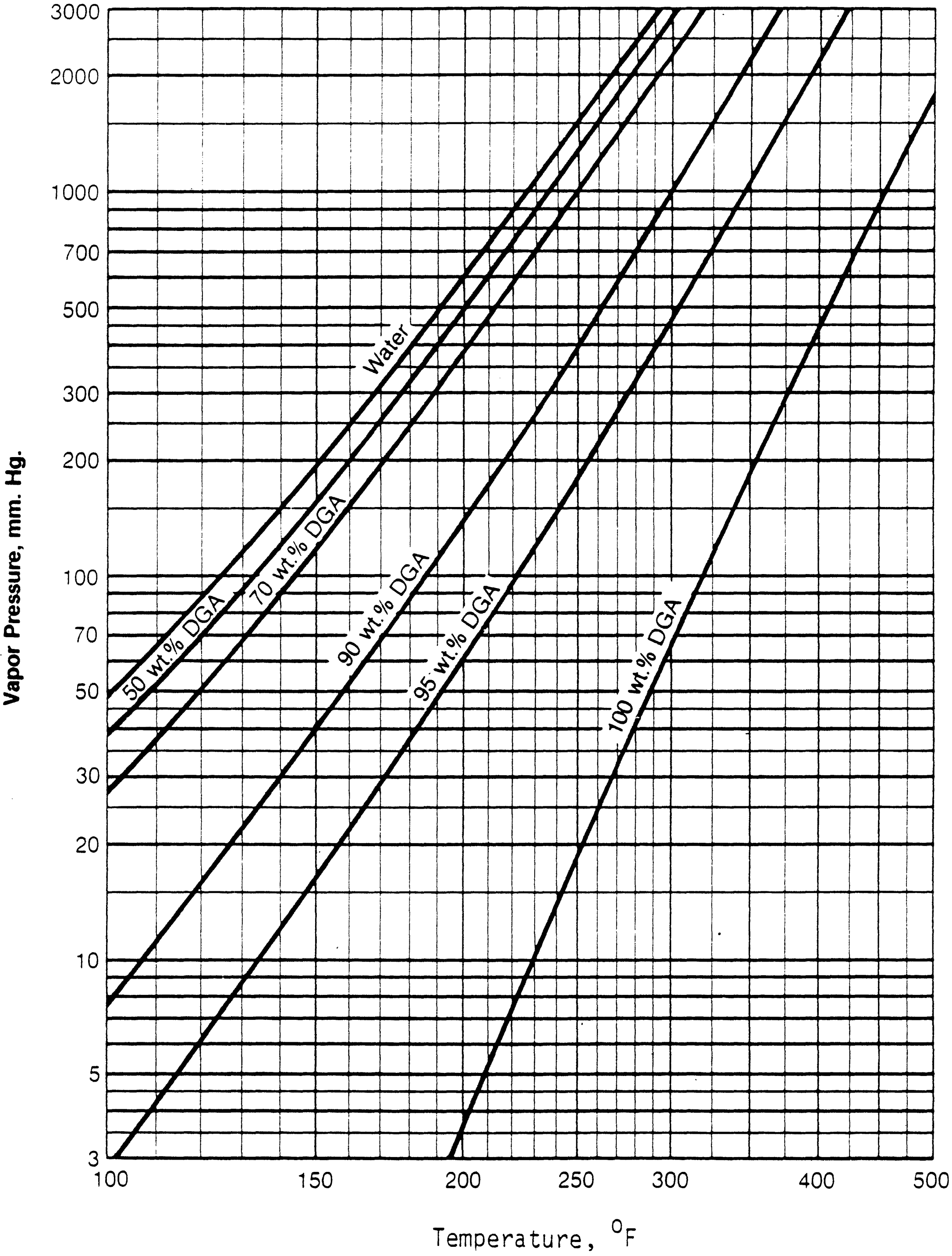

Figure 26. Vapor Pressure of DGA Aqueous Solutions (54)

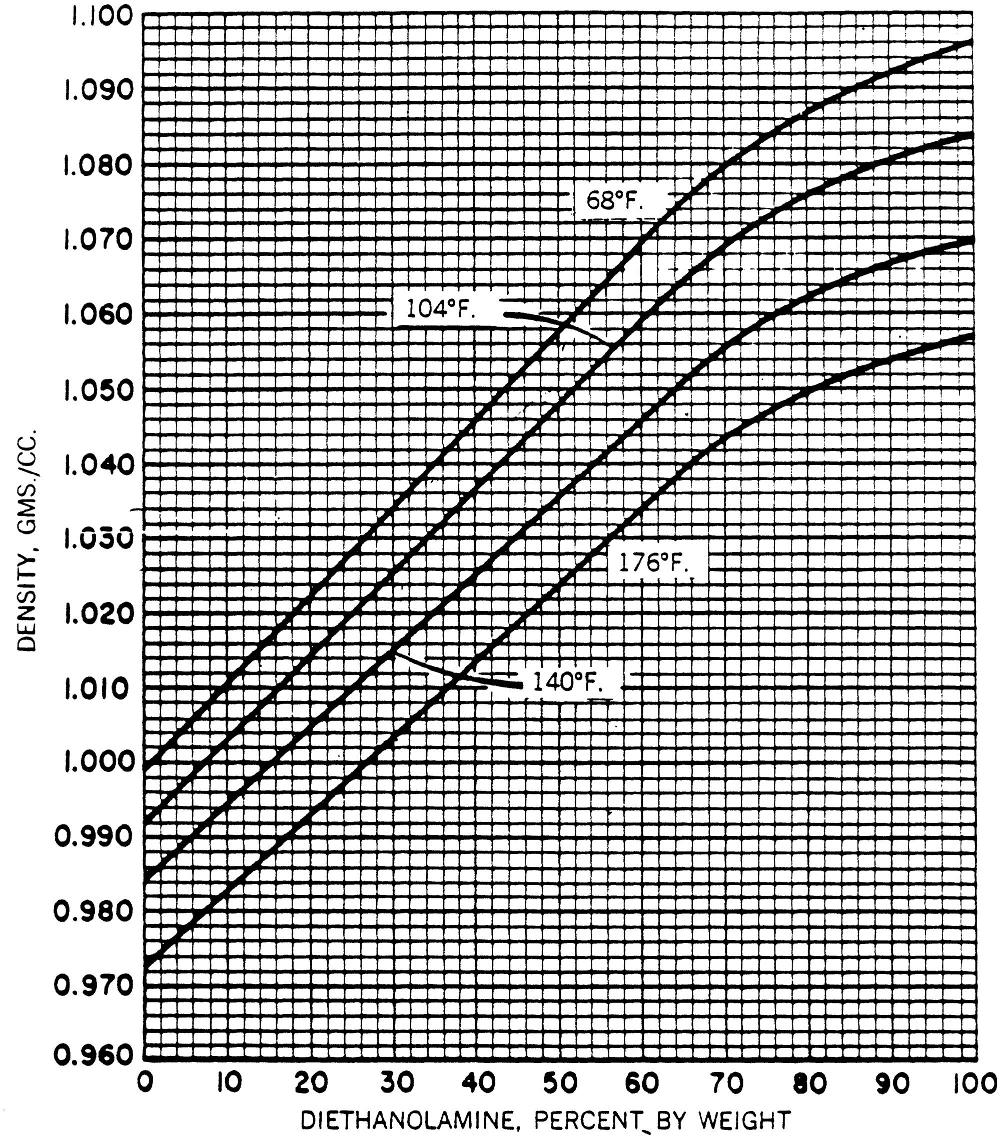

Figure 27. Density of DEA Aqueous Solutions (46)

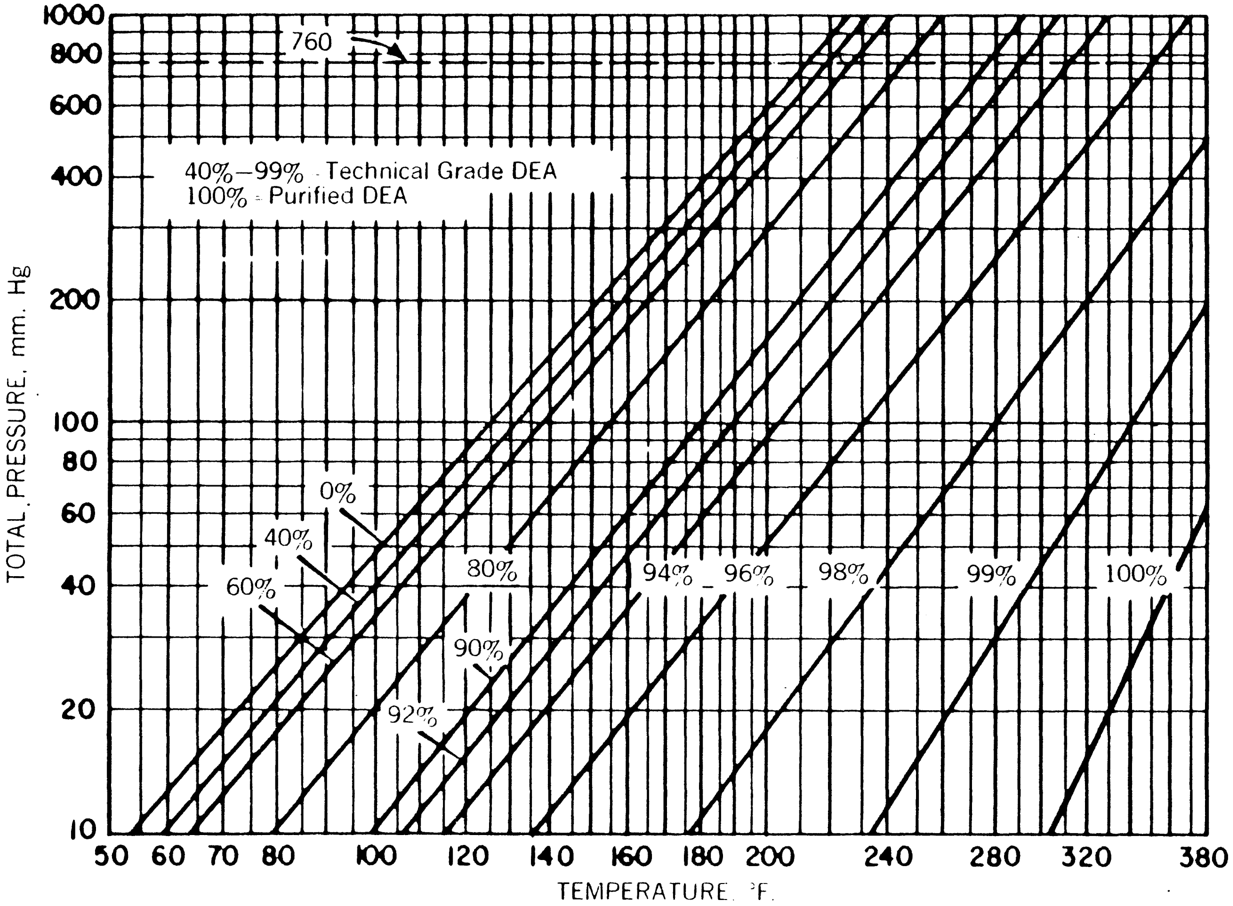

Figure 28: Vapor Pressure of DEA Aqueous Solutions (46)

Density of 20% by weight MDEA solution was measured by F.P.R.I. The smooth data are given by the following equation

$$D(gm/cm^3) = A \, . \, B^{[-(1-T/C)^{2/7}]}$$

where

$A = 0.72859$

$B = 0.65083$

$C = 909.27$

T = temperature in °R

The vapor pressure of the 20% solution was measured by the same apparatus at 100, 150 and 240°F. The results are shown

Temp °F	Solution Vapor Pressure psia
100	0.695
150	3.281
240	24.260

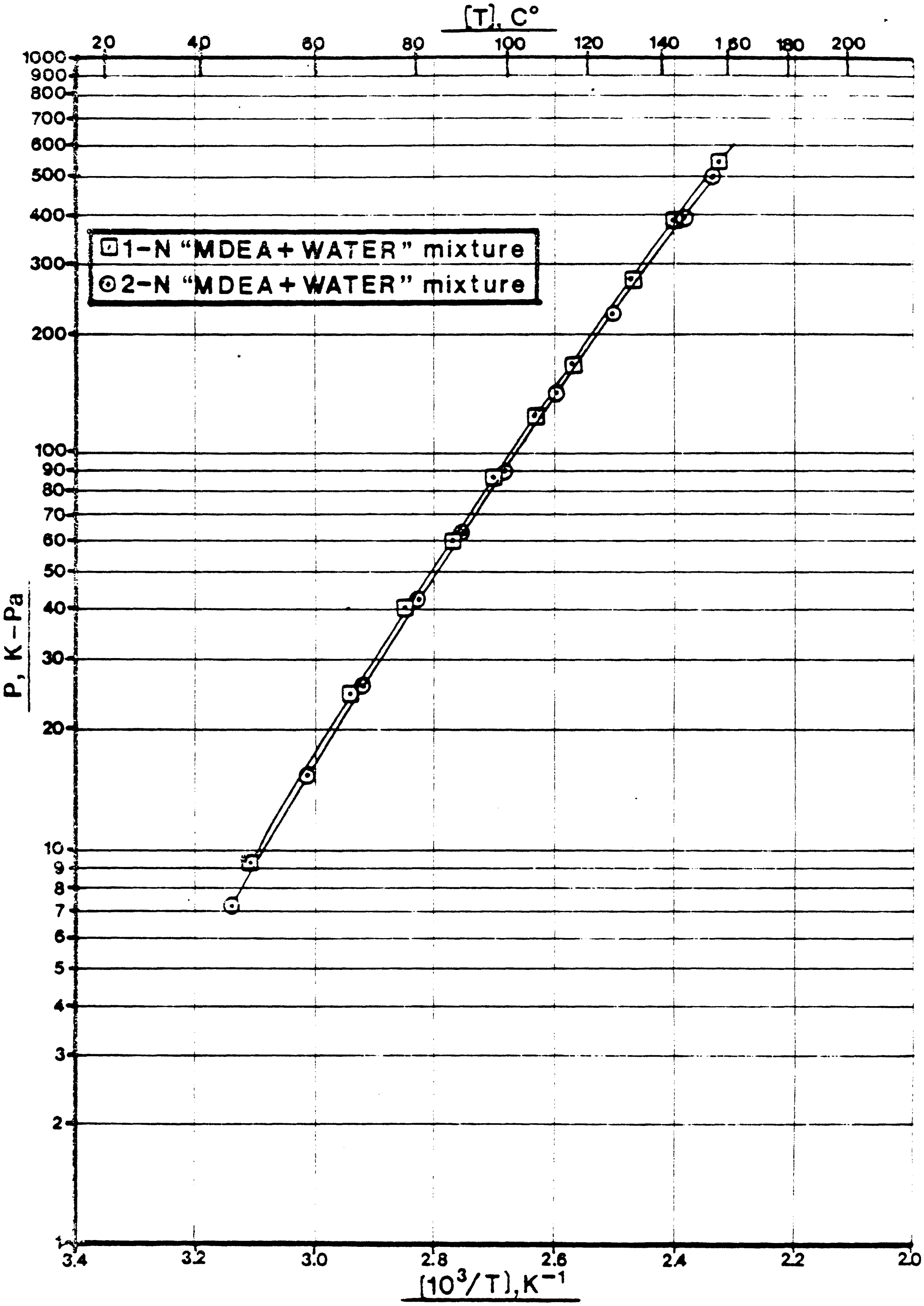

Figure 29: Vapor Pressure of 1 and 2 Normal "Methyldiethanolamine + Water" Mixtures (55)

APPENDIX F

SAMPLE CALCULATION

Sample Calculation

Solubility of H_2S in 1.0 N MDEA at 77°F

Cell volume = 1.0445 liter

Initial pressure = 207.27 psia

Initial solution (water) vapor pressure = 23.76 mm Hg

Initial water mole fraction = 0.0022

Initial H_2S mole fraction = 0.9978

Thus, H_2S mass fraction = 0.9988

From MINI*SIM output, density of the

vapor phase = 1.385 lb/ft^3

Initial mass of H_2S in the cell =

$$1.0445 \text{ liter} \times 3.531466 \times 10^{-2} \frac{\text{ft}^3}{\text{liter}} \times 0.9988 \frac{\text{lbs } H_2S}{\text{lbs vapor}}$$

$$\times 1.385 \frac{\text{lbs vapor}}{\text{ft}^3} = 5.102603 \times 10^{-2} \text{ lbs}$$

Amount of 1.0 N MDEA solution injected = 100 ml.

Final cell pressure = 164.88 psia

Solution vapor pressure at equilibrium = 22.0 mm Hg

Solution mole fraction in vapor phase = 0.0026

H_2S mole fraction in the vapor phase = 0.9974

H_2S mass fraction in the vapor phase = 0.9986

From MINI*SIM output (See Table XXXII), the 1.076562

Vapor phase density after solution injections = 1.070 lb/ft^3

Final mass of H_2S in the vapor phase after injection =

$$(1.0445 - 0.100) \text{ liter} \times 3.531466 \times 10^{-2}$$

$$\times\ 0.9986 \times 1.070 = 3.563956 \times 10^{-2} \text{ lbs}$$

$$\begin{aligned} \text{Dissolved } H_2S &= 5.102603 \times 10^{-2} - 3.56956 \times 10^{-2} \\ &= 1.538647 \times 10^{-2} \text{ lbs} \\ &= 2.048124 \times 10^{-1} \text{ g mole} \end{aligned}$$

Moles of MDEA used =

$$100 \text{ ml solution} \times 1.0213 \frac{\text{g}}{\text{ml}} \times 0.11885 \frac{\text{g MDEA}}{\text{g solution}}$$

$$\times \frac{0.97}{119.16} \text{ g/g mole} = 9.880837 \times 10^{-2} \text{ g mole}$$

where the purity of MDEA is 97%

$$\text{loading} = \frac{2.048124 \times 10^{-1}}{9.880837 \times 10^{-2}} = 2.0728 \frac{\text{mole } H_2S}{\text{mole MDEA}}$$

TABLE XXXII

MINI*SIM FLASH CALCULATION OUTPUT

```
TEMPERATURE=   77.00 DEG F ,PRESSURE=  164.88 PSIA


FEED/PRODUCT RATES ARE LB-MOLS

COMPONENT          FEED              .LIQUID              VAPOR       K
 NAME         MOLS MOL FR        MOLS MOL FR        MOLS MOL FR    VALUE

H2S            100.00   .0909      5.27   .0052      94.73   .9972 190.22139
H2O           1000.00   .9091    999.73   .9948        .27   .0028    .00286

TOTAL         1100.00 1.0000   1005.00 1.0000      95.00 1.0000

H;KBTU     -15161.84-13.783 -15542.81-15.466    380.98   4.010

S;KBTU/R        20.00    .018     15.81    .016      4.18    .044

MOL WT         19.462            18.084            34.036

D;LB/FT3                         62.089             1.070

MASS;LB       21408.2           18174.7            3233.5

MOL % VAP=     8.64;WT % VAP=    15.10;VOL % LIQ=    8.83
```

APPENDIX G

ERROR ANALYSIS

Error Analysis
Maximum Error in Solubility Determinations

High CO_2 Partial Pressure
0-3000 psi gauge
5 psi subdivisions

In determining the pressure a cathetometer was used to read the pressure accurately within a subdivision. The pointer was aligned with its mirror image in each reading to achieve consistency and accuracy. The pressure was easily read to less than 1 psi. However, to calculate the maximum error in the solubility a total deviation of 5 psi was assumed; 2.5 psi in the initial reading and 2.5 psi in the final reading. They were added or subtracted from the actual pressure so as to produce the maximum error in the solubility calculations.

The maximum deviation in the temperature and in the volume of the solution injected were also included. Their effects were counted to produce a maximum deviation in the solubility calculated.

Run 109 B
Solubility of CO_2 in 20% by weight MDEA aqueous solution at 100°F

Initial pressure, P_i = 710.28 psia

Initial temperature, T_i = 100°F

Initial pressure with maximum deviation, P_i^*

$= 710.28 + 2.5 = 712.28$ psia

Initial temperature with maximum deviation,

100.04

$T_i^* = 100 - 0.04 = 99.96^0F$

From MINI*SIM, the initial density of the vapor, $\rho_i^* = 6.972\ \mathrm{lb/ft^3}$

Final pressure after injection, $P_f = 721.28$ psia

Final temperature, $T_f = 100°F$

722.78

Final pressure with maximum deviation = 721.28 - 2.5 = 718.78 psia

99.96

Final temperature with maximum deviation = 100 + 0.04 = 100.04°F

From MINI*SIM, the final density of the vapor, $\rho_f^* = 7.053\ \mathrm{lb/ft^3}$

Initial mass of CO_2, M_i^* =

$$1.0296 \text{ liter} \times 3.531466 \times 10^{-2} \frac{\text{ft}^3}{\text{liter}} \times 6.972 \frac{\text{lbs vapor}}{\text{ft}^3}$$

$$\times\ 0.9996 \frac{\text{lb } CO_2}{\text{lb vapor}} = 2.530034 \times 10^{-1} \text{ lbs } CO_2$$

Solution injected = 150 ml at 68°F

Maximum error in measuring 50 ml = ± 0.1 ml

Maximum error in the volume injected = ± 0.3 ml

Maximum solution injected = 150.3 ml

Volume injected at 100°F = 151.5 ml

Remaining CO_2 in the vapor phase after injection, M_f^*

$= (1.0296 - 0.1515)\ 3.531466 \times 10^{-2} \times 7.053 \times 0.9996$

$= 2.1862466 \times 10^{-1}$ lbs

Dissolved $CO_2 = 3.4775682 \times 10^{-2}$ lbs

$= 3.5841818 \times 10^{-1}$ gmole

$$\text{MDEA used} = 150.3 \text{ ml} \times 1.0187 \ \frac{\text{g sol'n}}{\text{ml}} \times \frac{0.2 \text{ g MDEA}}{\text{f sol'n}}$$

$$\times \frac{0.97}{119.16 \text{ g/gmole}} = 2.4927374 \times 10^{-1} \text{ gmole}$$

$$\text{Loading} = \frac{3.58418 \times 10^{-1}}{2.4927374 \times 10^{-1}} = 1.4378 \text{ mole } CO_2\text{/mole MDEA}$$

compare to 1.3359

Maximum % deviation = 7.63%

Low CO_2 Partial Pressure
30" Hg Vac-0-60 psi gauge
0.2 psi subdivisions (0 - 60 psi range)
1" Hg subdivisions (30" - 0 range)

In determining the maximum error in the solubility a similar procedure is taken as discussed before. The maximum error associated with the pressure reading in the above atmospheric region is 0.1 psi. The maximum error in the subatmopsheric region is 0.5" Hg.

Run 112 C
Solubility of CO_2 in 20 by weight
MDEA aqueous solution at 100°F

Initial pressure, P_i = 69.61 psia

Initial temperature, T_i = 100°F

Initial pressure with maximum possible deviation, P_i^*

= 69.61 + 0.1 = 69.71 psia

Initial temperature with maximum deviation, T_i^*

= 100.0 - 0.04 = 99.96^{0}F

From MINI*SIM, the initial vapor density, ρ_i^*

= 0.518 lb/ft^3

Final pressure after injection, P_f^* = 14.5" Hg Vac

= 7.24 psia

Final pressure with maximum deviation, P_f^*

= 14.5" + 0.5" = 15.0" Hg Vac

= 6.99 psia

Final temperature with maximum derivation, T_f^*

= 100 + 0.04 = 100.04°F

From MINI*SIM, the density of the vapor phase, ρ_f^*

= 0.048 lb/ft^3

Initial mass of CO_2, M_i^* =

$1.0528 \times 3.531466 \times 10^{-2} \times 0.518 \times 0.9959$

$= 1.9179903 \times 10^{-2}$ lbs

Solution injected = 150 ml at 68°F

Maximum error = -0.3 ml

Solution injected = 149.7 ml at 68°F

= 150.9 ml at 100°F

Remaining CO_2 in the vapor phase after injection, M_f^* =

$(1.0528 - 0.1509)\ 3.531466 \times 10^{-2} \times 0.048 \times 0.9568$

$= 1.4627692 \times 10^{-3}$ lbs

CO_2 dissolved = 1.7717134×10^{-2} lbs

= 1.8260297×10^{-1} gmole

MDEA used = $149.7 \times 1.0187 \times 0.2 \times \frac{0.97}{119.16} = 2.4827863 \times 10^{-1}$ gmole

Loading = $\frac{1.8260297}{2.4827863}$ = 0.7355 mole CO_2/mole MDEA

compare to 0.7250

maximum % deviation = 1.45%

VITA

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Doctor of Philosophy

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