PHYSICAL SOLUBILITY OF HYDROGEN SULFIDE AND CARBON DIOXIDE IN ALKANOLAMINE SOLUTIONS

Thesis Approved:

R. N. Maddox
Thesis Advisor

Arland H. Johannes

Gary L. Foutch

C E [illegible]

Norman N. Durham
Dean of the Graduate College

PREFACE

A method is developed to measure directly the physical solubilities of acid gases, hydrogen sulfide and carbon dioxide, in aqueous alkanolamine solutions. The method is based on protonating alkanolamine solutions with hydrochloric acid prior to their contact with acid gases. Hydrogen sulfide and carbon dioxide physical solubilities in 20, 35, and 50% by weight protonated DEA aqueous solutions were measured. The solubility measurements were made at acid gas partial pressures to 1000 psia and temperatures of 80, 150, 240°F. The solubility of nitrous oxide in water and in protonated DEA solution was also determined at 80°F.

I wish to express my sincere gratitude to my thesis advisor, Dr. Robert N. Maddox, for his guidance, advisement and encouragement. I also thank the committee members who participated in one or all of my Ph.D. examinations, Dr. Arland J. Johannes, Dr. Gary L. Foutch, Dr. Kenneth J. Bell, Dr. Faye C. McQuiston, and Dr. C. Eric Price.

I appreciate the acceptance of Dr. Johannes to oversee the completion of the thesis during Dr. Maddox' absence. Mr. Erardo M. Elizondo's friendship and help in every way is gratefully acknowledged.

I like to thank the faculty and staff of the School of Chemical Engineering for their help and encouragement. My graduate colleagues' help and friendships are acknowledged. Special thanks are due to Dr. Yousef H. Zurigat and Mr. Tushar K. Ghosh for their constant help and encouragement.

Thanks are due to the School of Chemical Engineering and the Gas

Processors Association for their financial support.

I am very thankful to Daleene Caldwell for typing this thesis on short notice and for the overtime to complete it.

The moral and financial support throughout my education by my parents, brothers and sisters deserves my sincere gratitude and appreciation.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

Table Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Removal of the acid gases, hydrogen sulfide (H_2S) and carbon dioxide (CO_2), from natural gas is commonly accomplished by absorption in a suitable solvent. The process is classified as either physical absorption or physical absorption followed by chemical reaction (29). In the first case, the solvent dissolves the acid gases. Typical physical solvents are selexol and propylene carbonate (3, 29). In the second case the solvent contains components that react with the acid gases after they dissolve or dissociate in the liquid phase. Aqueous alkanolamine solutions, which are employed in many processes, fall under the second category. Their introduction into the gas sweetening industry is credited to Bottoms (9) who was granted a patent in 1930 covering their use for sweetening natural gas.

All alkanolamines have at least one hydroxyl group and one amino group which provide the necessary alkalinity for their reactions with acid gases (21). CO_2 reacts to form a weak acid in aqueous solution, while H_2S dissociates to give hydrogen and acid sulfide ions. When the acid gas is in contact with the weak base (amine solution), they combine chemically to form an acid-base complex called a salt (28).

Two approaches have been made to model the absorption of CO_2 and H_2S in aqueous alkanolamine solutions: the mass transfer approach and the reaction equilibrium approach. In both approaches, the physical solubility of these gases in aqueous alkanolamine solution is needed.

The reactivity of CO_2 and H_2S with alkanolamine makes the direct measurement of their physical solubility impossible. This led many researchers in this field (7, 10, 13, 16, 18, 22-23, 30, 33-35, 38-39) to use the solubility of nitrous oxide (N_2O) in water and in aqueous alkanolamine solution to estimate CO_2 physical solubility in these solutions. This has been referred to as the "N_2O analogy". N_2O has similar molecular properties to those of CO_2. Also for the lack of information on H_2S physical solubility, the "N_2O analogy" has been employed to estimate H_2S physical solubility (39).

In an effort to correlate the reaction equilibrium of the H_2S-CO_2-water-alkanolamine system, several models have been proposed (4, 11, 19, 20). In all of these models, since the physical solubility of CO_2 and H_2S in the aqueous alkanolamine solutions is not known, it has been assumed to be the same as for pure water.

The objectives of this study were:

1. Develop a method to measure directly the physical solubility of CO_2 and H_2S in aqueous alkanolamine solutions.
2. Measure CO_2 and H_2S physical solubilities in aqueous diethanolamine solutions. The solubility measurements were made at acid gas partial pressure to 1000 psia and temperatures of 80, 150, and 240°F. These conditions cover the range of conditions under which gas-treating plants operate.
3. Investigate whether CO_2 and H_2S physical solubilities in aqueous diethanolamine solutions are the same as in pure water.

4. Check the validity of the "N_2O analogy" under conditions similar to those used commercially and other than the conditions (25°C, 1 atm) at which the analogy was inferred.

CHAPTER II

LITERATURE SURVEY

The chemical reaction equilibrium models, the experimental techniques used to measure the physical solubility of CO_2 and H_2S in reacting and non-reacting solvents, and the consistency method used in smoothing the data, are reviewed in this chapter.

Chemical Reaction Equilibrium Models

According to Maddox (27), many attempts have been made to model the alkanolamine-acid gas equilibrium to make the process and design of gas treating plants easier. Most of these attempts postulate that certain reactions occur in solution and propose a thermodynamic model for the reaction equilibrium. The first of these attempts was made by Atwood et al. (4). To model the H_2S-H_2O-ethanolamine system, and to estimate the amount of H_2S dissociated, they assumed that solubility of free, physically dissolved, hydrogen sulfide in an amine solution is the same as that in water. Later Danckwerts and McNeil (11) studied the equilibrium of CO_2-water-ethanolamine solutions. Those two models were concerned with only one acid gas and the aqueous ethanolamine solution.

According to Vaz (37), Klyamer et al. (20) extended the models to the CO_2-H_2S-water-ethanolamine system. Their thermodynamic equilibrium constants were expressed in terms of the average ion activity coefficients and the chemical species concentration. Knowledge of the average ion activity coefficients is required to determine the concentration of the species in solution. This led Kent and Eisenberg (19) to modify previous attempts, mainly the Danckwerts-McNeil approach. They proposed a set of equations that describe the H_2S-CO_2-water-ethanolamine system at equilibrium. With RR'NH representing an ethanolamine, these equations are:

$$RR'NH_2^+ \overset{K_1}{\rightleftharpoons} H^+ + RR'NH \tag{1}$$

$$RR'NCOO^- + H_2O \overset{K_2}{\rightleftharpoons} RR'NH + HCO_3^- \tag{2}$$

$$H_2O + CO_2 \overset{K_3}{\rightleftharpoons} H^+ + HCO_3^- \tag{3}$$

$$H_2O \overset{K_4}{\rightleftharpoons} H^+ + OH^- \tag{4}$$

$$HCO_3^- \overset{K_5}{\rightleftharpoons} H^+ + CO_3^= \tag{5}$$

$$H_2S \overset{K_6}{\rightleftharpoons} H^+ + HS^- \tag{6}$$

$$HS^- \overset{K_7}{\rightleftharpoons} H^+ + S^= \tag{7}$$

$$P_{CO_2} = H_{CO_2} [CO_2] \tag{8}$$

$$P_{H_2S} = H_{H_2S} [H_2S] \tag{9}$$

where K_1 through K_7 are the equilibrium constants for the reactions in equations (1) through (7). Even though the proposed reactions by Kent and Eisenberg account for all the species in the solution, they do not describe the reaction between CO_2 and amines correctly. This reaction has been found to occur in two steps, the insertion of CO_2 into the N-H bond followed by the very rapid protonation of another amine molecule (28).

$$CO_2 + R_2NH \longleftrightarrow R_2HN{:}CO_2 \longrightarrow R_2NCOOH \qquad (10)$$

$$R_2NH + HOOCNR_2 \longrightarrow [R_2NH_2^+][^-OOCNR_2] \qquad (11)$$

In the Danckwerts-McNeil, Klyamer et al. and Kent-Eisenberg models, the equilibrium partial pressures of CO_2 and H_2S in the gas phase are related to the free concentration of CO_2 and H_2S in solution by a Henry's law relationship as shown above in equations (8) and (9). The Henry constants for CO_2 (H_{CO_2}) and for H_2S (H_{H_2S}) in amine aqueous solutions were assumed to be the same as the Henry constants for these gases in water. Details of these models and how they are applied are given by Vaz (36) and Loh (26).

Kent and Eisenberg tested the performance of their model for only two amines (MEA and DEA) and for limited concentration of the amines and for limited acid gas loadings. Vaz (36), Loh (26), Batt et al. (5), Moshfeghian et al. (31) and Elizondo (15) have extended and improved the application of the Kent and Eisenberg model to cover the other amines with wider ranges of concentration, acid gas partial pressure and temperature.

Experimental Techniques for Physical Solubility Studies

Several experimental techniques, which allow short contact-time (about 10^{-3} sec.) between gas and liquid, are summarized by Danckwerts (12). These techniques are the rotating drum, the moving-band absorber, the wetted-sphere column, the laminar jet and the wetted-sphere apparatus. The short contact-time provided by these techniques is not short enough to avoid the fast reactions (reaction times are typically of the order of 10^{-13} sec.) between acid gases and amines (3, 10). This inability led Clarke (10) to suggest the use of nitrous oxide to estimate CO_2 physical solubility.

Consistency Method

A consistency method developed by Elizondo (15), was used to smooth the experimental data. In this method, plotting the common logarithm of the acid gas partial pressure divided by the acid gas loading against the loading gives a straight line relationship as follows:

$$\log_{10} \left(\frac{P_i}{\beta_i}\right) = a + b\beta_i \qquad (12)$$

where a and b are the intercept and slope of the straight line equation, P_i and β_i are the acid gas partial pressure and loading, respectively. This method was applied to all of the raw data obtained in this study to get smoothed curves when plotting the acid gas partial pressure versus the acid gas loading. This will be shown in Chapter V.

CHAPTER III

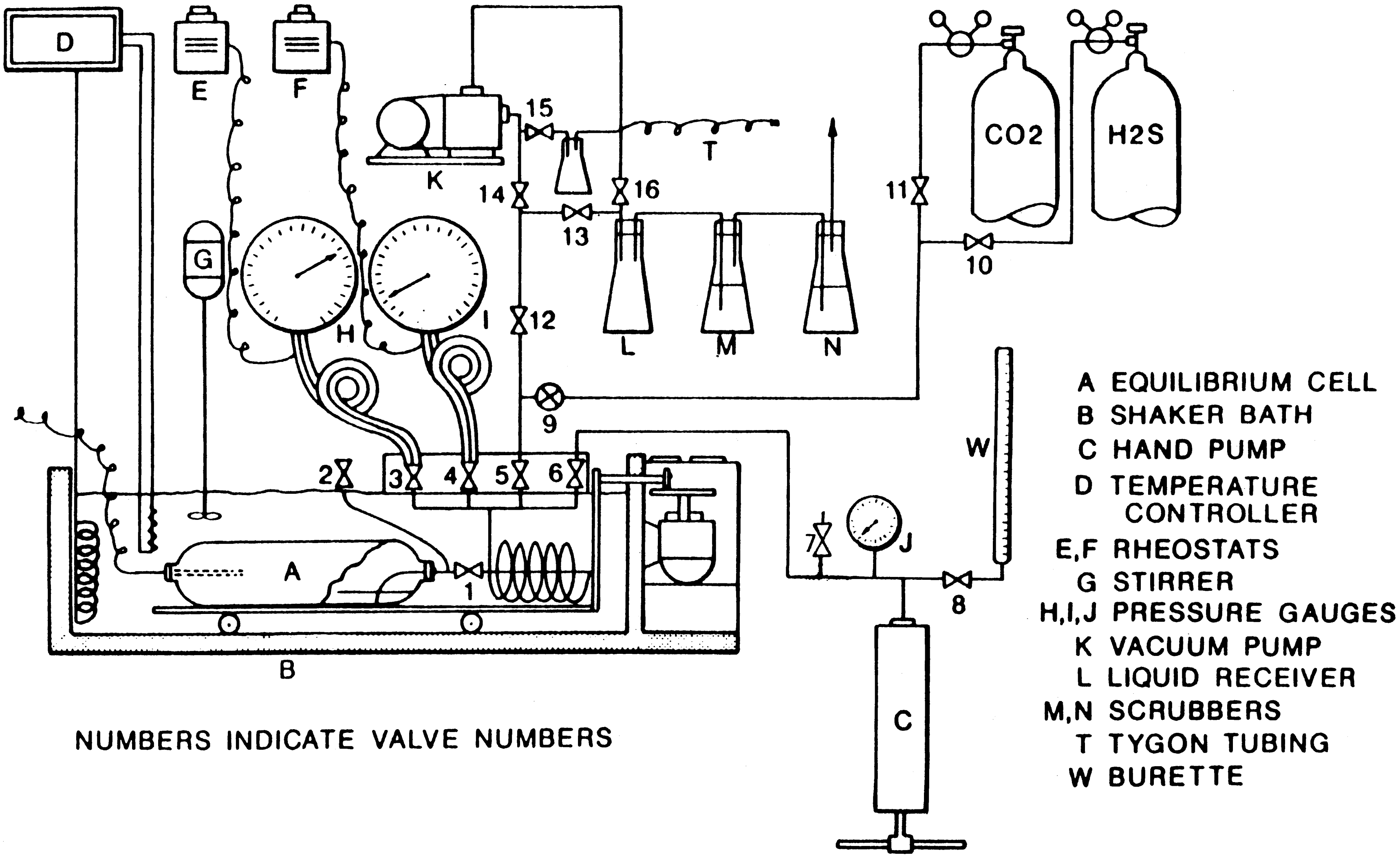
EXPERIMENTAL APPARATUS

The apparatus used here is an improvement of a similar one suggested by Woertz (40), and used by Akashah (2), Adeyiga (1) and Bhairi (6). Akashah and Adeyiga reported CO_2 and H_2S solubilities in physical solvents, while Bhairi reported CO_2 and H_2S solubilities in alkanolamines solutions. A schematic diagram of the apparatus is shown in Figure 1.

The apparatus consists of a constant temperature shaker bath housing the equilibrium cell, gas and liquid feed lines that are attached to the cell, pressure gauges, a thermocouple that is inserted inside the cell, and tubing that connects the equilibrium cell to the scrubbing flasks. Description of the major parts is given below:

Constant Temperature Shaker Bath

The bath made by Precision Scientific, GCA (Model 50 Cat. #66802) is rectangular shaped with a capacity of 9 gallons. It has a built-in reciprocal motion which shakes the shaker tray and a variable speed tachometer that indicates 20 to 200 oscillations per minute. The stroke length of the shaker tray can be adjusted from 0.5 to 1.5 inch per cycle. To keep the temperature constant in the bath, two immersion heaters made by Watlow (Model 8444, Catalog #G11EX4A) were connected through a rheostats to a Fisher temperature controller. The controller



NUMBERS INDICATE VALVE NUMBERS

Figure 1. Schematic Diagram of the Apparatus Used (6).

(Model 44, Catalog #15-177) has a temperature range of -40 to 300°F and was able to control the bath temperature to ±0.5°F when working at 80°F and ±1°F when working at 150 - 240°F. An electric stirrer was used to insure temperature uniformity throughout the bath. Polyalkylene glycol (supplied by Union Carbide) was used as the bath fluid.

Equilibrium Cell

The equilibrium cell, made by Whitey (304-HDF4), is a stainless steel cylinder of 1010 cc volume. The volume with glass beads inside was determined by displacement of distilled water at room temperature. The cell has two 1/4" ports. One is connected to a 60" long coil of 1/16" stainless steel tubing. This coil allows the cell to be rocked while connected to a head that contains four valves. Two of the valves are connected to the pressure gauges, and the other two are used for gas and liquid charging. In the second port, a 1/8" stainless steel closed end tubing supplied by Omega is installed. This tubing extends 6" inside the cell. The tubing protects a copper-constantan thermocouple that is inserted inside it. The tubing also serves to prevent any leakage from the cell. The calibration data for the thermocouple are in Appendix B.

Liquid Feed System

The liquid amine feed system is a 100 ml burette, in which the solution under study is placed, is connected to a 3-way junction. One of the junctions is connected to a high pressure displacement pump made by High Pressure Equipment Company (Model 87-6-5), with 60 ml capacity. The other side is connected to the equilibrium cell.

The amount of liquid injected via the high pressure pump is determined by taking the difference between the initial and final reading of the graduated burette.

Gas Feed System

The gas feed system consists of CO_2, H_2S and N_2O cylinders connected to the equilibrium cell through 1/8" tubing. Each cylinder is equipped with a pressure regulator and 1/8" valve. The desired pressure was attained by a needle metering valve. The system is connected to a 1/3 hp Welch Dow-Seal vacuum pump (Model 1392) which was used to evacuate the cell before injecting the desired gas. The guaranteed vacuum pressure by the manufacturer on the pump is 2×10^{-4} Torr. The oil was changed at least every 45 days.

Pressure Gauges

Two pressure gauges were used depending on the system pressure. For the low pressure measurements, a 0-300 psi Heise gauge (Solid Front-B-45141R) was used. The diameter of the dial is 16" with 0.2 psi subdivisions. The internal volume of the Bourdon tube is 19.4 ml. The accuracy is reported to be 0.1% of full scale reading throughout the entire range.

The high pressure measurements were taken by a 0-5000 psi Heise gauge (Solid Front-C-52143). The diameter of the dial is 16" with 5 psi subdivision. The internal volume of the Bourdon tube is 10.3 ml. The accuracy is also 0.1% of full scale reading throughout the entire range. Both gauges are designed to tolerate full vacuum.

The pressure gauges were calibrated using a dead weight tester

(Ruska Model 2400). The gauges were tested periodically to check the calibration. The calibration data are in Appendix C.

Auxiliary Equipment

The auxiliary equipment consisted of a potentiometer, a vacuum pump, sodium hydroxide scrubbers, glass beads, a barometer, a digital thermometer, heating tapes, rheostats, an electric balance, and valves and fittings.

The potentiometer is a Leeds and Northrup Company (Model #8686). It has a range of -10.0 to 100.1 millivolts with the smallest division being 0.005 millivolts. It is capable of measuring potential to within a temperature of 0.04°F. The sodium hydroxide scrubbers were two 1 liter plastic Ehrlenmeyer flaskes connected in series. The solution used was 15% by weight NaOH. The discharged gas was bubbled through the solution. To prevent sucking the solution into the equilibrium cell, an empty flask was put in the line ahead of the scrubbers.

The digital thermometer made by Omega, type T, (Model #2160A) was used as a quick check when setting the temperatures of the bath and the lines leading to the pressure gauges. Two 24" long tapes made by Sargent Welch (Briskheat 3/4") were used to heat the lines connecting the pressure gauges to the equilibrium cell. Rheostats made by Aloe Scientific, 110 V, were used to control the temperature of the tapes on the lines to the pressure gauges.

Valves and fitting were all 1/8" stainless steel made by Parker C.P.I.

Materials

The compressed gases were CO_2 and H_2S supplied by Matheson Co., Inc. and N_2O supplied by Buriten Bennet. Minimum purities of the gases were given as: carbon dioxide and hydrogen sulfide 99.5%; nitrous oxide 99.97%.

DEA was obtained from two companies; Aldrich Chemical Company with 97% purity and Kodak Chemical Company with 99.5% purity. The diethanolamine and the acid gases were used as received without further purification.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The procedure followed in amine protonation, measuring the experimental data, and calculating the acid gas solubility is described in this chapter.

Amine Protonation

Hydrochloric acid solution (~ 12N) made by Fisher Scientific Company was used for diethanolamine protonation. The protonation eliminated diethanolamine reactivity with the acid gases. To cover the range of diethanolamine concentrations used commercially, protonated 20, 35, and 50% by weight DEA aqueous solutions were prepared and used in the measurements. The amount of pure DEA, distilled water and HCl solution needed to prepare each concentration was determined from acid-base standard calculations. Small adjustment to the calculations were made to get the desired pH.

Operational Procedure

The following steps were followed in carrying out the experiment:

1 - The equilibrium cell was cleaned with distilled water before starting a new run and dried using the vacuum pump. Glass beads (1/4" diameter) were then placed inside the cell to improve the liquid mixing.

2 - Place the equilibrium cell in the bath and attach it to the system. Heat the bath (with polyalkylene glycol as the heat transfer fluid) to the desired temperature. Also heat the lines connecting the equilibrium cell to the pressure gauges using heating tapes and rheostats.

3 - Turn on the shaker and the stirrer.

4 - Admit the desired acid gas into the system with valves 1,3 or 4,5,9 and 10 or 11 open and 2,6 and 12 close, to a pressure of about 100 psi.

5 - Check for leaks using soap, then vent the system through the scrubbers with valves 5,12 and 13 opened and 9,14 and 16 closed. Evacuate the system with the vacuum pump.

6 - Repeat steps 4 and 5 three times. This will insure an air free system.

7 - Charge the system with the acid gas to the desired pressure using the metering valve (#9). Close valves 5,9,10 or 11, 12 to isolate the equilibrium cell from the scrubbing and the gas systems.

8 - Leave the system, after the temperature and pressure stabilize, for a few hours with periodical recording of the temperature and pressure to insure a leak free system. The system was left pressurized for 6 to 10 hours when working with CO_2 and for 1 to 2 hours when working with H_2S.

9 - Place the protonated amine solution in the clean burette with valve 8 closed. Evacuate the lines between valves 6 and 8 and the hand pump by connecting the tygon tubing to valve 7. Open valve 8 to fill the lines with the solution with valve 7 closed. Evacuate the lines again (to make sure the lines are cleaned), then fill with

the solution. The system is now ready for solution injection.

10 - Withdraw the predetermined amount of solution from the burette using the hand pump. Close valve 8, then pressurize the solution to a pressure higher than the pressure inside the equilibrium cell. This will prevent the gas from flowing into the liquid feed system as valve 6 is opened. Close valves 3 and 4 to prevent the solution from entering the pressure gauges. Open valve 6 and introduce the solution to the equilibrium cell.

11 - As the introduction of the solution is over, close valve 6, then open valve 8. Record the final reading on the burette, to determine exactly the amount of solution injected.

12 - Wait for a few minutes before opening valve 3 or 4. The higher pressure in the lines to the pressure gauge (only when H_2S is the acid gas) will force the small amount of solution out of the coil into the cell. When CO_2 or N_2O is the gas, the pressure in the cell increased after the injection of either the protonated DEA solution or water.

13 - Wait for a few hours, but record the pressure and temperature on a regular basis. When equilibrium is reached, no change in pressure will be observed.

14 - In some cases, another injection of fluid can be made to get another equilibrium point. Injection to get another equilibrium point can only be done when working at high pressure (above 400 psi) and the gas is CO_2 or N_2O. At these conditions, injecting liquid, increases the pressure (~ 100 psi for injecting ~ 200 ml), then another equilibrium point can be taken. The increase in pressure is due to the reduction of volume as more liquid is

injected and the low solubility of these gases in water or in protonated DEA solution.

15 - Discharge the gas by opening valves 5, 12 and 13. If H_2S is in use, fill the scrubbers to about 2/3 with 15% by weight sodium hydroxide solution. Evacuate the system with the vacuum pump. Introduce nitrogen into the cell and evacuate for three times before opening it to the room. Remove the cell from the bath and clean it with distilled water. Clean the lines to the pressure gauges and the bourdon tube with acetone with the aid of the vacuum pump.

Determination of Experimental Solubility

The solubility of the acid gas in the protonated DEA solution or in water was determined by mass balance. The amount of acid gas dissolved is determined once the cell volume, gas temperature and pressure before and after the injection of the solution are known. The SRK equation of state is used to calculate the density of the vapor phase. Other necessary data to determine the solubility were:

1 - solution vapor pressure at the equilibrium temperature,

2 - the barometric pressure,

3 - weight percent of amine in solution,

4 - amount of solution injected, and

5 - density of the solution at room temperature and at the equilibrium temperature.

The following assumptions were made in the calculations:

1 - protonated DEA solution density was the same as DEA solution density,

2 - the liquid was assumed incompressible,

3 - the volume of the dissolved acid gas does not change the liquid volume, and

4 - in calculating the vapor phase density, only water vapor was assumed to be present with the acid gas above the liquid, even though the experimental vapor pressure of the amine solution was used. This is a reasonable assumption, since the vapor pressure of the amines are very small compared to that of water. Physical properties of DEA solution used in the calculations are presented in Appendix D.

A detailed sample calculation is presented in Appendix E. Error analysis is shown in Appendix F.

CHAPTER V

RESULTS AND DISCUSSION

This chapter is divided into three sections. The first section deals with the experimental solubility data and how the data was smoothed. The second section discusses the treatment applied to the data to investigate the relationship between the solubility of CO_2 and H_2S in water and in aqueous DEA solutions. In the third section, the solubility of N_2O in water and in protonated DEA solution is investigated.

Solubility Data

Data Smoothing

The consistency method described in Chapter II was used to smooth the raw experimental data. Figures 2 and 3 show the solubility of CO_2 and H_2S in 35% by weight protonated DEA aqueous solution at 80°F. As can be seen, plotting acid gas partial pressure divided by the acid gas loading in the solution against the loading on a semi-log coordinate gives a straight line. The straight line equation obtained from such plots was used to calculate the partial pressure for a given loading. The solid lines in all of the subsequent figures are obtained using this method.

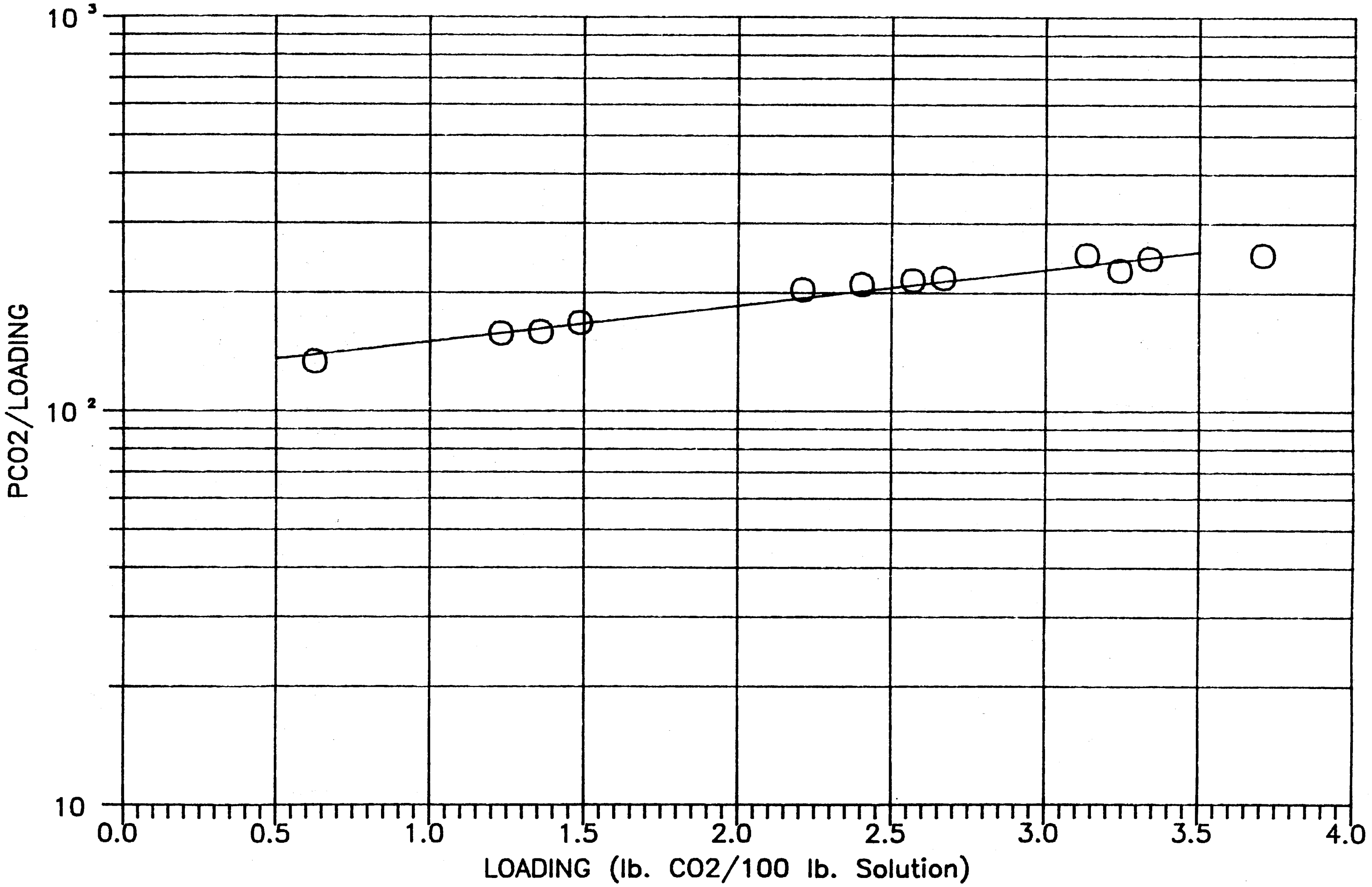


Figure 2. Data Consistency Test for CO2 Solubility in Protonated (pH=7.3) 35% by Weight DEA Aqueous Solution at 80 F.

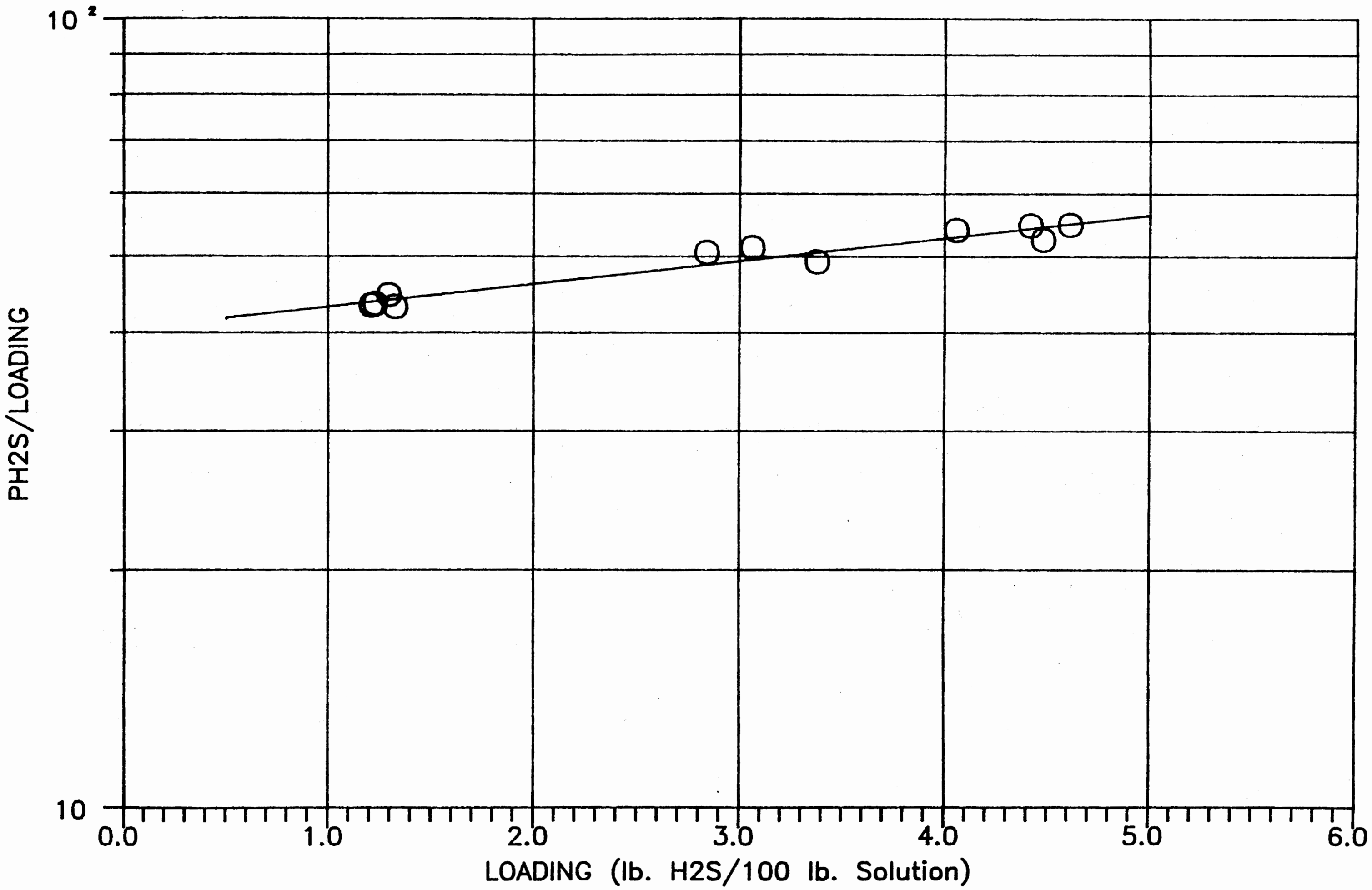


Figure 3. Data Consistency Test for H2S Solubility in Protonated (pH=7.3) 35% by Weight DEA Aqueous Solution at 80 F.

Experimental Solubility Data

Before taking any measurements for acid gases physical solubility in aqueous diethanolamine, the solubility of CO_2 and H_2S in water at 80°F were determined. This was done to ensure that the procedure followed in carrying out the experiment and the method of calculating the acid gas solubility (based on mass balance), as explained in Chapter IV and shown in Appendix F, were correct. The partial pressure of CO_2 ranged from 115.4 to 782.2 psia and H_2S partial pressure ranged from 70.9 to 240.3 psia. The results of these measurements are shown in Tables XV and XVI and Figures 4 and 5. The literature data for the solubility of H_2S in water was obtained by interpolating between the data reported by Lee and Mather (24) at 68°F and 86°F. For CO_2 solubility, the literature data are obtained from three different sources where each has limited partial pressure range. The agreement between the results of this work and the literature for both CO_2 and H_2S is excellent. Water has higher capacity to absorb H_2S than to absorb CO_2 at any acid gas partial pressure.

CO_2 Data. To eliminate the reactivity of diethanolamine, it was protonated with hydrochloric acid to a pH that is equivalent to reacting one mole of CO_2 or H_2S with one mole of diethanolamine. Since hydrochloric acid is a strong acid and diethanolamine is a weak base, the pH obtained from their reaction at the equivalence point is different from the pH that would be obtained when diethanolamine is protonated with the acid gases. For example, the pH obtained from reacting one mole of CO_2 with one mole of DEA is 7.33 at 80°F. This is based on reaction equilibrium calculations using the Kent-Eisenberg

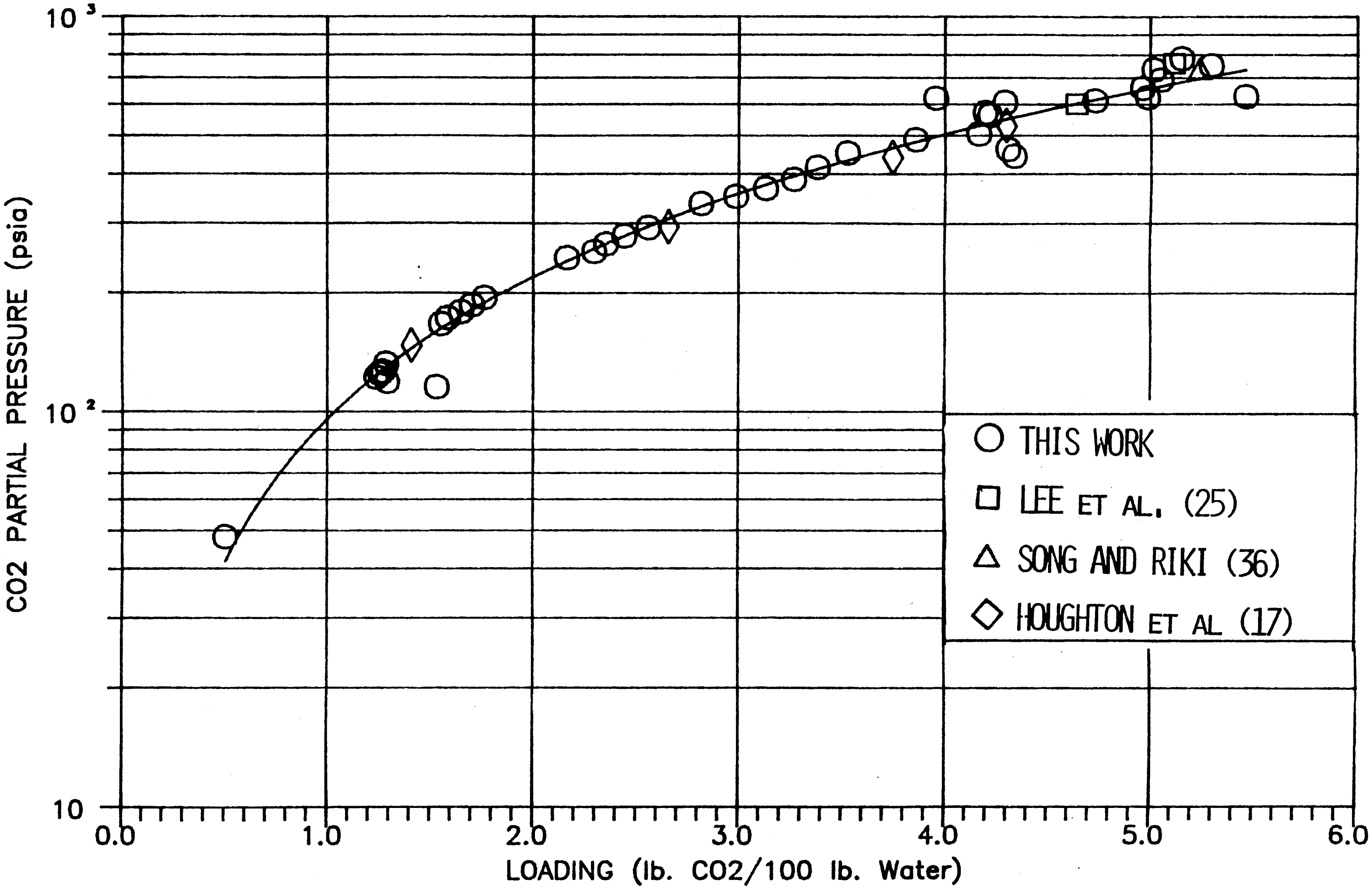


Figure 4. Solubility of CO2 in Water at 80 F.

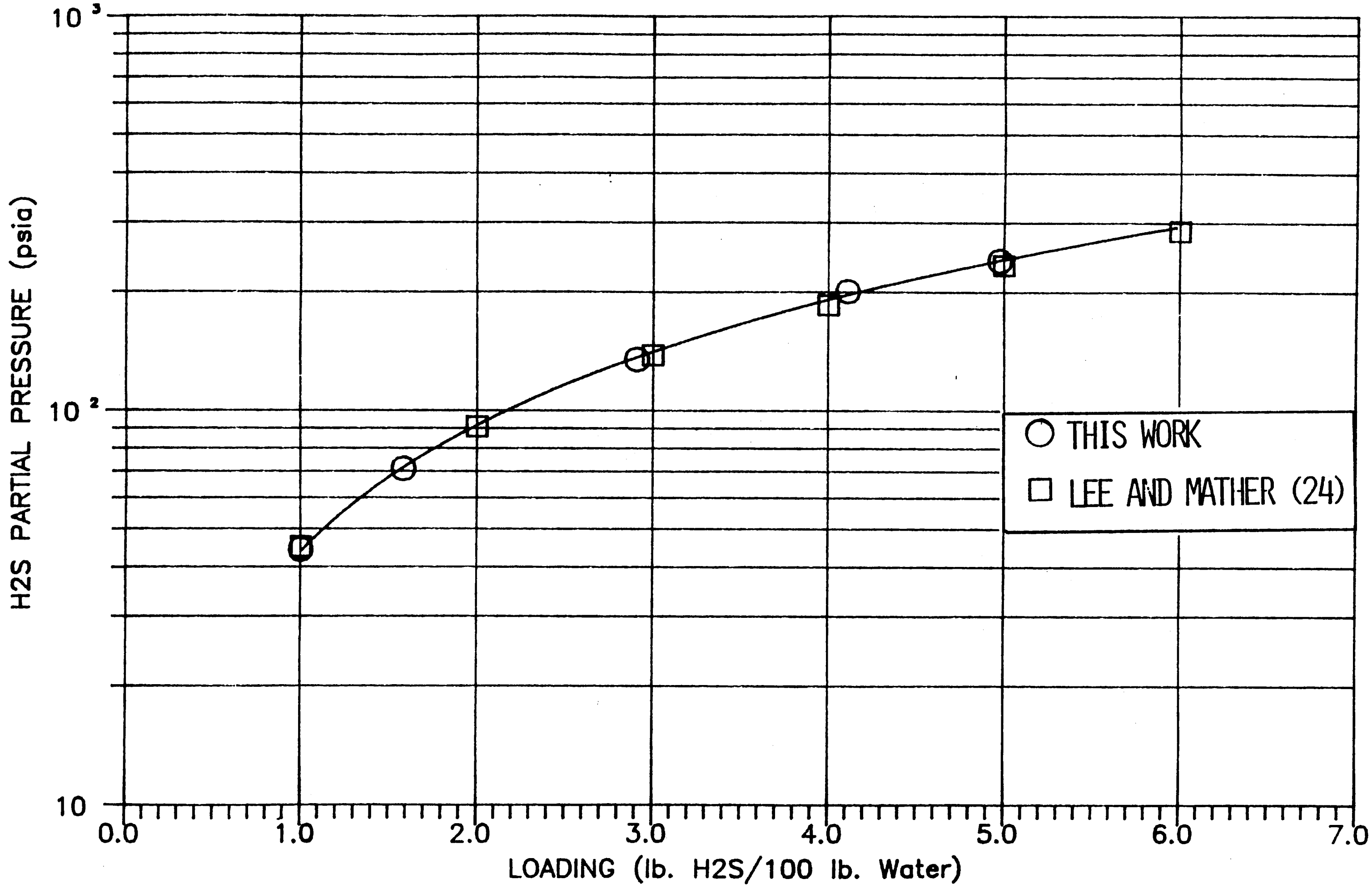


Figure 5. Solubility of H2S in Water at 80 F.

model. Complete protonation of the diethanolamine with HCl occurred at pH = 2.45. The solubility of CO_2 in protonated (pH = 7.3) and in acidic (pH = 2.35) 17% by weight DEA aqueous solutions was measured to check if there were changes in CO_2 solubility.

The experimental data for these measurements are shown in Figure 6 and Tables XVII and XVIII. The data were taken at 80°F and CO_2 partial pressures from 107 to 945 psia. The results indicate very small differences in solubilities. These differences are due to the presence of a small amount of free amine left after protonating the solution to pH = 7.3. Appendix G shows a calculation of the amount of free amine.

All the rest of the measurements were made in protonated (pH = 7.3) aqueous diethanolamine solutions. The data are shown in Figures 7 to 11 and Tables XIX through XXVI of Appendix A. The concentration of the solutions was 17, 20, 26, 34, 35 and 50 percent by weight protonated DEA. The measurements were made at 80, 150, and 240°F and at CO_2 partial pressure to 1000 psia. Some of the data sets show a small amount of scattering mainly at high temperatures. However, most of the data show good agreement internally.

CO_2 solubility in water and in aqueous protonated DEA solutions behaved differently than CO_2 solubility in aqueous DEA solutions. The pressure increased as the solution was injected. The amount of increase depended on the working pressure. The increase in the pressure was due to the low solubility of CO_2 in these solutions and the reduction in the volume as more liquid was injected. The low solubility of CO_2 in these solutions made the measurements difficult. Any small error in reading the pressure affected the solubility resulting in scattered data. Therefore, many runs were repeated to ensure reproducibility.

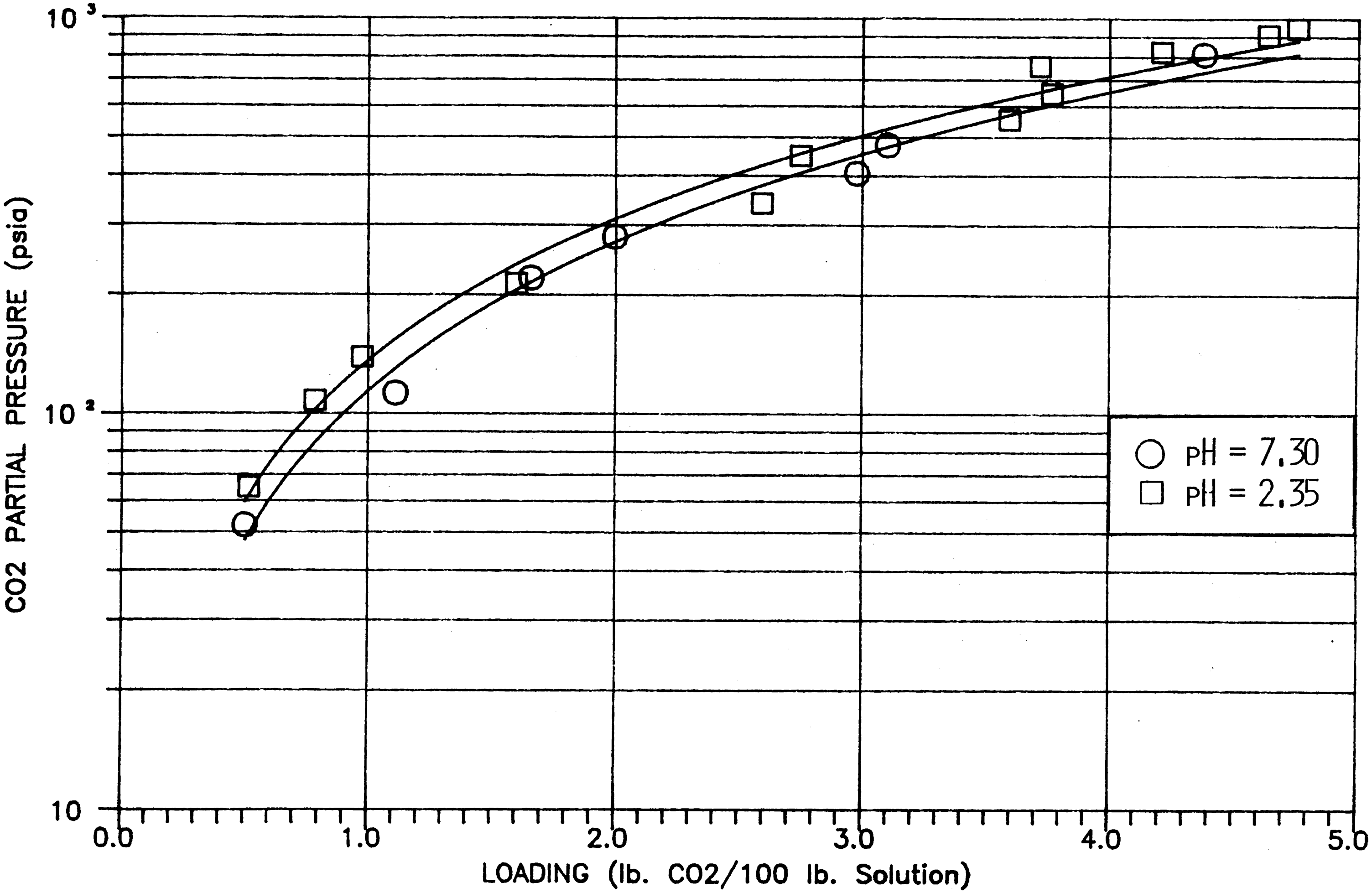


Figure 6. Solubility of CO2 in Protonated (pH = 7.3) and in Acidic (pH = 2.35) 17% by Weight DEA Aqueous Solution at 80 F.

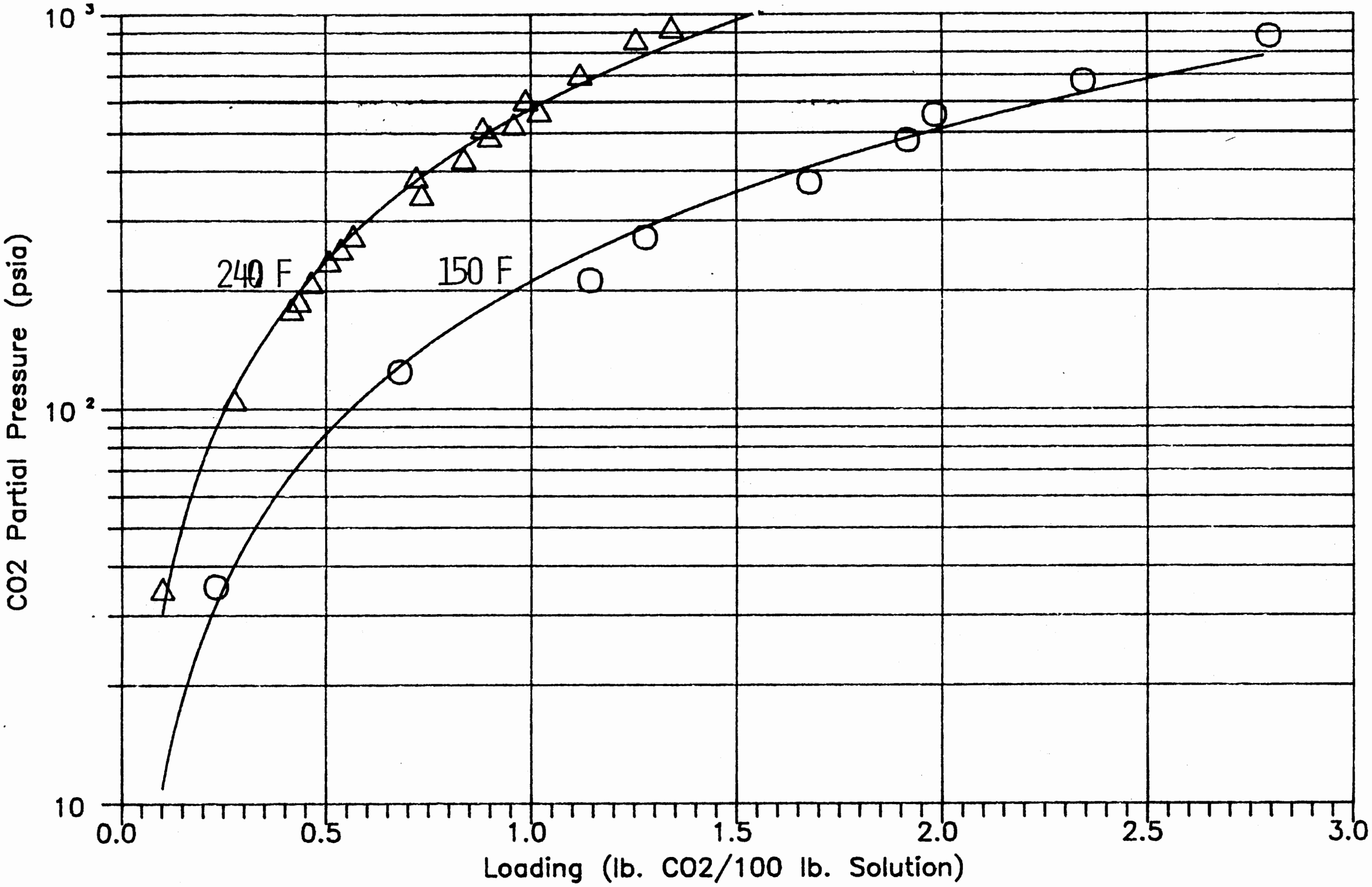


Figure 7. Solubility of CO2 in Protonated (pH=7.3) 17% by Weight DEA Aqueous Solution at 150 and 240 F.

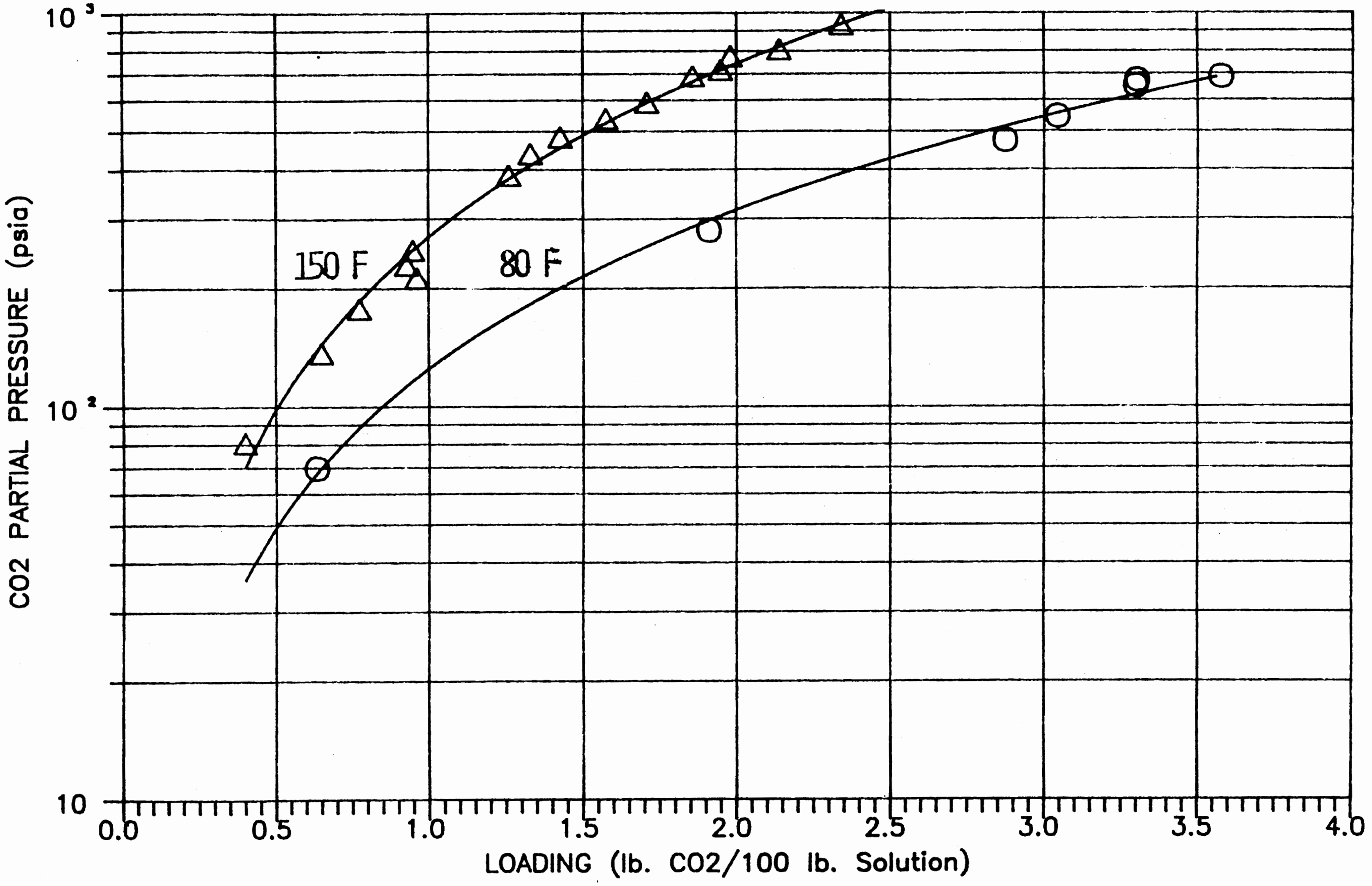


Figure 8. Solubility of CO2 in Protonated (pH=7.3) 26% by Weight DEA Aqueous Solution at 80 and 150 F.

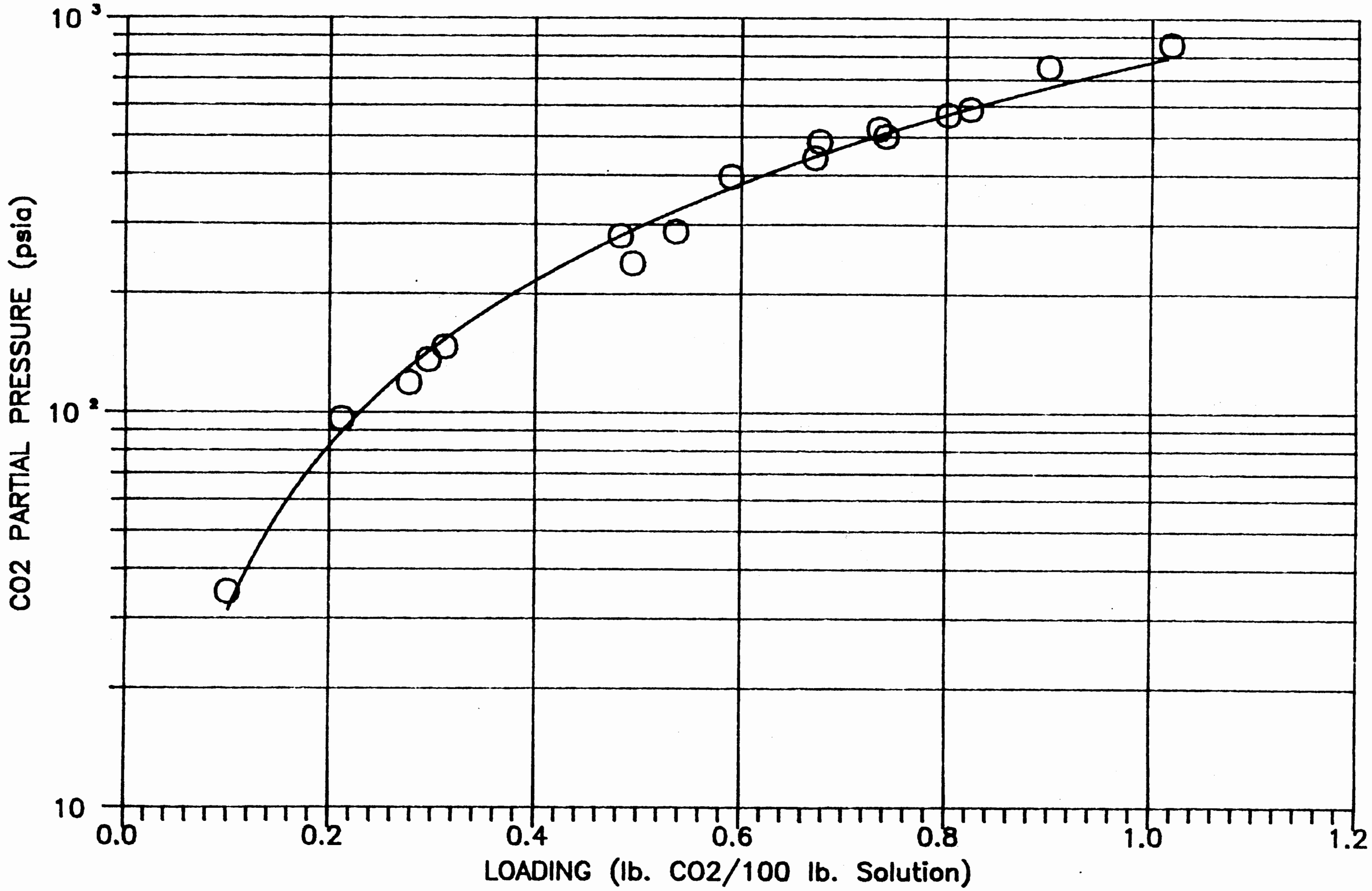


Figure 9. Solubility of CO2 in Protonated (pH=7.3) 35% by Weight DEA Aqueous Solution at 240 F.

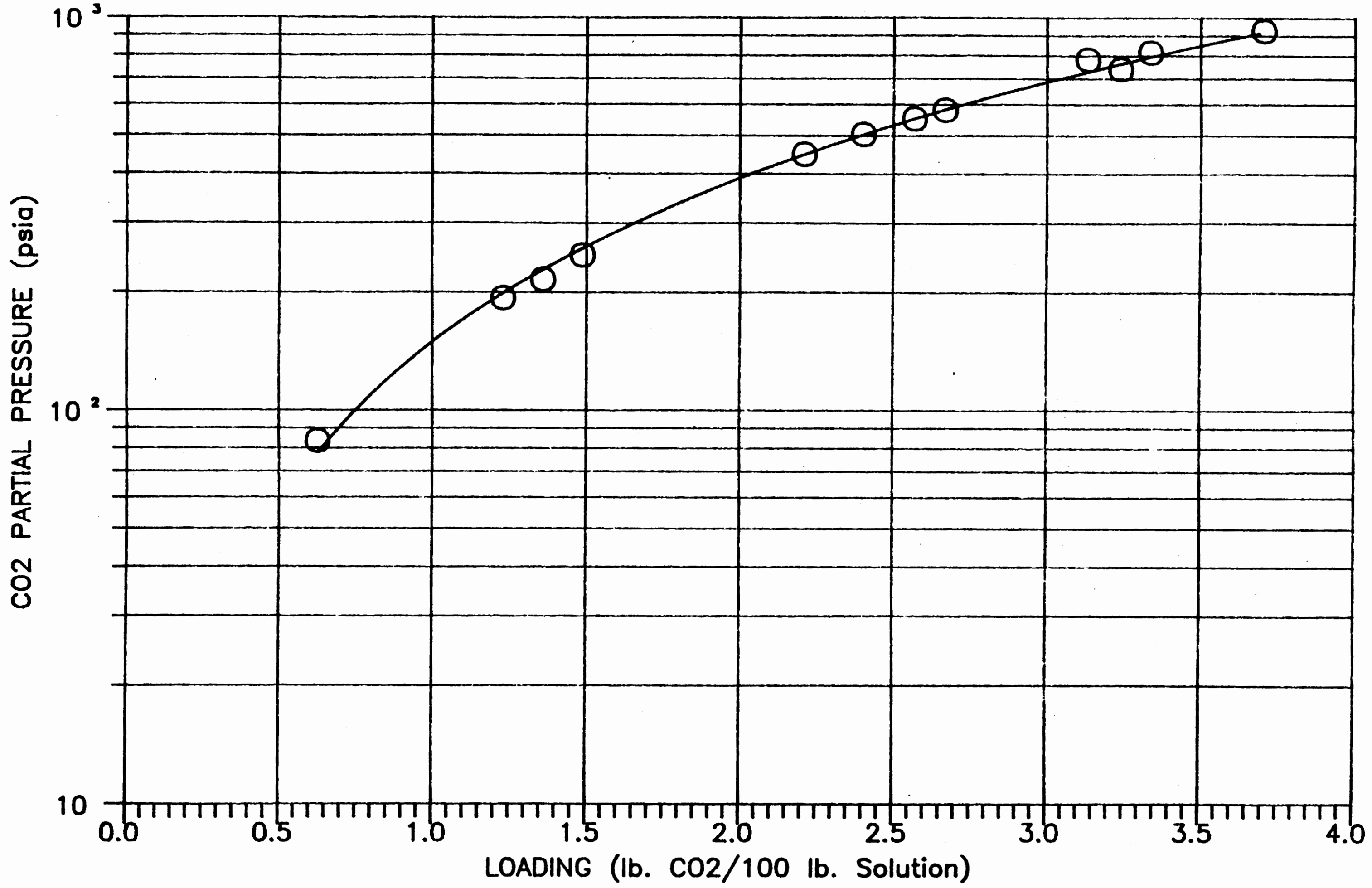


Figure 10. Solubility of CO2 in Protonated (pH=7.3) 34% by Weight DEA Aqueous Solution at 80 F.

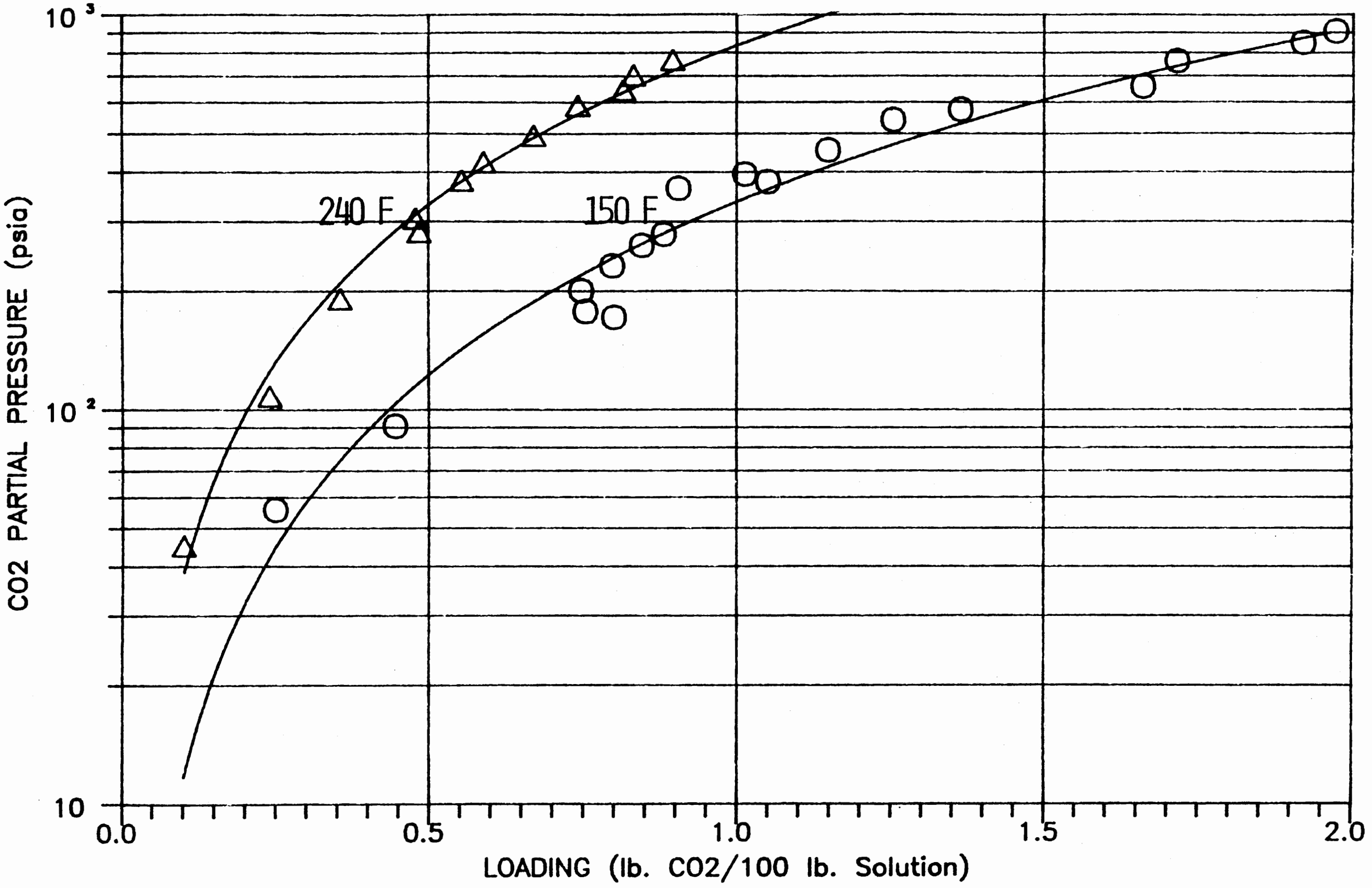


Figure 11. Solubility of CO2 in Protonated (pH=7.3) 50% by Weight DEA Aqueous Solution at 150 and 240 F.

The physical solubility of CO_2 in aqueous protonated diethanolamine solutions decreases as the temperature or the solution concentration increases as can be seen from Figures 12 and 13.

$\underline{H_2S \text{ Data}}$. The physical solubility of H_2S in protonated 20, 35, and 50% by weight DEA aqueous solutions at 80, 150 and 240°F was measured. The partial pressure of H_2S ranged from ~ 40 to ~ 272 psia. The results of these measurements are shown in Figures 14 through 19 and Tables XXVII through XXXV of Appendix A. The data for H_2S physical solubility in protonated 20 and 50% by weight DEA aqueous solutions at 150°F were obtained by linear interpolation using the data measured at 80 and 240 °F. One experimental data point was measured for the 20% solution as shown in Figure 14.

The data seem to be consistent which is shown by the good agreement between the smoothed and the measured data. At any partial pressure of CO_2 or H_2S, the physical solubility of H_2S is greater than that of CO_2.

The physical solubility of H_2S decreases as the temperature increases, as illustrated in Figure 20, but increases as the solution concentration increases. The increase in H_2S physical solubility occurred at all temperatures. Figure 21 shows this behavior at 80°F.

Relationship Between the Solubility of CO_2 and H_2S in Water and in Aqueous Diethanolamine Solutions

As mentioned in Chapter II, in all of the reaction equilibrium models, the physical solubility of the acid gases in aqueous alkanolamines is assumed to be the same as their solubility in water. Here, this assumption is investigated.

For CO_2, calculation of CO_2 solubility based on the water portion

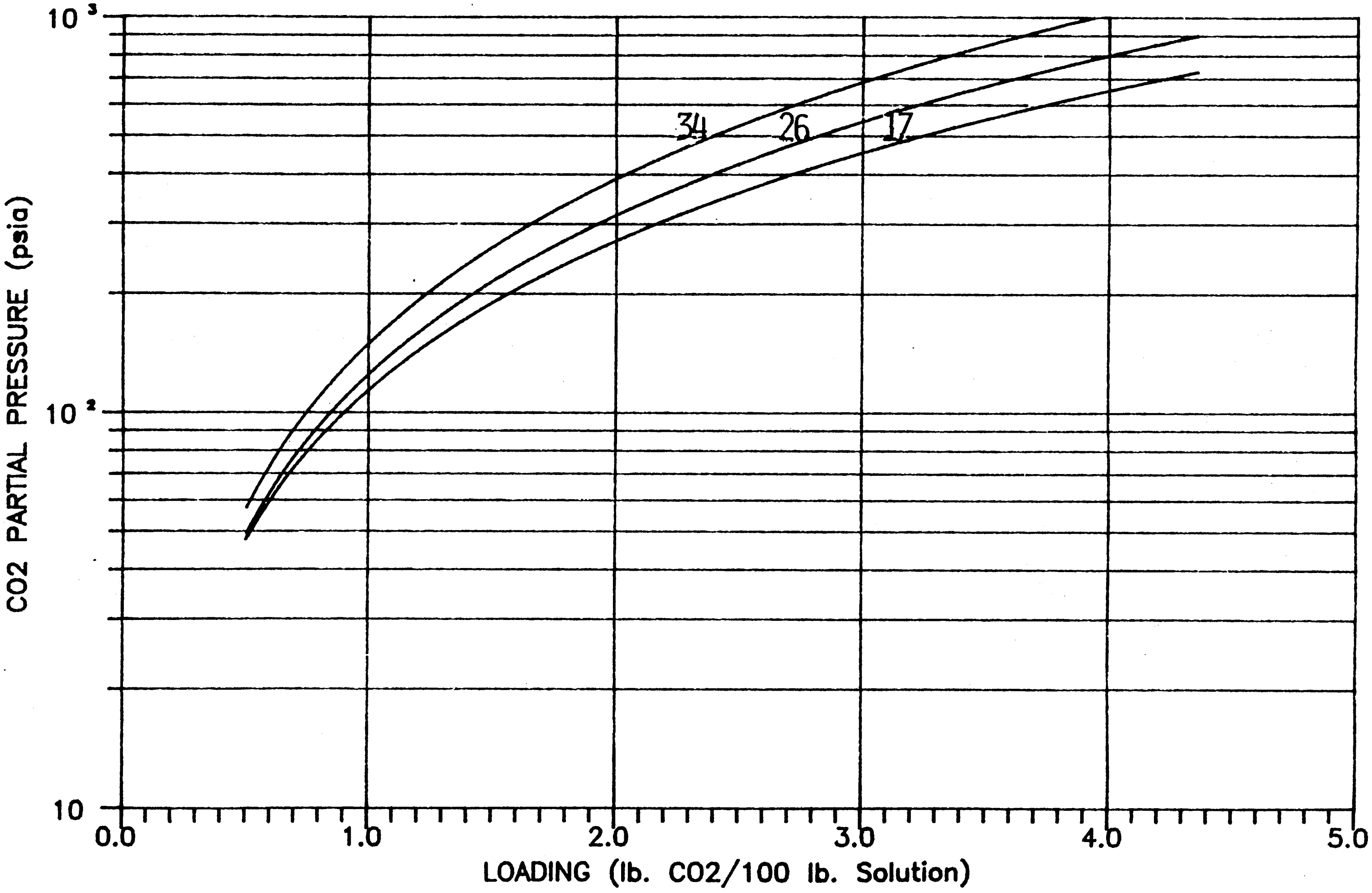


Figure 12. Solubility of CO2 in Protonated (pH=7.3) 17, 26 and 34% by Weight DEA Aqueous Solution at 80 F.

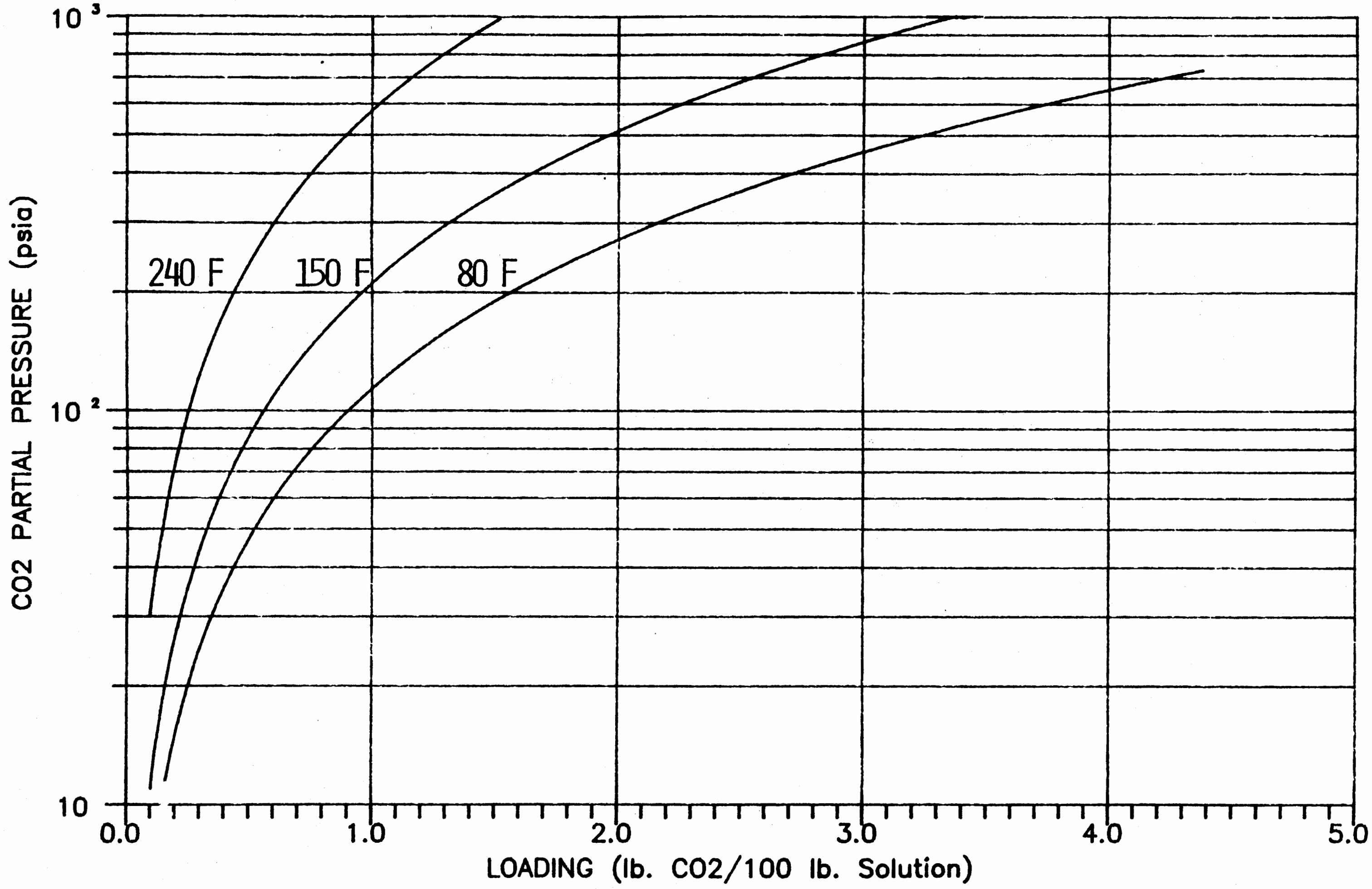


Figure 13. Solubility of CO2 in Protonated (pH=7.3) 17% by Weight DEA Aqueous Solution at 80, 150 and 240 F.

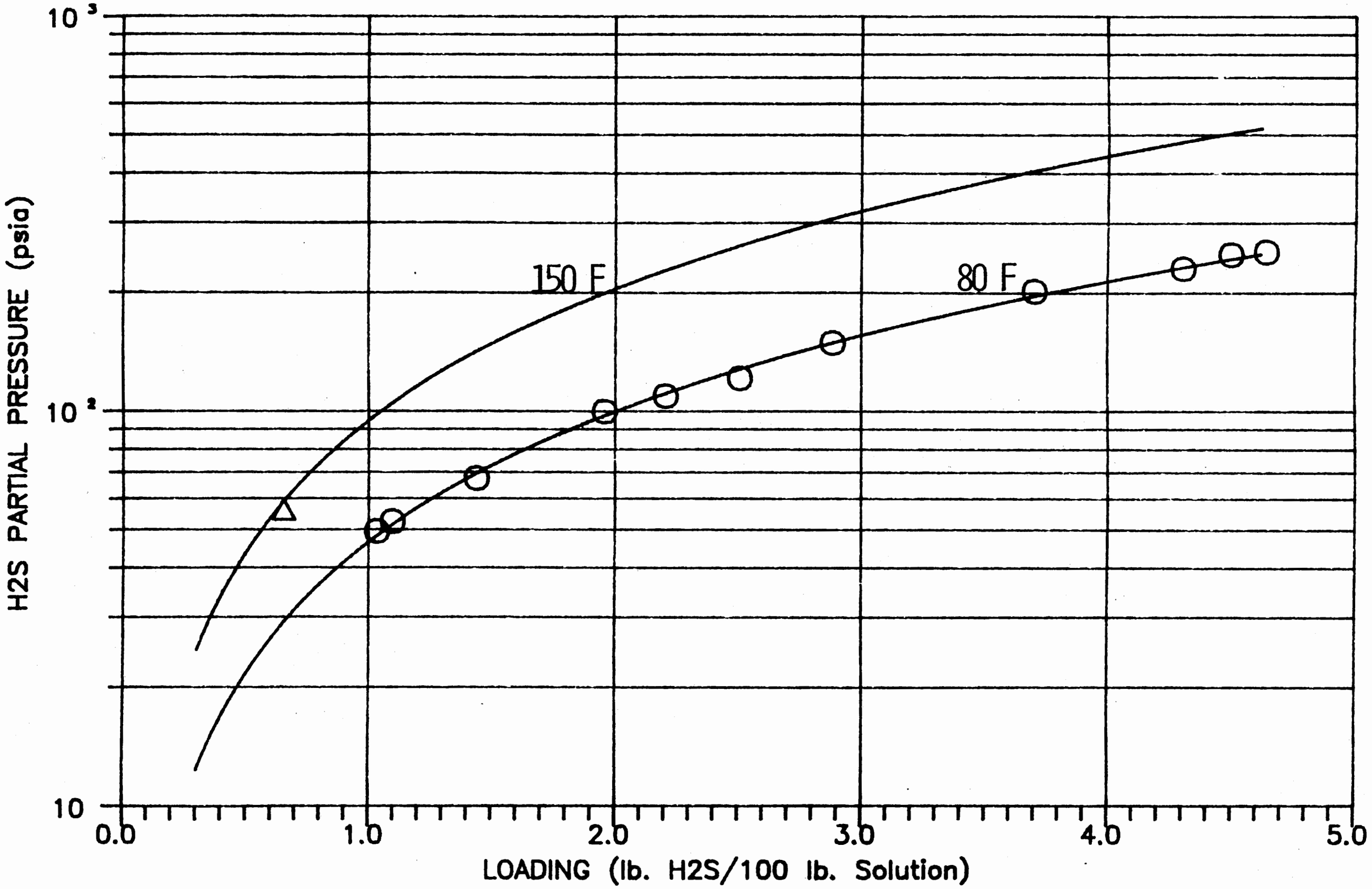


Figure 14. Solubility of H2S in Protonated (pH=7.3) 20% by Weight DEA Aqueous Solution at 80 and 150 F.

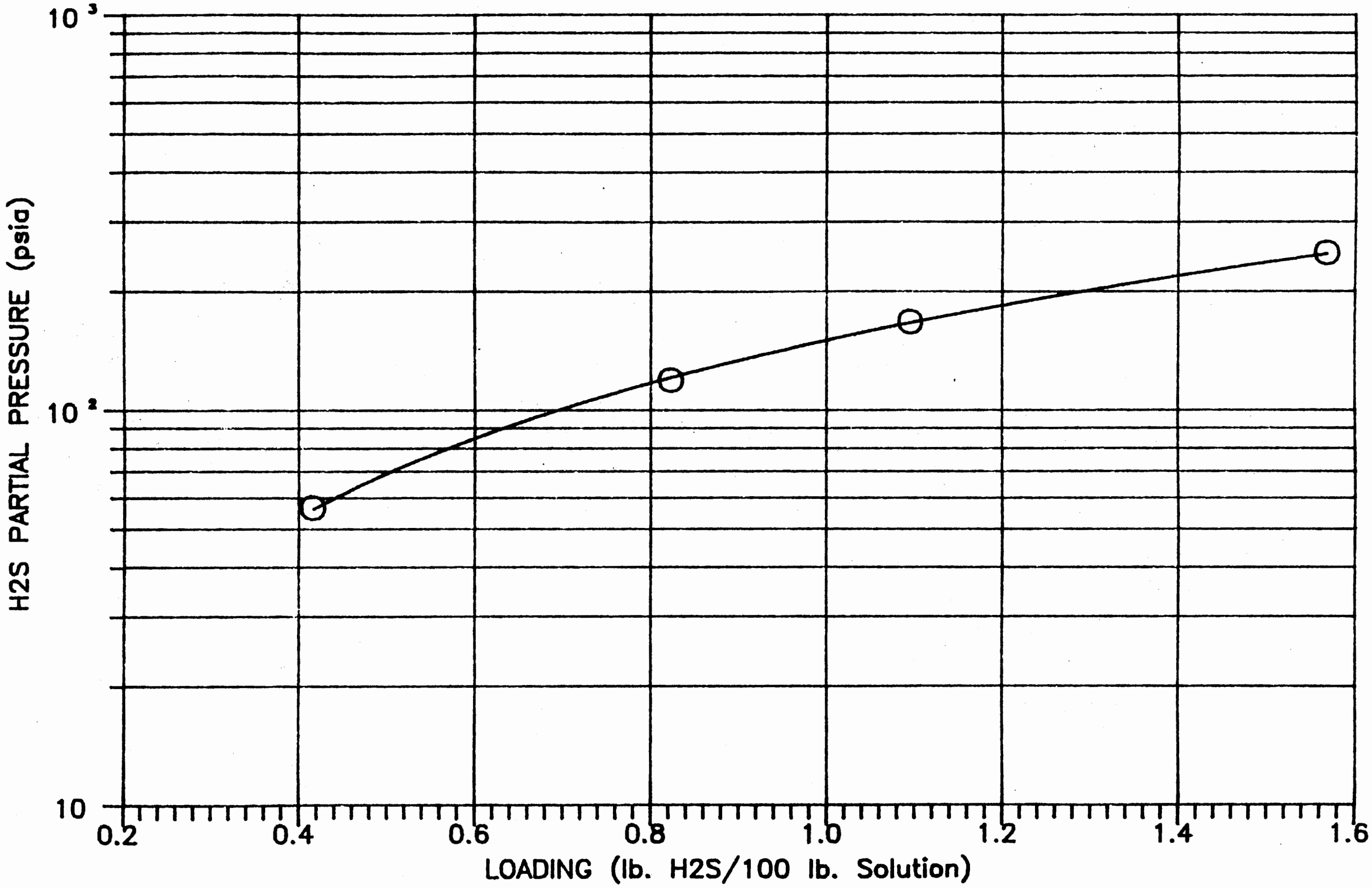


Figure 15. Solubility of H2S in Protonated (pH=7.3) 20% by Weight DEA Aqueous Solution at 240 F.

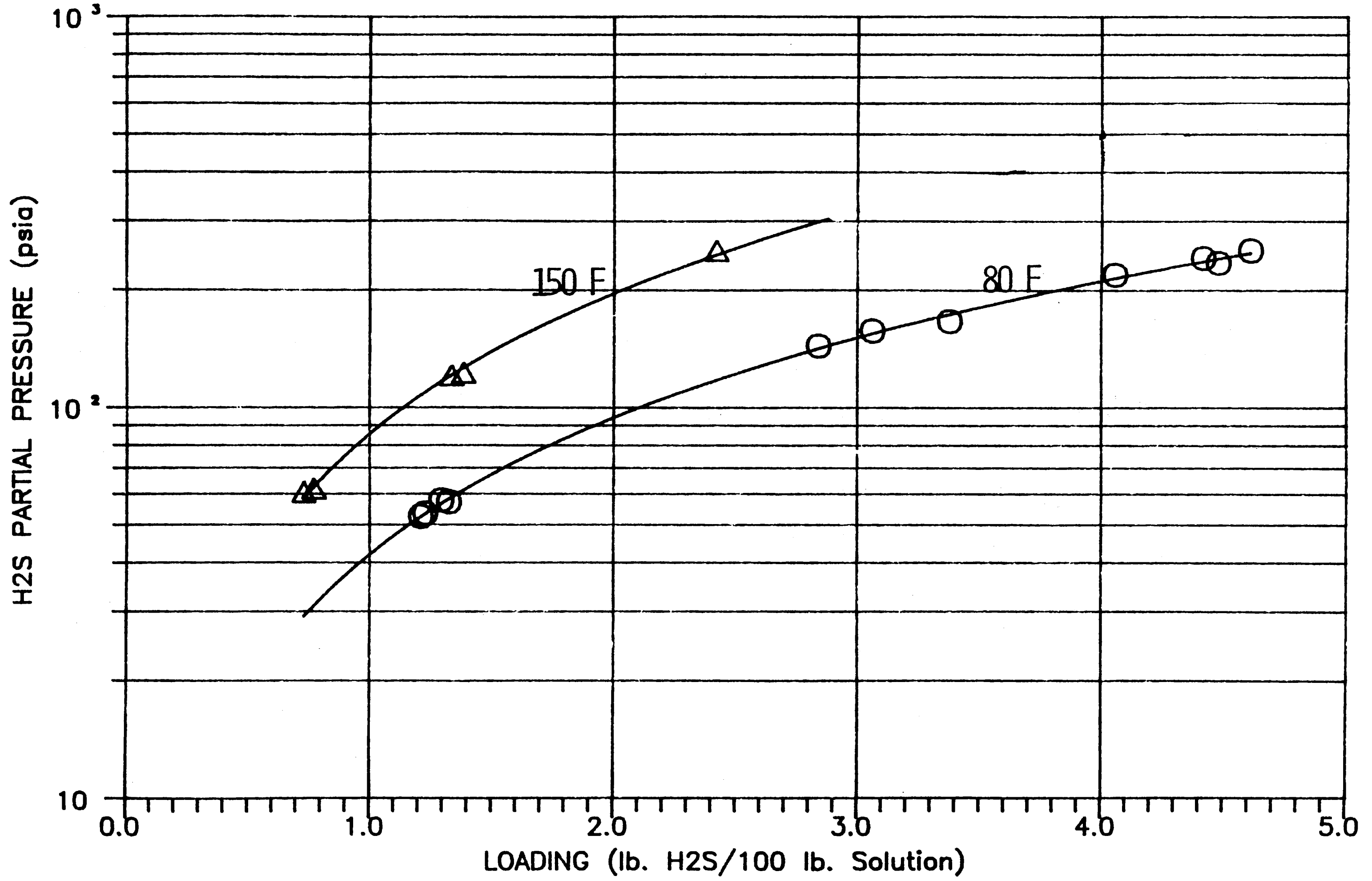


Figure 16. Solubility of H2S in Protonated (pH=7.3) 35% by Weight DEA Aqueous Solution at 80 and 150 F.

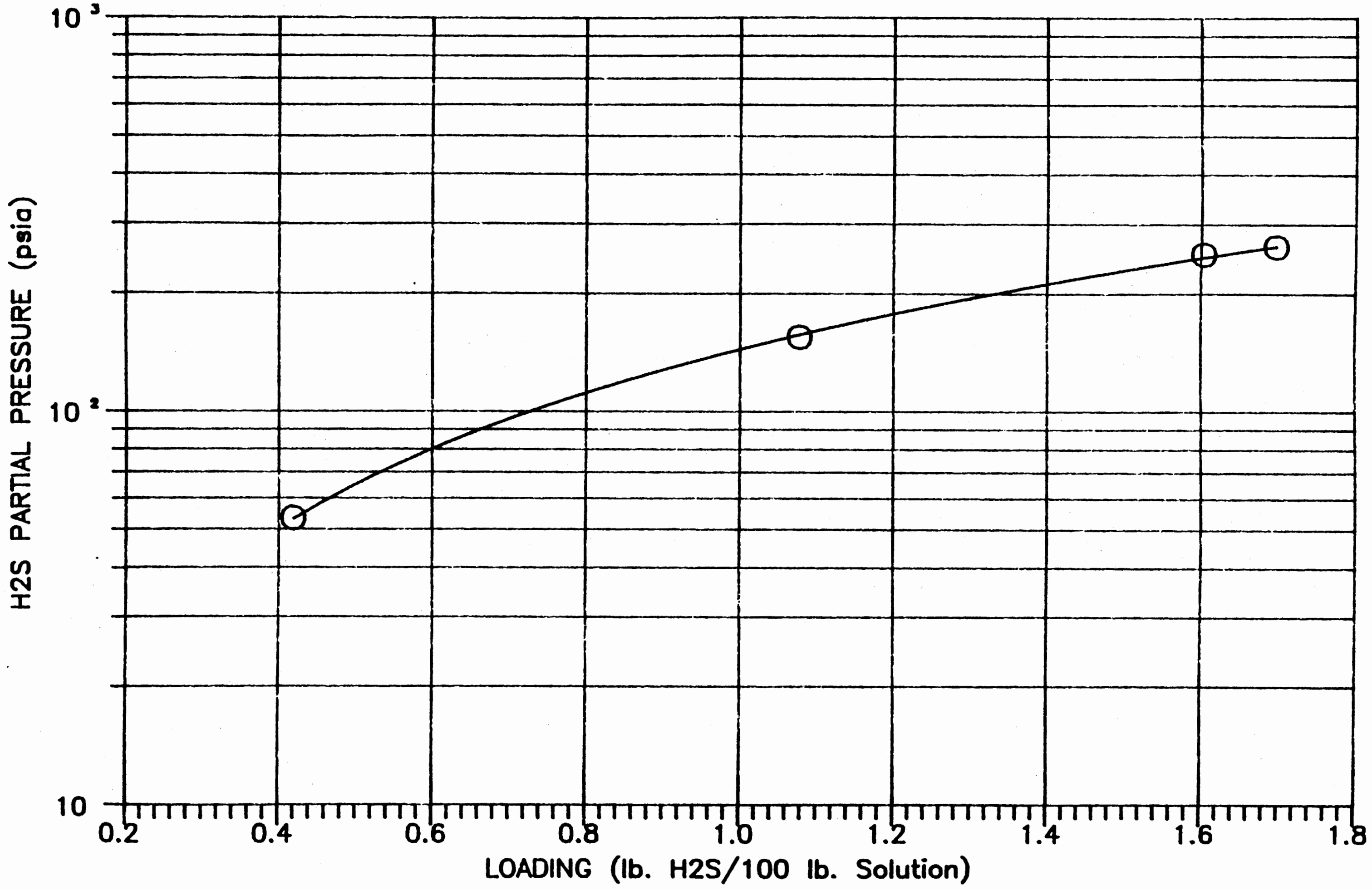


Figure 17. Solubility of H2S in Protonated (pH=7.3) 35% by Weight DEA Aqueous Solution at 240 F.

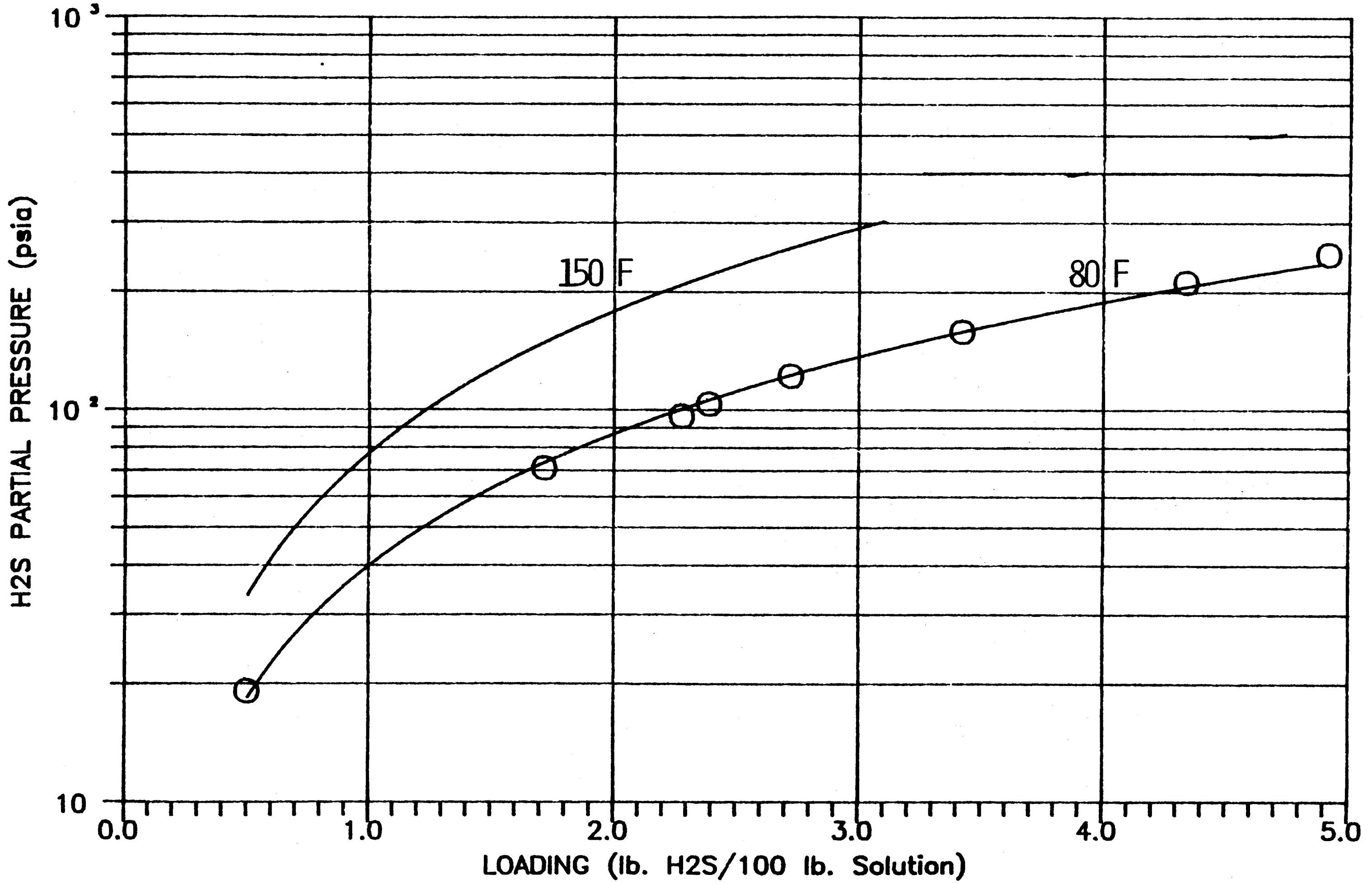


Figure 18. Solubility of H2S in Protonated (pH=7.3) 50% by Weight DEA Aqueous Solution at 80 and 150 F.

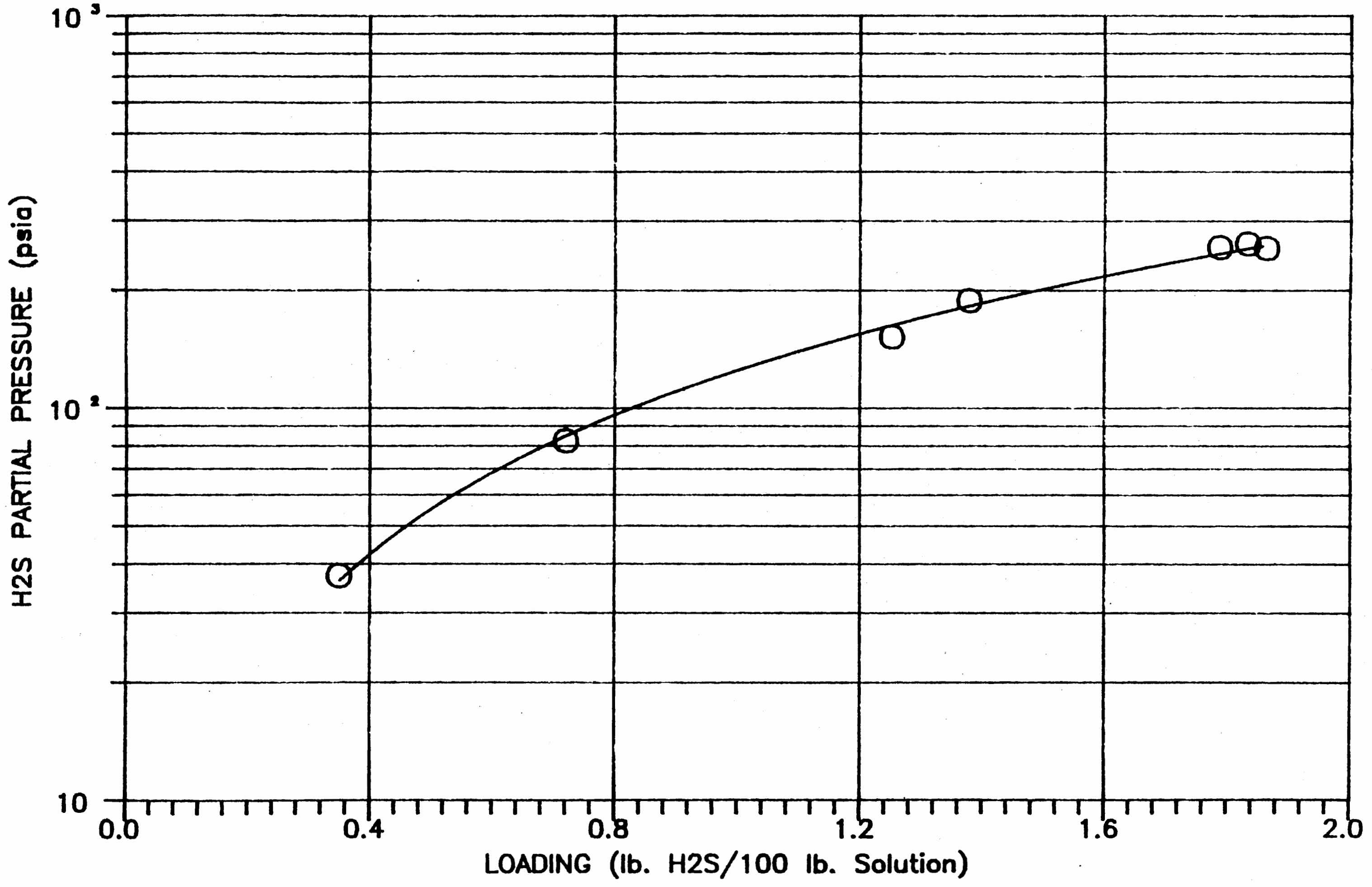


Figure 19. Solubility of H2S in Protonated (pH=7.3) 50% by Weight DEA Aqueous Solution at 240 F.

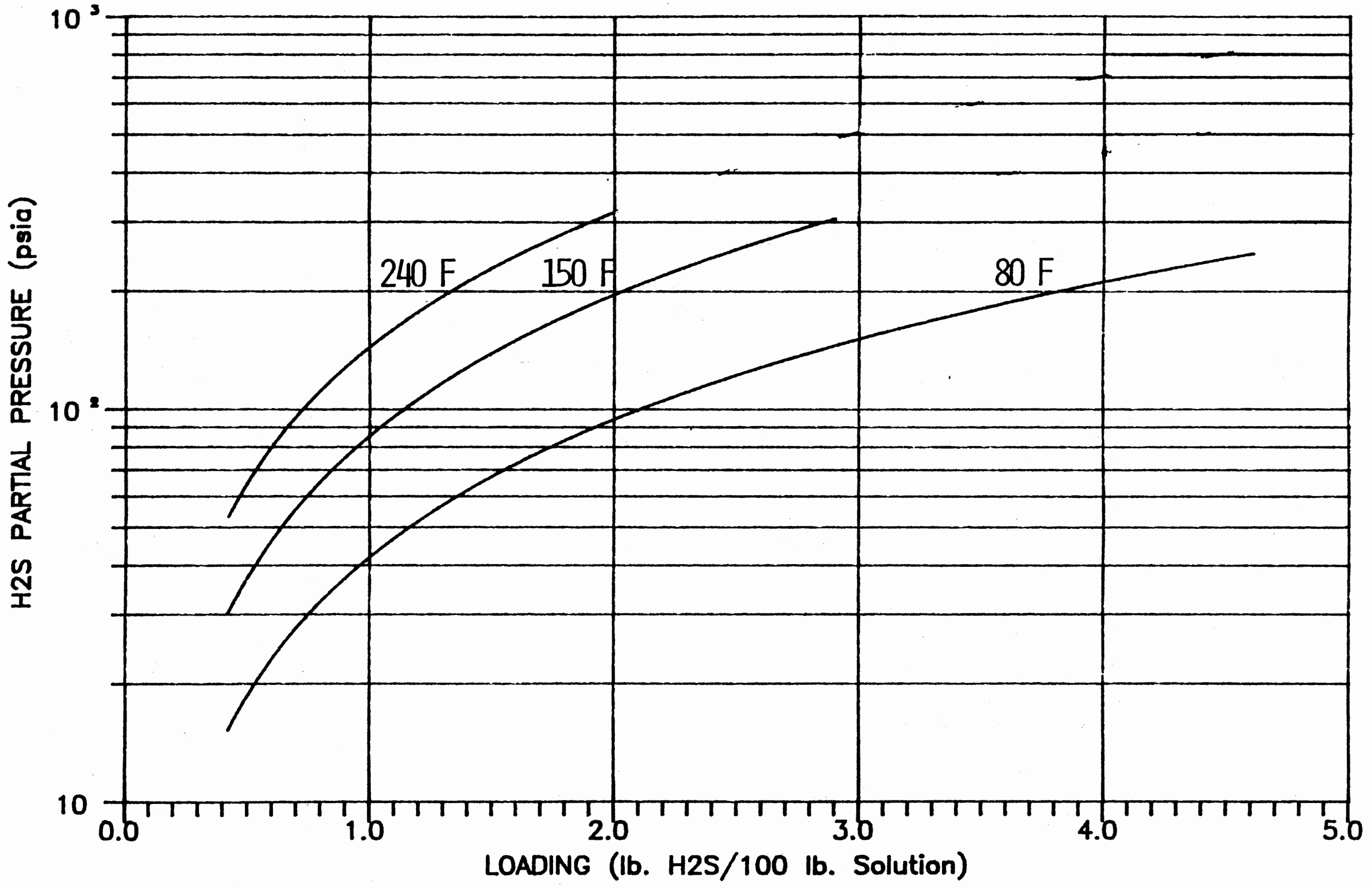


Figure 20. Solubility of H2S in Protonated (pH=7.3) 35% by Weight DEA Aqueous Solution at 80, 150 and 240 F.

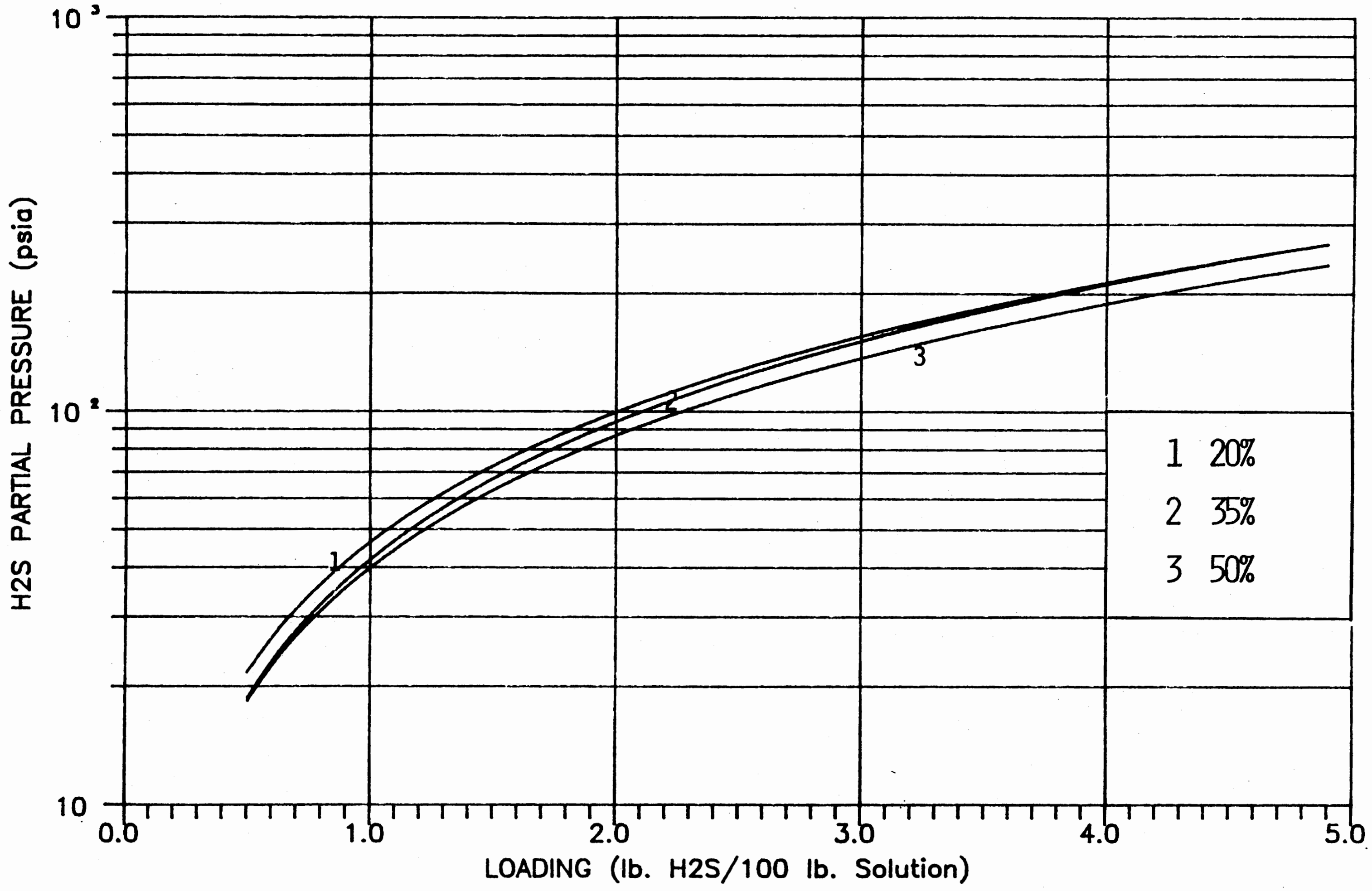


Figure 21. Solubility of H2S in Protonated (pH=7.3) 20, 35, and 50% by Weight DEA Aqueous Solution at 80 F.

of the protonated DEA solution shows that the solubility is mostly contributed by water. As mentioned earlier, after protonating the amine solution to pH = 7.3, a small amount of amine remained in the solution unprotonated. In the calculation, it was assumed that the free (unprotonated) amine reacted with equal moles of CO_2 according to the following reactions (28):

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \tag{13}$$

$$H^+ + \text{amine} \longrightarrow (\text{H:amine})^+ \tag{14}$$

The solubility of CO_2 was calculated based on the amount of water in the solution after subtracting the amount of CO_2 reacted with the free amine from the measured physical solubility of CO_2 in the solution. This solubility was compared to the solubility of CO_2 in pure water. Details of the calculations are presented in Appendix G. Tables I through VI show the comparisons between the solubility of CO_2 in pure water and that calculated as described above at 80 and 150 °F. In all of these tables, smoothed data are used. The solubility of CO_2 in pure water at 80 °F are measured in this study, while that at 150 °F was obtained by interpolating between the data reported by Houghton et al. (17) at 122 and 167 °F and then was smoothed. There is a small difference between the solubility in pure water and that calculated from the measurements for the four solutions at 80 °F, but at 150 °F, there is quite a difference at low pressure. The interpolation and the smoothing to get the data at 150 °F could be responsible for these differences.

For H_2S, such calculations gave a large difference between the solubility calculated as mentioned above and the solubility in pure water. The difference was 20% for the H_2S-protonated 20% by weight DEA

TABLE I

COMPARISON BETWEEN CO_2 SOLUBILITY CALCULATED ON WATER BASIS FROM CO_2 PHYSICAL SOLUBILITY MEASUREMENTS IN ACIDIC (pH = 2.35) 17% BY WEIGHT DEA AQUEOUS SOLUTION AND IN WATER AT 80 °F

CO_2 Partial Pressure, Psia	β_{CO_2} in Water[1]	β_{CO_2} Calculated[2]	% Difference
100.0	1.00	0.99	0.85
200.0	1.87	1.85	1.09
300.0	2.64	2.61	1.28
400.0	3.34	3.29	1.44
500.0	3.98	3.92	1.57
600.0	4.56	4.49	1.68
700.0	5.11	5.02	1.78
800.0	5.61	5.51	1.86
900.0	6.09	5.97	1.94
1000.0	6.53	6.40	2.00

β_{CO_2} = Lb. CO_2 Absorbed/100 Lb. Water

[1] Smoothed Data

[2] From Smoothed Data

TABLE II

COMPARISON BETWEEN CO_2 SOLUBILITY CALCULATED ON WATER BASIS FROM CO_2 PHYSICAL SOLUBILITY MEASUREMENTS IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION AND IN WATER AT 80 °F

CO_2 Partial Pressure, Psia	β_{CO_2} in Water[1]	β_{CO_2} Calculated[2]	% Difference
100.0	1.00	1.07	-6.94
200.0	1.87	1.95	-4.44
300.0	2.64	2.71	-2.55
400.0	3.34	3.38	-1.07
500.0	3.98	3.97	0.14
600.0	4.56	4.51	1.14
700.0	5.11	5.00	2.01
800.0	5.61	5.46	2.75
900.0	6.09	5.88	3.40
1000.0	6.53	6.27	3.98

β_{CO_2} = Lb. CO_2 Absorbed/100 Lb. Water

[1] Smoothed Data

[2] From Smoothed Data

TABLE III

COMPARISON BETWEEN CO_2 SOLUBILITY CALCULATED ON WATER BASIS FROM CO_2 PHYSICAL SOLUBILITY MEASUREMENTS IN PROTONATED (pH = 7.3) 26% BY WEIGHT DEA AQUEOUS SOLUTION AND IN WATER AT 80 °F

CO_2 Partial Pressure, Psia	β_{CO_2} in Water[1]	β_{CO_2} Calculated[2]	% Difference
200.0	1.87	2.03	-8.71
400.0	3.34	3.47	-3.81
600.0	4.56	4.59	-0.66
800.0	5.61	5.52	1.59
1000.0	6.53	6.32	3.29

β_{CO_2} = Lb. CO_2 Absorbed/100 Lb. Water

[1] Smoothed Data

[2] From Smoothed Data

TABLE IV

COMPARISON BETWEEN CO_2 SOLUBILITY CALCULATED ON WATER BASIS FROM CO_2 PHYSICAL SOLUBILITY MEASUREMENTS IN PROTONATED (pH = 7.3) 34% BY WEIGHT DEA AQUEOUS SOLUTION AND IN WATER AT 80 °F

CO_2 Partial Pressure, Psia	β_{CO_2} in Water[1]	β_{CO_2} Calculated[2]	% Difference
200.0	1.87	1.96	-4.73
400.0	3.34	3.48	-4.17
600.0	4.56	4.74	-3.79
800.0	5.61	5.81	-3.50
1000.0	6.53	6.75	-3.27

β_{CO_2} = Lb. CO_2 Absorbed/100 Lb. Water

[1] Smoothed Data

[2] From Smoothed Data

TABLE V

COMPARISON BETWEEN CO_2 SOLUBILITY CALCULATED ON WATER BASIS FROM CO_2 PHYSICAL SOLUBILITY MEASUREMENTS IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION AND IN WATER AT 150 °F

CO_2 Partial Pressure, Psia	β_{CO_2} in Water[1]	β_{CO_2} Calculated[2]	% Difference
200.0	0.88	1.22	-27.77
400.0	1.68	2.07	-23.35
600.0	2.42	2.74	-13.45
800.0	3.10	3.29	-6.33
1000.0	3.73	3.76	-0.91

β_{CO_2} = Lb. CO_2 Absorbed/100 Lb. Water

[1] Smoothed Data

[2] Interpolated and Smoothed from Houghton et al. (7) Data.

TABLE VI

COMPARISON BETWEEN CO_2 SOLUBILITY CALCULATED ON WATER BASIS FROM CO_2 PHYSICAL SOLUBILITY MEASUREMENTS IN PROTONATED (pH = 7.3) 26% BY WEIGHT DEA AQUEOUS SOLUTION AND IN WATER AT 150 °F

CO_2 Partial Pressure, Psia	β_{CO_2} in Water[1]	β_{CO_2} Calculated[2]	% Difference
200.0	0.88	1.05	-19.40
400.0	1.68	1.84	-9.44
600.0	2.42	2.48	-2.53
800.0	3.10	3.01	2.62
1000.0	3.73	3.48	6.64

β_{CO_2} = Lb. CO_2 Absorbed/100 Lb. Water

[1] Smoothed Data

[2] Interpolated and Smoothed from Houghton et al. (7) Data.

solution and more than 40% for the other solutions. However, comparing the solubility of H_2S in water to that in solution for the protonated 20, 35 and 50% by weight DEA solutions at 80 and 150 °F, as shown in Figures 22 and 23, indicates that the solubility of H_2S in these solutions is very close to that in pure water.

These results show that CO_2 is only soluble in the water portion of the protonated amine solution, while H_2S seems to be soluble in both water and the amine. This behavior could be due to the fact that most of the physically absorbed CO_2 remains as CO_2 molecules which may make it harder to penetrate through the bulky protonated DEA. On the other hand, a large portion of H_2S dissociates to give hydrogen and acid sulfide ions. These ions probably react with some of the species in the solution or it is easier for them to penetrate than it is for CO_2 molecules.

Solubility of N_2O in Water and in Protonated DEA Aqueous Solution

To accurately design and simulate acid gas-amine contactors, information is needed on the mass transfer coefficient, gas-liquid contact area, reaction rates, and physical parameters (physical absorption and diffusivity). As mentioned before, since H_2S and CO_2 react with the amine their physical solubilities and diffusivities can not be measured directly in aqueous solutions of amine. This led Clarke (10) to suggest the use of nonreacting gases (like Nitrous Oxide, N_2O) that have similar molecular properties to those of the reacting gases to estimate the physical parameters.

The similarities of N_2O and CO_2 with regard to configuration,

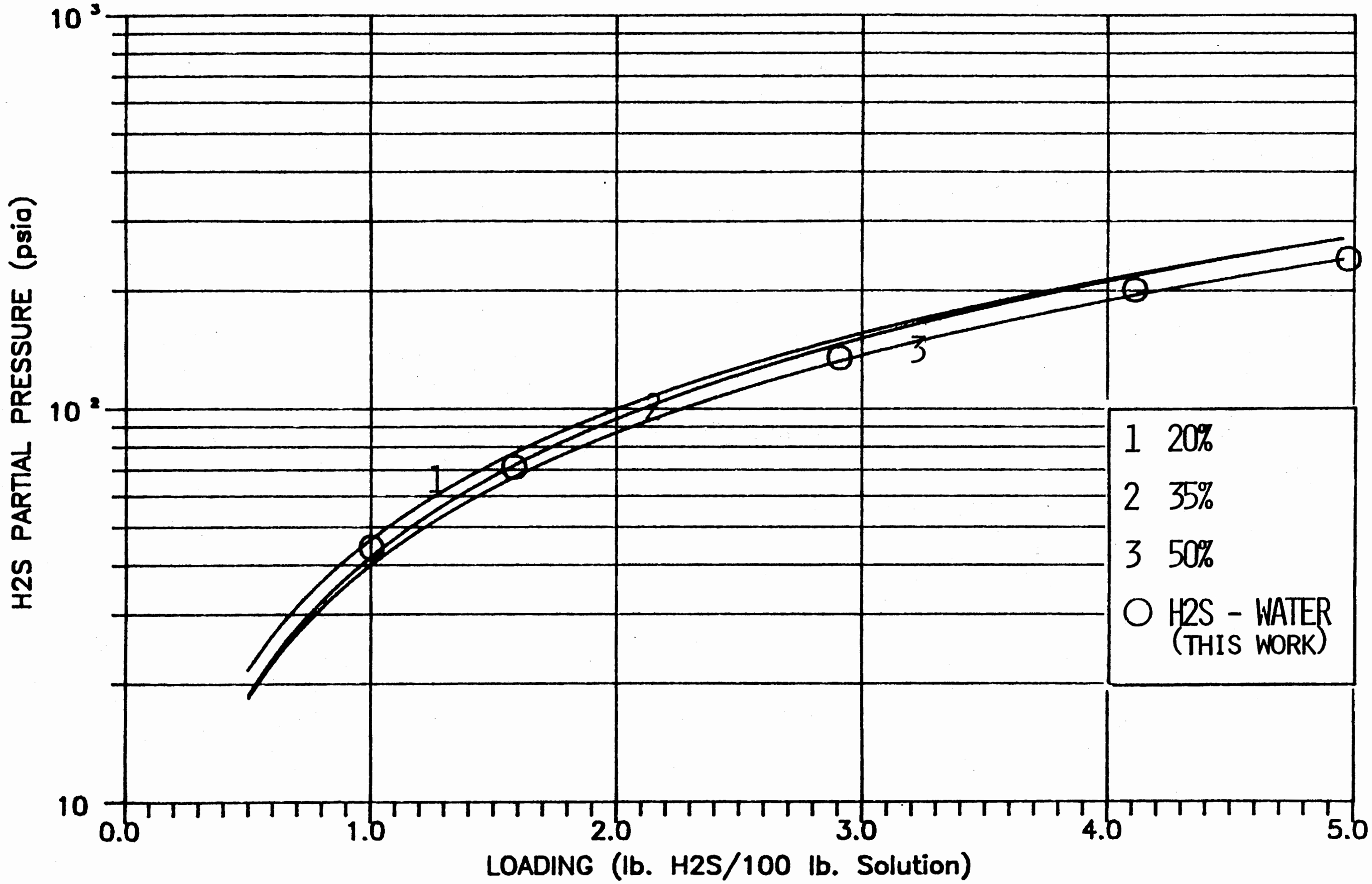


Figure 22. Solubility of H2S in Water and in Protonated (pH=7.3) 20, 35, and 50% by Weight DEA Aqueous Solutions at 80 F.

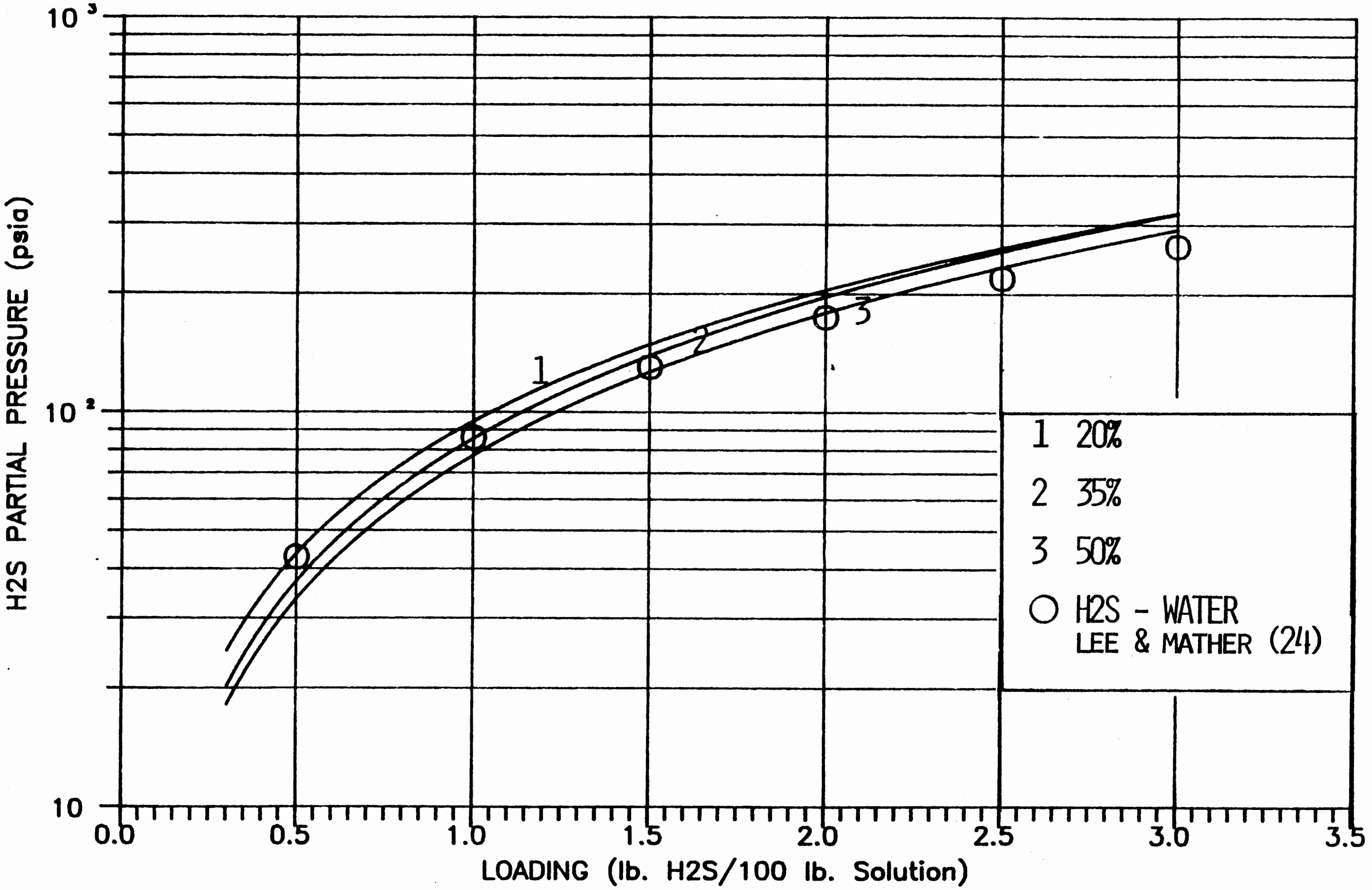


Figure 23. Solubility of H2S in Water and in Protonated (pH=7.3) 20, 35, and 50% by Weight DEA Aqueous Solutions at 150 F.

molecular volume, and electronic structure, led many researchers (7, 13, 16, 18, 22-23, 33-35, 38-39) to believe that the ratio of the solubilities of the two gases is the same in an aqueous solution of amine as in water. All the researchers found a ratio of 1.37 for water and 1.37 ± 5% for other solutions at 25°C and 1 atm, and assumed this ratio would hold for other conditions. This has been referred to by these researchers as the "N_2O analogy".

Some of those researchers like Sada et al. (33-35) measured N_2O solubility in MEA, DEA, TEA, and Ethylenediamine (EDA) at 25°C and 1 atm and based on that proposed the following relationship to estimate CO_2 physical solubility.

$$\log(\alpha/\alpha_w)_{CO_2} = \log(\alpha/\alpha_w)_{N_2O} \tag{15}$$

where α and α_w are solubility of CO_2 and N_2O in a solution and in water, respectively.

Versteeg et al. (38) also measured the solubility of N_2O in DEA, DIPA, DMMEA, and DIPA at various temperatures and concentrations. They proposed the following equation:

$$\text{solubility of } CO_2 = C_1 \text{ (solubility of } N_2O) \tag{16}$$

with

$$C_1 = (\text{solubility of } CO_2 \text{ in water/solubility of } N_2O \text{ in water})$$

which is the same as Eq. (15). They correlated C_1 in terms of temperature as follows:

$$C_1 = 3.04 \exp(-240/T) \tag{17}$$

where T is in °K.

Also for the lack of information on H_2S physical parameters, Versteeg (39) used the "N_2O analogy" to estimate H_2S physical solubility in intrepretation of his experimental results and in the design of a contactor.

Table VII gives the properties of N_2O and the acid gases. Some of these properties (mass and molecular interaction parameters) were the basis for Clarke (10) to propose the use of the "N_2O analogy". As can be seen, there are a lot of differences between N_2O and H_2S properties.

In this study, the solubility of N_2O in water and in protonated 17% by weight DEA at 80°F was measured. The partial pressure ranged from ~ 66 to 853 psia. The results are shown in Figures 24 and 25 and Tables XXXVI and XXXVII of Appendix A. Literature data on the solubility of N_2O (10, 14, 16, 18, 30, 34, 38) in water are all reported at 25°C and 1 atm. These are tabulated in Table VIII along with the value from this work at 80°F and 1 atm, which is obtained from the smoothed data. The value from this work seems to be very close to that of Duda and Vrentas (14) and overall the agreement is good with all of the literature data.

Sada et al. (34) measured N_2O solubility in aqueous solutions of DEA with different concentration at 25°C and 1 atm. Their result in 2 M solution is shown in Figure 25 for comparison with the result of this work. The agreement is good.

N_2O Analogy

In this section, the validity of the "N_2O analogy" to estimate CO_2 and H_2S physical solubility under conditions similar to the conditions

TABLE VII

PROPERTIES OF N_2O AND THE ACID GASES (32)

Property	Nitrous Oxide (N_2O)	Carbon Dioxide (CO_2)	Hydrogen Sulfide (H_2S)
Molecular weight	44.013	44.010	34.080
Dipole moment (debyes)	0.20	0.00	0.90
Potential length constant (A°)	3.828	3.941	3.623
ε/k (°K)	232.4	195.2	301.1
Acentric factor	0.160	0.225	0.100
Critical Temperature (°K)	309.6	304.2	373.2
Critical Pressure (atm)	71.5	72.8	88.2

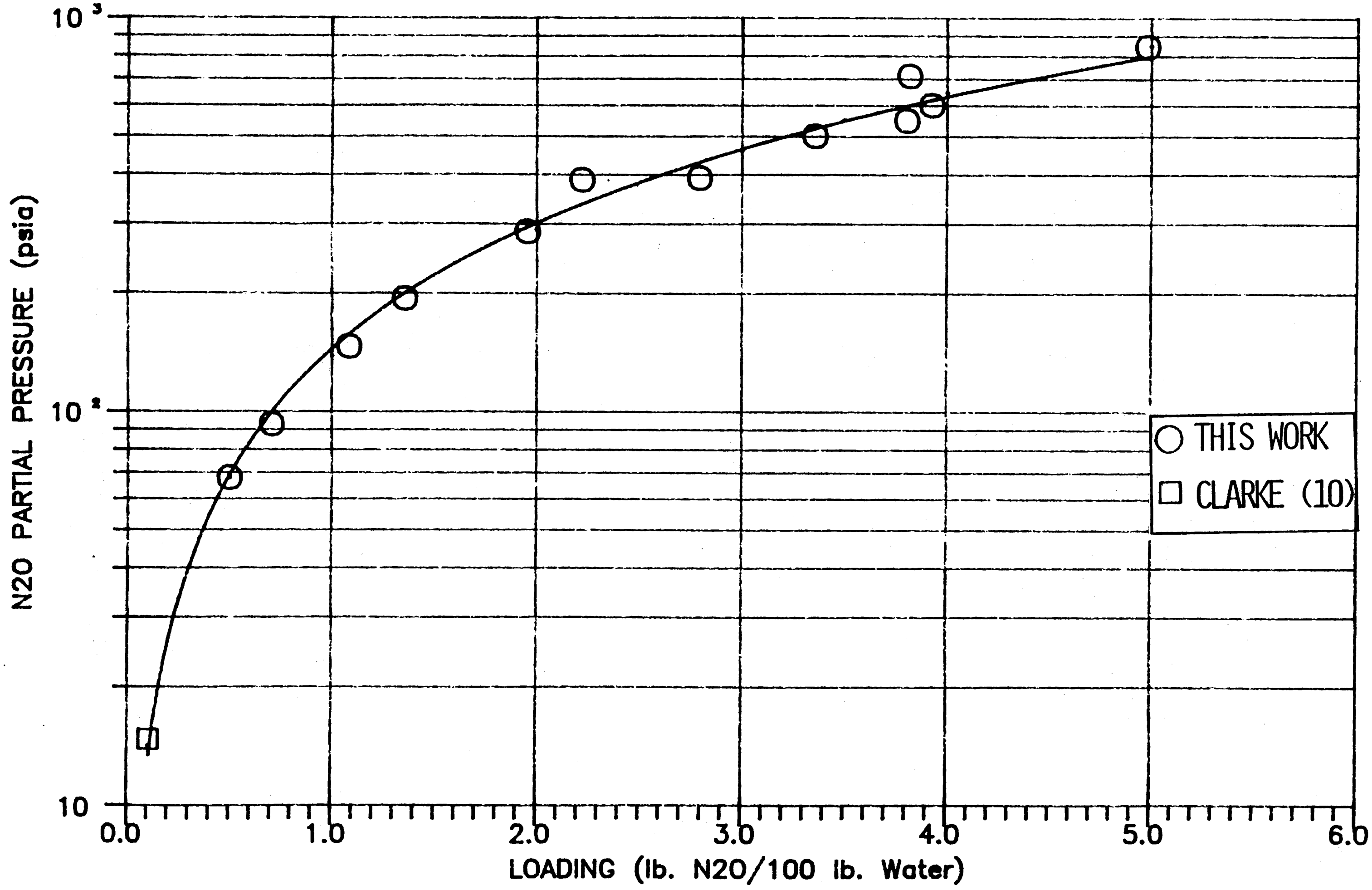


Figure 24. Solubility of N2O in Water at 80 F.

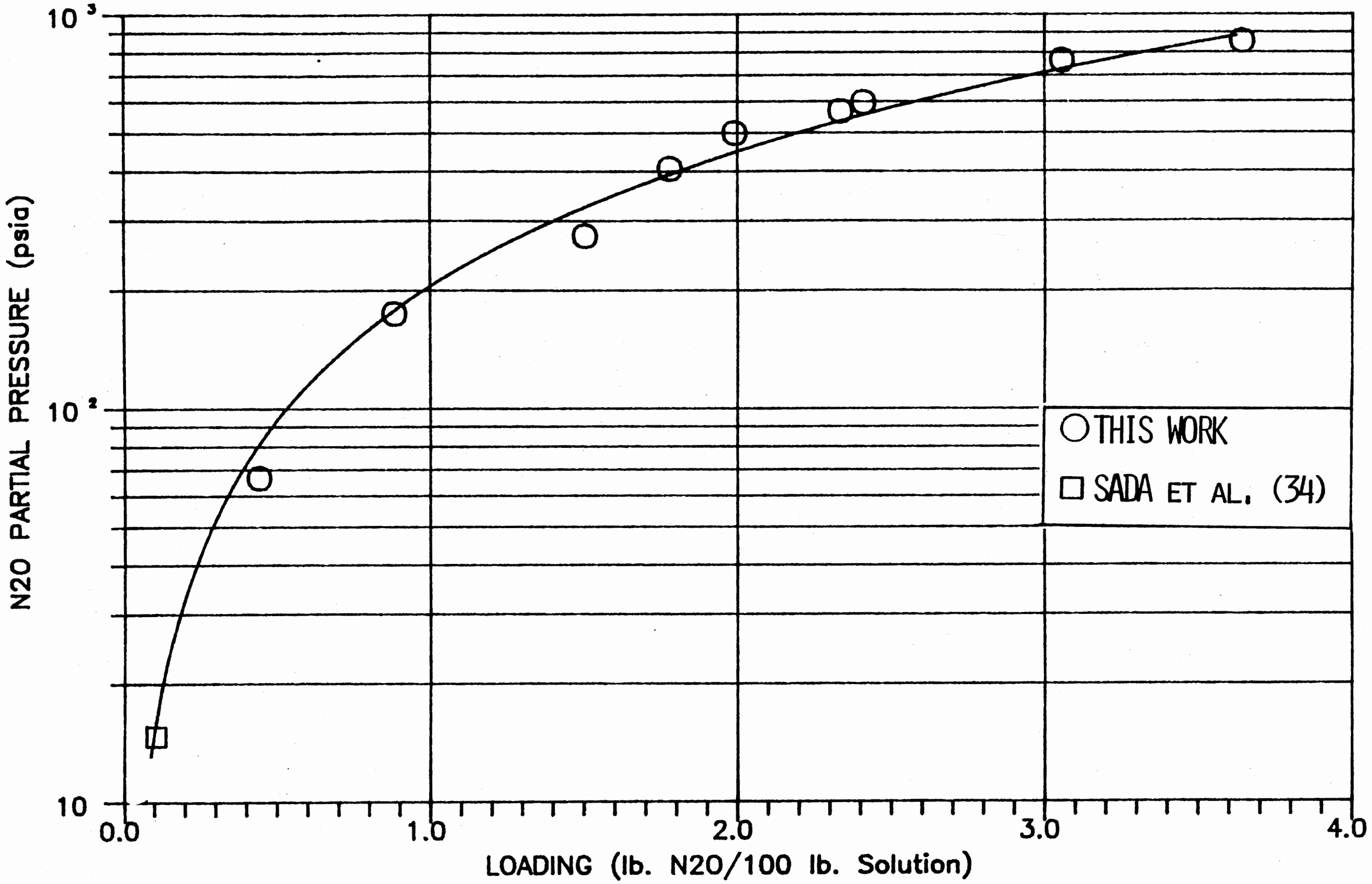


Figure 25. Solubility of N2O in Protonated (pH=7.3) 17% by Weight DEA Aqueous Solution at 80 F.

TABLE VIII

SOLUBILITY OF N_2O IN WATER AT 25°C AND 1 ATM

Reference	Loading $(\frac{\text{Lb } N_2O}{\text{100 Lb Water}})$
Clarke (10)	0.107
Joosten and Danckwerts (19)	0.107
Sada et al. (34)	0.106
Markham and Kobe (30)	0.108
Haimour and Sandell (16)	0.107
Versteeg and Van Swaaij (38)	0.108
Duda and Vrentas (14)	0.114
This work	0.111*

*At 80°F (26.67°C)

at which gas treating plants operates is checked. The solubility of N_2O, CO_2 and H_2S in water and in protonated 20% by weight DEA aqueous solution at such conditions are shown in Figures 26 and 27. These figures show a big difference in the solubility of N_2O and H_2S. Tables IX and X give the ratio of CO_2 physical solubility to N_2O solubility in water and in protonated 20% by weight DEA at 80 °F as a function of the gas partial pressure. Tables XI and XII give the ratio of H_2S solubility to N_2O solubility in the two solutions at similar conditions. The results show that the ratio does not remain constant as has been reported in the literature. Also, for H_2S, the ratio changes in water and in protonated 20% by weight DEA solution.

Several equations stated in the previous section have been proposed in the literature (34, 38) based on the "N_2O analogy". The solubility predicted by these equations along with the results of this work and the percent difference are shown in Tables XIII and XIV. Both equations underestimate the physical solubility of CO_2. Equation 15 gives 15.5% average difference. This difference is as much as 17.7% at high pressure. Equation 16 gives 6.1% average difference and, surprisingly, as high as 15.7% at low pressure. Since the analogy was inferred from measurements at atmospheric pressure, one would think that it would give lower difference at low pressure.

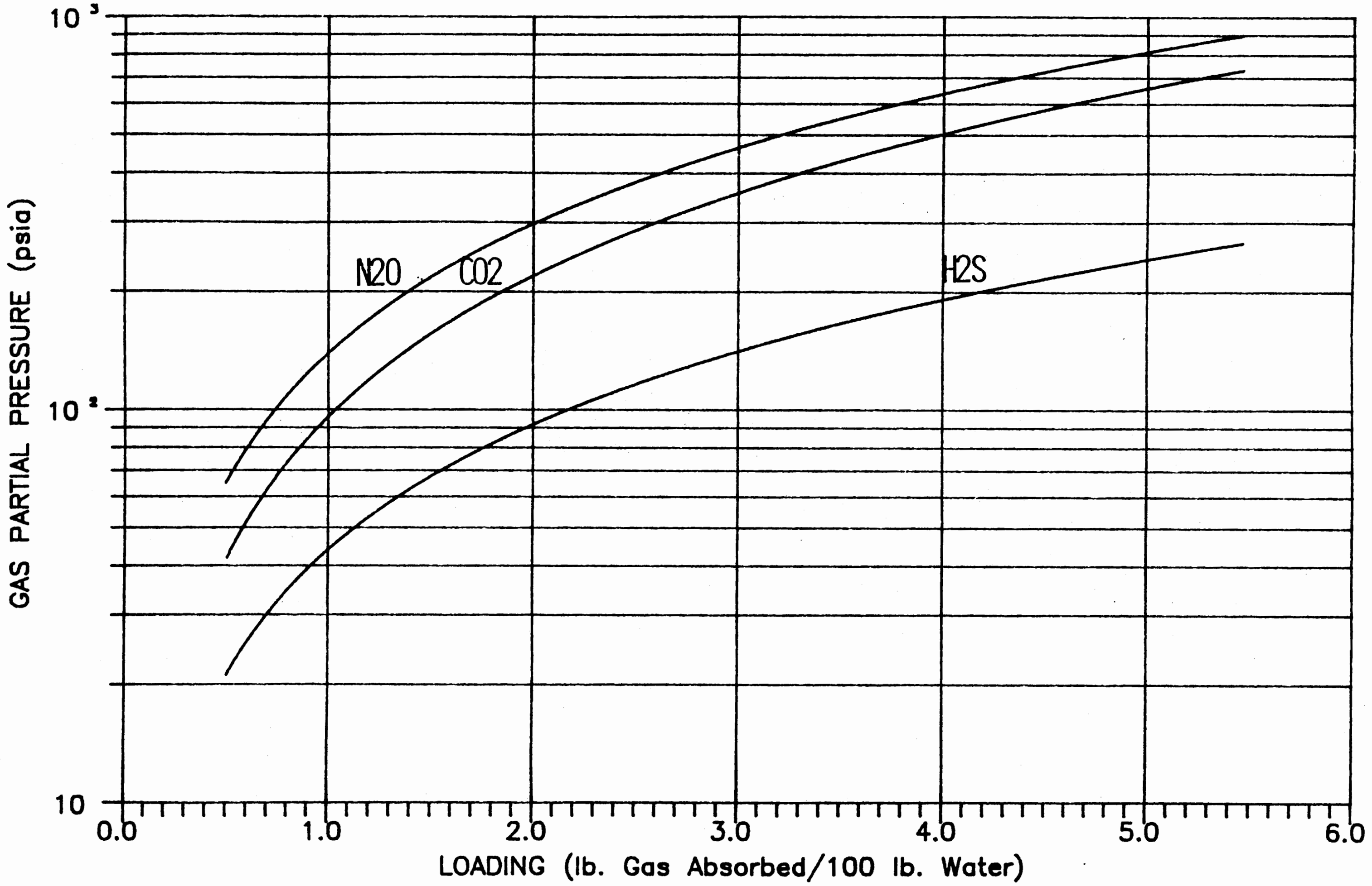


Figure 26. Solubility of N2O, CO2 and H2S in Water at 80 F.

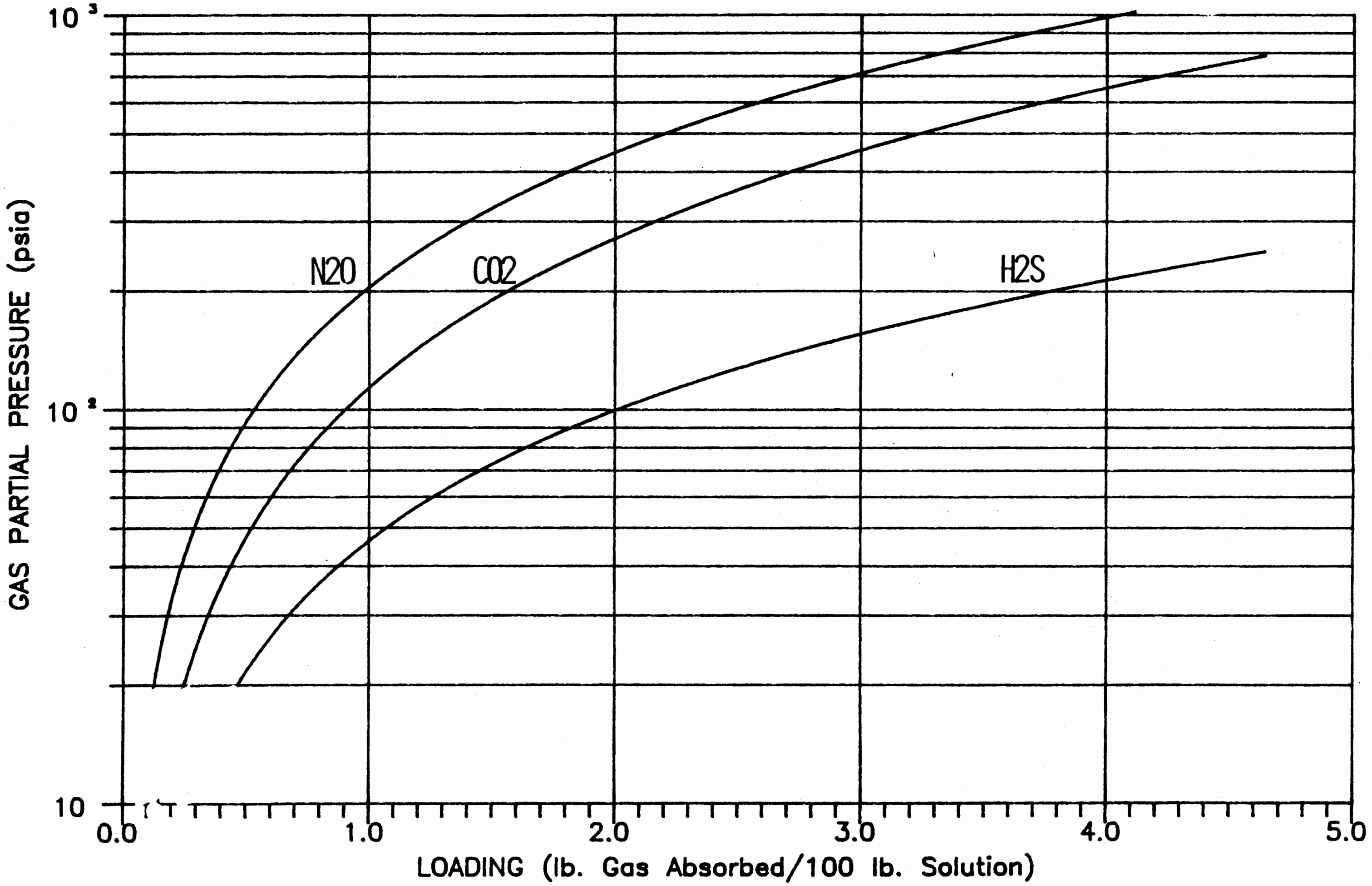


Figure 27. Solubility of N2O, CO2 and H2S in Protonated (pH=7.3) 20% by Weight DEA Aqueous Solution at 80 F.

TABLE IX

SOLUBILITY OF CO_2 AND N_2O IN WATER AT 80 °F

Gas Partial Pressure (psia)	CO_2 Loading[1] (β_{CO_2})	N_2O Loading[1] (β_{N_2O})	Ratio $\beta_{CO_2}/\beta_{N_2O}$
50.0	0.52	0.37	1.39
100.0	1.00	0.73	1.37
150.0	1.45	1.08	1.34
200.0	1.87	1.42	1.32
250.0	2.27	1.74	1.30
300.0	2.64	2.06	1.29
350.0	3.00	2.36	1.27
400.0	3.34	2.66	1.26
450.0	3.67	2.95	1.24
500.0	3.98	3.23	1.23
550.0	4.28	3.52	1.22
600.0	4.56	3.78	1.21
650.0	4.84	4.04	1.20
700.0	5.11	4.29	1.19
750.0	5.36	4.54	1.18
800.0	5.61	4.79	1.17
850.0	5.85	5.02	1.16
900.0	6.09	5.26	1.16
950.0	6.31	5.49	1.15
1000.0	6.53	5.71	1.14

Loading = Lb. Gas Absorbed/100 Lb. Water

[1] Smoothed Data

TABLE X

SOLUBILITY OF CO_2 AND N_2O IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION

Gas Partial Pressure (psia)	CO_2 Loading[1] (β_{CO_2})	N_2O Loading[1] (β_{N_2O})	Ratio $\beta_{CO_2}/\beta_{N_2O}$
50.0	0.49	0.30	1.37
100.0	0.91	0.58	1.43
150.0	1.29	0.83	1.46
200.0	1.64	1.07	1.46
250.0	1.96	1.29	1.46
300.0	2.25	1.50	1.45
350.0	2.53	1.70	1.44
400.0	2.78	1.89	1.43
450.0	3.02	2.07	1.42
500.0	3.25	2.24	1.42
550.0	3.46	2.40	1.41
600.0	3.67	2.57	1.40
650.0	3.86	2.71	1.40
700.0	4.05	2.85	1.39
750.0	4.23	2.99	1.38
800.0	4.40	3.13	1.38
850.0	4.56	3.26	1.37
900.0	4.72	3.39	1.37
950.0	4.88	3.51	1.37
1000.0	5.02	3.63	1.36

Loading = Lb. Gas Absorbed/100 Lb. Solution

[1] Smoothed Data.

TABLE XI

SOLUBILITY OF H_2S AND N_2O IN WATER AT 80 °F

Gas Partial Pressure (psia)	H_2S Loading[1] (β_{H_2S})	N_2O Loading[1] (β_{N_2O})	Ratio $\beta_{H_2S}/\beta_{N_2O}$
30.0	0.68	0.23	3.03
60.0	1.34	0.45	3.01
90.0	1.98	0.66	3.00
120.0	2.60	0.87	2.98
150.0	3.21	1.08	2.97
180.0	3.79	1.28	2.96
210.0	4.36	1.48	2.94
240.0	4.91	1.68	2.93
270.0	5.45	1.87	2.92
300.0	5.98	2.06	2.91

Loading = Lb. Gas Absorbed/ 100 Lb. Water

[1] Smoothed Data.

TABLE XII

SOLUBILITY OF H_2S AND N_2O IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION AT 80 °F

Gas Partial Pressure (psia)	H_2S Loading[1] (β_{H_2S})	N_2O Loading[1] (β_{N_2O})	Ratio $\beta_{H_2S}/\beta_{N_2O}$
30.0	0.65	0.18	3.17
60.0	1.26	0.36	3.28
90.0	1.84	0.52	3.37
120.0	2.40	0.68	3.41
150.0	2.93	0.83	3.43
180.0	3.44	0.97	3.46
210.0	3.93	1.11	3.47
240.0	4.40	1.25	3.46
270.0	4.86	1.38	3.46
300.0	5.30	1.50	3.48

Loading = Lb. Gas Absorbed/ 100 Lb. Solution

[1] Smoothed Data.

TABLE XIII

COMPARISON BETWEEN SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION OBTAINED EXPERIMENTALLY AND CALCULATED USING N_2O ANALOGY AT 80 °F

Gas Partial Pressure (psia)	(β_{CO_2}) Actual[1]	(β_{CO_2}) Calculated[2]	% Difference[3]
50.0	0.49	0.42	14.1
100.0	0.91	0.79	13.6
150.0	1.29	1.11	14.1
200.0	1.64	1.41	14.1
250.0	1.96	1.68	14.4
300.0	2.25	1.94	14.1
350.0	2.53	2.16	14.6
400.0	2.78	2.38	14.5
450.0	3.02	2.56	15.2
500.0	3.25	2.75	15.3
550.0	3.46	2.93	15.5
600.0	3.67	3.09	15.7
650.0	3.86	3.25	15.9
700.0	4.05	3.40	16.2
750.0	4.23	3.53	16.5
800.0	4.40	3.66	16.8
850.0	4.56	3.78	17.2
900.0	4.72	3.93	16.9
950.0	4.88	4.03	17.3
1000.0	5.02	4.13	17.7

[1] Smoothed Data

[2] According to Equation (15)

[3] $$\%\ \text{Difference} = \frac{(\beta_{CO_2}\text{actual} - \beta_{CO_2}\text{calculated})}{\beta_{CO_2}\text{actual}}$$

TABLE XIV

COMPARISON BETWEEN SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION OBTAINED EXPERIMENTALLY AND CALCULATED USING N_2O ANALOGY AT 80 °F

Gas Partial Pressure (psia)	(β_{CO_2}) Actual[1]	(β_{CO_2}) Calculated[2]	% Difference[3]
50.0	0.49	0.41	15.7
100.0	0.91	0.79	13.9
150.0	1.29	1.13	12.5
200.0	1.64	1.46	10.9
250.0	1.96	1.76	10.1
300.0	2.25	2.05	9.1
350.0	2.53	2.32	8.2
400.0	2.78	2.58	7.4
450.0	3.02	2.82	6.7
500.0	3.25	3.05	6.0
550.0	3.46	3.28	5.4
600.0	3.67	3.49	4.8
650.0	3.86	3.70	4.3
700.0	4.05	3.90	3.8
750.0	4.23	4.09	3.4
800.0	4.40	4.27	2.9
850.0	4.56	4.45	2.5
900.0	4.72	4.62	2.1
950.0	4.88	4.79	1.8
1000.0	5.02	4.95	1.4

[1] Smoothed Data

[2] According to Equation (16).

[3] $$\%\ \text{Difference} = \frac{(\beta_{CO_2}\text{actual} - \beta_{CO_2}\text{calculated})}{\beta_{CO_2}\text{actual}}$$

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

From the measurement of the solubility of CO_2 and H_2S in aqueous diethanolamine solutions and solubility of N_2O in water and in protonated 17% by weight DEA solution, the following conclusions can be drawn.

1. A method that allows for direct measurements of acid gases physical solubilities has been developed. The method eliminates amines reactivity with acid gases. The physical solubility data are needed in modeling acid gases absorption in aqueous alkanolamine solutions via the reaction equilibrium model or the mass transfer model. So far, acid gases physical solubilities have been estimated from their solubilities in pure water or using the "N_2O analogy".
2. The ratio of H_2S physical solubility to N_2O solubility in aqueous DEA solutions does not remain constant at all conditions. The ratio of these gases solubility in water also does not remain constant at all conditions. These ratios are different in amines solutions compared to those in pure water.
3. The ratio of CO_2 physical solubility to N_2O solubility in aqueous DEA solutions within experimental error is a constant, but the ratio of these gases in water is not constant and those ratios are different in water compared to those in DEA solutions.

4. Both CO_2 and H_2S physical solubility decreases with an increase in temperature.
5. CO_2 physical solubility decreases as a function of solution concentration while that of H_2S increases slightly.
6. At any acid gas partial pressure, the physical solubility of H_2S is higher than that of CO_2 for the same solution concentration and for the same temperature. This is also true for their solubilities in water.
7. CO_2 physical solubility in aqueous DEA solutions occurs mainly in the water portion of the solution. Therefore, the physical solubility of CO_2 in an aqueous DEA solution must be corrected based on the fraction of water in the solution.
8. H_2S physical solubility in aqueous DEA solutions is the same as H_2S solubility in water.

Recommendations

1. Investigation of the ability of the "N_2O analogy" to estimate CO_2 diffusivity in amines should be considered.
2. Acid gases physical solubilities in other aqueous amine solutions should be measured using the developed method.
3. Regarding the apparatus, installing a stirrer inside the equilibrium cell might reduce the time needed to reach equilibrium significantly.

BIBLIOGRAPHY

1. Adeyiga, A. A., G. J. Mains, and R. N. Maddox, "Vapor-Liquid Equilibrium Coefficients for Acid Gas Consistents and Physical Solvent," Proceedings 30th Canadian Conference on Chemical Engineering, Calgary, October, 1980.

2. Akashah, S. A., "Gas Sweetening; Determination of Equilibrium Distribution Coefficients for Hydorgen Sulfide, Carbon Dioxide and Methane in Methanol," M.Sc. Thesis, Oklahoma State University, Stillwater, OK, 1978.

3. Astarita, G., D. W. Savage, and A. Bisio, Gas Treating With Chemical Solvents, John Wiley & Sons, New York, 1983.

4. Atwood, K., M. R. Arnold, and R. C. Kindrick, "Equilibrium for the System, Ethanolamines-Hydrogen Sulfide-Water," Ind. Eng. Chem., 49 (9), pp. 1439-1444, Sept. 1957.

5. Batt, W. T., R. N. Maddox, G. J Mains, M. Rahman, and R. N. Vaz, "Chemical and Engineering Fundamentals of Ethanolamine Sweetening," Proceedings of the Gas Conditioning Conference, University of Oklahoma, Norman, OK, 1980.

6. Bhairi, A. M., "Experimental Equilibrium Between Acid Gases and Ethanolamine Solutions," Ph.D. Thesis, Oklahoma State University, Stillwater, OK, 1984.

7. Blauwhoff, P. M. M., G. F. Versteeg, and W. P. M. Van Swaaij, "A Study on the Reaction Between CO_2 and Alkanolamines in Aqueous Solutions," Chem. Eng. Sci., 39 (2), pp. 207-225, 1984.

8. Blauwhoff, P. M. M., "Selective Absorption of Hydrogen Sulphide from Sour Gases by Alkanolamine Solutions," Ph.D. Thesis, Techinsche Hogeschool Twente, Amsterdam, The Netherlands, 1982.

9. Bottoms, R. R., "Organic Bases for Gas Purification," Ind. Eng. Chem., 22 (5), pp. 501-504, May 1931.

10. Clarke, J. K. A., "Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times," Ind. Eng. Che. Fundamentals, 3 (3), pp. 239-245, August 1964.

11. Danckwerts, P. V., and K. M. McNeil, "The Absorption of Carbon Dioxide into Aqueous Amine Solutions and the Effects of Catalysis," Trans. Instn Chem. Engrs, 45 (19), pp. T32-T39, 1967.

12. Danckwerts, P. V., Gas-Liquid Reactions, McGraw-Hill Book Co., New York, 1970.

13. Diaz, J. M., A. Vega, and J. Coca, "Diffusivities of CO_2 and N_2O in Aqueous Alcohol Solutions," J. Chem. Eng. Data, 33, pp. 10-12, 1988.

14. Duda, J. L., and J. S. Vrentas, "Laminar Liquid Jet Diffusion Studies," AIChE J., 14 (2), pp. 286-294, March, 1968.

15. Elizondo, E. V., "Experimental Equilibrium and Modeling for the Absorption of Acid Gases in Diethanolamine Solution at Low and High Partial Pressure," Ph.D. Thesis, Oklahoma State University, Stillwater, OK, 1988.

16. Haimour, N., and O. C. Sandell, "Absorption of Carbon Dioxide into Aqueous Methyldiethanolamine," Chem. Eng. Sci., 39 (12), pp. 1791-1796, 1984.

17. Houghton, G., A. M. McLean, and P. D. Ritchie, "Compressibility, Fugacity, and Water-Solubility of Carbon Dioxide in the Region 0-36 atm. and 0-100°C," Chem. Eng. Sci., 6, pp. 132-137, 1957.

18. Joosten, G. E. H., and P. V. Danckwerts, "Solubility and Diffusivity of Nitrous Oxide in Equimolar Potassium Carbonate-Potassium Bicarbonate Solutions at 25°C and 1 atm," J. Chem. Eng. Data, 17 (4), pp. 452-454, 1972.

19. Kent, R. L., and B. Eisenberg, "Better Data for Amine Treating," Hydrocarbon Processing, February 1976.

20. Klyamer, S. D., and T. L. Kolesnikova, "General Mathematical Description of Experimental Data for the Thermodynamic Equilibrium in Carbon Dioxide-Monoethanolamine (Diethanolamine) -Water Systems," Russian J. f Physical Chemistry, 46 (2), 1972.

21. Kohl, A. L., and F. C. Riesenfeld, Gas Purification, Fourth Edition, Gulf Publishing Co., Houston, Texas, 1985.

22. Laddha, S. S., J. M. Diaz, and P. V. Danckwerts, "The N_2O Analogy: The Solubilities of CO_2 and N_2O in Aqueous Solutions of Organic Compounds," Chem. Eng. Sci., 36, pp. 228-229, 1981.

23. Laddha, S. S., and P. V. Danckwerts, "Reaction of CO_2 with Ethanolamines: Kinetics from Gas-Absorption," Che. Eng. Sci., 36 (3), pp. 479-482, 1981.

24. Lee, J. I., and A. E. Mather, "Solubility of Hydrogen Sulfide in Water," *Ber. Bunsenges. Phys. Chem.*, 81 (10\), pp. 1020-1023, 1977.

25. Lee, J. I., F. D. Oto, and A. E. Mather, "Solubility of Carbon Dioxide in Aqueous Diethanolamine Solutions at High Pressures," *J. Chem. Eng. Data*, 17 (4), pp. 465-468, 1972.

26. Loh, H. L., "Simulation of Alkanolamine Sweetening Processes," Ph.D. Thesis, Oklahoma State University, Stillwater, OK, 1987.

27. Maddox, R. N., *Gas Conditioning and Processing*, Vol. 4, *Gas and Liquid Sweetening*, Fourth Edition, Campbell Petroleum Series, Norman, OK, 1985.

28. Maddox, R. N., G. J. Mains, and M. A. Rahman, "Reactions of Carbon Dioxide and Hydrogen Sulfide with Some ALkanolamines," *Ind. Eng. Chem. Res.*, 26, pp. 27-31, 1987.

29. Maddox, R. N., "Private Communication", November 1988.

30. Markham, A. E., and K. A. Kobe, "The Solubility of Carbon Dioxide and Notrous Oxide in Aqueous Salt Solutions," *J. Am. Chem. Soc.*, 63, pp. 449-466, February, 1941.

31. Moshfeghian, M., K. J. Bell, and R. N. Maddox, "Reaction Equilibria for Acid Gas Systems," *Proceedings of the Gas Conditioning Conference*, University of Oklahoma, Norman, OK, 1977.

32. Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, Third Edition, McGraw-Hill Book Co., New York , 1977.

33. Sada, E., H. Kumazawa, and M. A. Butt, "Gas Absorption with Consecutive Chemical Reaction: Absorption of Carbon Dioxide into Aqueous Amine Solutions," *The Canadian J. Chem. Eng.*, 54, pp. 421-424, October, 1976.

34. Sada, E., H. Kumazawa, and M. A. Butt, "Solubilities of Gases in Aqueous Solutions of Amine," *J. Chem. Eng. Data*, 22 (3), pp. 277-278, 1977.

35. Sada, E., H. Kumazawa, and M. A. Butt, "Solubility and Diffusivity of Gases in Aqueous Solutions of Amines," *J. Chem. Eng. Data*, 23 (2), pp. 161-164, 1978.

36. Song, K. Y., and K. Riki, "Water Contents of CO_2-Rich Fluids in Equilibrium Water and Hydrate," Research Report-80, *Gas Processors Association*, May 1984.

37. Vaz, R. N., "Design of Ethanolamine Sweetening Processes Using a Reaction Equilibrium Model," Ph.D. Thesis, Oklahoma State University, Stillwater, OK, 1980.

38. Versteeg, G. F., W. P. M. Van Swaaij, "Solubility and Diffusivity of Acid Gases (CO_2, N_2O) in Aqueous Alkanolamine Solutions," J. Chem. Eng. Data, 33, pp. 29-34, 1988.

39. Versteeg, G. F., "Mass Transfer and Chemical Reactions in Acid Gas Treataing Process," Ph.D. Thesis, Universiteit Twente, Hengelo, The Netherlands, 1986.

40. Woertz, B. B., "Experiments With Solvent-Amine-Water for Removing CO_2 from Gas," The Canadian J. Chem. Eng., 50, pp. 425-427, June, 1976.

APPENDIX A

EXPERIMENTAL DATA

TABLE XV

SOLUBILITY OF CO_2 IN WATER AT 80°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Water
115.93	799.09	115.43	795.64	1.5320
119.55	824.04	119.05	820.59	1.2890
122.44	843.96	121.94	840.50	1.2355
125.18	862.85	124.68	859.40	1.2543
126.84	874.29	126.34	870.84	1.2673
132.72	914.82	132.22	911.37	1.2849
167.29	1153.11	166.79	1149.66	1.5521
173.27	1194.33	172.77	1190.88	1.5849
179.32	1236.03	178.82	1232.58	1.6489
186.63	1286.41	186.13	1282.97	1.7020
195.08	1344.66	194.58	1341.21	1.7630
246.16	1696.75	245.66	1693.30	2.1606
254.99	1757.61	254.49	1754.16	2.2928
266.40	1836.26	265.90	1832.81	2.3505
279.22	1924.62	278.72	1921.18	2.4398
293.05	2019.95	292.55	2016.51	2.5566
337.14	2323.86	336.64	2320.41	2.8154
351.62	2423.67	351.12	2420.22	2.9853
368.25	2538.29	367.75	2534.85	3.1299
388.34	2676.77	387.84	2673.33	3.2661
416.41	2870.25	415.91	2866.81	3.3801
443.62	3057.81	443.12	3054.36	4.3350
452.60	3119.71	452.10	3116.26	3.5255
461.70	3182.43	461.20	3178.99	4.3041
488.74	3368.82	488.24	3365.37	3.8563
504.81	3479.58	504.31	3476.14	4.1635
561.88	3872.96	561.38	3869.51	4.2172
571.47	3939.06	570.97	3935.61	4.1945
606.64	4181.48	606.14	4178.04	4.2918
612.08	4218.98	611.58	4215.53	4.7307
621.04	4280.74	620.54	4277.29	3.9539
624.03	4301.35	623.53	4297.90	4.8950
627.00	4321.82	626.50	4318.38	5.4623
658.56	4539.36	658.06	4535.91	4.9596
690.95	4762.62	690.45	4759.17	5.0510
733.81	5058.05	733.31	5054.60	5.0160
750.80	5175.16	750.30	5171.71	5.2950
782.74	5395.32	782.24	5391.87	5.1520

TABLE XVI

SOLUBILITY OF H_2S IN WATER AT 80°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Water
71.44	492.43	70.93	488.91	1.5830
135.03	930.74	134.52	927.23	2.9070
200.99	1385.40	200.48	1381.88	4.1104
240.78	1659.66	240.27	1656.15	4.9747

TABLE XVII

SOLUBILITY OF CO_2 IN ACIDIC (pH = 2.35) 17% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
108.12	745.26	107.76	742.77	0.7881
139.35	960.52	138.89	957.35	0.9764
213.94	1474.66	213.48	1471.49	1.6002
341.11	2351.22	340.67	2348.19	2.5948
449.71	3099.79	449.25	3096.62	2.7507
553.96	3818.37	553.50	3815.20	3.5929
646.00	4452.79	645.54	4449.62	3.7657
756.35	5213.41	755.89	5210.24	3.7174
823.73	5677.85	823.27	5674.68	4.2104
908.34	6261.06	907.88	6257.89	4.6383
945.10	6514.44	944.64	6511.27	4.7572

TABLE XVIII

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
112.77	777.31	112.33	774.27	1.1100
220.73	1521.46	220.29	1518.43	1.6589
280.27	1931.86	279.83	1928.83	1.9940
405.98	2798.36	405.54	2795.33	2.9761
478.28	3296.72	477.84	3293.68	3.1000
810.80	5580.73	810.36	5585.70	4.3776
894.48	6165.52	894.04	6162.49	4.7619

TABLE XIX

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION AT 150°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
127.72	880.36	124.16	855.82	0.6802
215.30	1484.03	211.64	1458.80	1.1427
274.83	1894.36	271.27	1869.83	1.2762
377.26	2600.40	373.70	2575.86	1.6770
481.25	3317.19	477.59	3291.96	1.9153
558.38	3848.83	554.72	3823.61	1.9819
678.84	4679.15	675.28	4654.61	2.3440
882.41	6082.33	878.85	6057.79	2.7941

TABLE XX

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 20% BY WEIGHT DEA AQUEOUS SOLUTION AT 240°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
129.05	889.52	105.45	726.85	0.2761
202.41	1395.18	178.81	1232.51	0.4148
211.26	1456.19	187.66	1293.51	0.4336
232.88	1605.21	209.28	1442.54	0.4627
260.63	1796.49	237.03	1633.81	0.5060
277.41	1912.15	253.81	1749.48	0.5356
297.54	2050.90	273.94	1888.23	0.5657
372.13	2565.04	348.53	2402.37	0.7337
410.00	2826.07	386.40	2663.40	0.7194
453.13	3123.36	429.53	2960.69	0.8364
513.11	3536.79	489.51	3374.12	0.8992
537.66	3706.01	513.98	3542.79	0.8824
548.64	3781.70	525.04	3619.03	0.9580
591.12	4074.51	567.52	3911.83	1.0194
629.13	4336.50	605.45	4173.28	0.9862
726.87	5010.21	703.19	4846.99	1.1180
887.44	6117.00	863.84	5954.33	1.2540
947.60	6531.67	924.00	6369.00	1.3407

TABLE XXI

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 26% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
72.89	502.42	72.45	499.39	0.6331
280.74	1935.10	280.30	1932.07	1.9107
474.36	3269.70	473.93	3266.73	2.8729
545.32	3758.81	544.88	3755.78	3.0435
652.28	4496.07	651.84	4493.04	3.2982
674.33	4648.06	673.90	4645.10	3.3027
687.25	4737.12	686.81	4734.08	3.5760

TABLE XXII

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 26% BY WEIGHT DEA AQUEOUS SOLUTION AT 150°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
83.87	578.10	80.64	555.84	0.3967
140.53	968.65	136.34	939.77	0.6487
180.44	1243.75	176.96	1219.76	0.7723
215.14	1482.93	211.91	1460.67	0.9605
231.86	1598.18	228.63	1575.91	0.9270
252.37	1739.55	249.14	1717.29	0.9472
389.12	2682.15	385.89	2659.88	1.2587
441.20	3041.13	437.97	3018.86	1.3285
485.71	3347.93	482.36	3324.84	1.4257
540.25	3723.87	536.92	3700.91	1.5744
592.85	4086.43	589.62	4064.17	1.7082
692.20	4771.24	688.72	4747.25	1.8564
717.21	4943.63	713.98	4921.36	1.9474
777.22	5357.27	773.99	5335.00	1.9795
809.20	5577.70	805.97	5555.44	2.1379
934.54	6441.65	931.31	6419.39	2.3399

TABLE XXIII

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 35% BY WEIGHT DEA AQUEOUS SOLUTION AT 240°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
113.93	785.30	96.27	663.58	0.2113
140.94	971.48	118.62	817.63	0.2773
158.16	1090.17	135.84	936.33	0.2958
168.64	1162.41	146.32	1008.56	0.3117
261.44	1802.07	239.12	1648.22	0.4941
303.05	2088.88	280.73	1935.03	0.4821
310.46	2139.96	288.14	1986.11	0.5359
419.04	2888.38	396.72	2734.53	0.5895
464.60	3202.42	442.28	3048.57	0.6719
508.66	3506.12	486.34	3352.27	0.6764
524.15	3612.89	501.83	3459.04	0.7411
546.17	3764.67	523.85	3610.82	0.7343
589.99	4066.72	567.67	3912.87	0.8011
609.62	4202.02	587.30	4048.18	0.8225
774.70	5339.90	752.38	5186.05	0.8990
880.48	6069.02	858.16	5915.17	1.0184

TABLE XXIV

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 34% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
83.71	577.00	83.35	574.52	0.6250
193.55	1334.11	193.19	1331.63	1.2290
215.90	1488.17	215.54	1485.69	1.3580
248.98	1716.18	248.62	1713.70	1.4862
449.26	3096.69	448.90	3094.20	2.2099
504.28	3475.93	503.92	3473.45	2.4022
551.77	3803.27	551.41	3800.79	2.5680
580.28	3999.79	579.92	3997.31	2.6673
738.41	5089.75	738.05	5087.27	3.2408
781.19	5384.63	780.83	5382.15	3.1319
814.56	5614.65	814.20	5612.16	3.3375
923.44	6365.14	923.08	6362.66	3.7040

TABLE XXV

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 50% BY WEIGHT DEA AQUEOUS SOLUTION AT 150°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
93.40	643.79	90.52	623.94	0.4449
174.08	1199.91	171.20	1180.06	0.7994
180.14	1241.68	177.26	1221.83	0.7529
202.74	1397.46	199.86	1377.61	0.7459
234.03	1613.14	231.15	1593.28	0.7965
263.21	1814.27	260.33	1794.42	0.8449
281.00	1936.89	278.11	1916.97	0.8808
366.18	2524.03	363.30	2504.18	0.9052
380.19	2620.60	377.31	2600.74	1.0507
397.18	2737.71	394.30	2717.85	1.0132
456.18	3144.38	453.30	3124.53	1.1484
543.48	3746.13	540.60	3726.28	1.2541
577.16	3978.28	574.28	3958.43	1.3638
659.63	4546.74	656.74	4526.82	1.6599
764.22	5267.66	761.34	5247.81	1.7154
852.23	5874.30	849.35	5854.45	1.9196
909.26	6267.40	906.38	6247.55	1.9724

TABLE XXVI

SOLUBILITY OF CO_2 IN PROTONATED (pH = 7.3) 50% BY WEIGHT DEA AQUEOUS SOLUTION AT 240°F

Total Pressure		CO_2 Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb CO_2/100 lb Solution
128.49	885.66	107.82	743.19	0.2402
211.09	1455.01	190.42	1312.54	0.3545
301.79	2080.20	281.11	1937.65	0.4847
325.19	2241.49	304.52	2099.01	0.4787
400.48	2760.45	379.81	2617.98	0.5532
443.56	3056.71	422.89	2914.92	0.5890
514.95	3549.48	494.27	3406.93	0.6698
607.67	4188.58	586.99	4046.04	0.7412
663.59	4574.03	642.92	4431.56	0.8150
720.89	4968.99	700.22	4826.52	0.8314
785.31	5413.03	764.64	5270.55	0.8954

TABLE XXVII

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 20% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
49.81	343.33	49.37	340.30	1.0336
52.71	363.32	52.27	360.29	1.0976
67.75	466.99	67.31	463.96	1.4391
99.88	688.46	99.43	685.36	1.9567
109.41	754.15	108.96	751.05	2.2041
121.44	837.07	121.00	834.04	2.5071
149.04	1027.31	148.60	1024.28	2.8836
201.84	1391.25	201.39	1388.15	3.7031
229.97	1585.15	229.53	1582.12	4.3060
249.92	1722.66	249.47	1719.56	4.4995
253.57	1747.82	253.13	1744.79	4.6407

TABLE XXVIII*

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 20% BY WEIGHT DEA AQUEOUS SOLUTION AT 150°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
46.69	321.83	43.25	298.12	0.50
59.41	409.50	55.97	385.79	0.6534**
94.93	654.34	91.49	630.63	1.00
148.67	1024.76	145.23	1001.05	1.50
208.48	1437.02	205.04	1413.31	2.00
274.61	1892.85	271.17	1869.14	2.50

* All the data points presented in this table are obtained by linear interpolation from the data obtained for this solution at 80 and 240°F.

** Experimental data point.

TABLE XXIX

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 20% BY WEIGHT DEA AQUEOUS SOLUTION AT 240°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
80.18	552.67	56.50	389.45	0.4154
142.52	982.37	118.84	819.15	0.8223
190.76	1314.88	167.08	1151.66	1.0950
273.86	1887.68	250.18	1724.46	1.5675

TABLE XXX

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 35% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
52.77	363.74	52.37	360.98	1.2097
53.78	370.70	53.38	367.94	1.2278
57.52	396.48	57.12	393.72	1.3252
58.13	400.68	57.73	397.92	1.2936
143.87	991.68	143.47	988.92	2.8391
157.34	1084.52	156.94	1081.77	3.0617
166.48	1147.52	166.08	1144.77	3.3770
219.07	1510.02	218.67	1507.26	4.0557
235.13	1620.72	234.74	1618.03	4.4781
241.72	1666.14	241.32	1663.38	4.4160
252.75	1742.17	252.36	1739.48	4.6085

TABLE XXXI

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 35% BY WEIGHT DEA AQUEOUS SOLUTION AT 150°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
63.62	438.52	60.40	416.33	0.7295
64.85	447.00	61.62	424.74	0.7708
123.56	851.68	120.33	829.42	1.3362
125.35	864.02	122.12	841.76	1.3849
255.21	1759.13	251.98	1736.86	2.4195

TABLE XXXII

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 35% BY WEIGHT DEA AQUEOUS SOLUTION AT 240°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
75.65	521.44	53.33	367.60	0.4189
176.70	1217.97	154.38	1064.12	1.0778
273.88	1887.82	251.56	1733.97	1.6032
285.01	1964.53	262.69	1810.68	1.6968

TABLE XXXIII

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 50% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
71.13	490.29	70.77	487.81	1.7510
96.55	665.51	96.20	663.09	2.2743
103.63	714.31	103.20	711.34	2.3864
122.20	842.31	121.85	839.89	2.7207
158.58	1093.07	158.22	1090.59	3.4215
211.83	1460.11	211.47	1457.63	4.3363
249.88	1722.39	249.52	1719.91	4.9153

TABLE XXXIV*

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 50% BY WEIGHT DEA AQUEOUS SOLUTION AT 150°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
37.57	258.96	34.69	239.11	0.50
77.86	536.68	74.98	516.83	1.00
124.56	858.57	121.68	838.72	1.50
178.54	1230.65	175.66	1210.80	2.00
240.82	1659.94	237.94	1640.09	2.59

* All the data presented in this table are obtained by linear interpolation from the data obtained for this solution at 80 and 240°F.

TABLE XXXV

SOLUBILITY OF H_2S IN PROTONATED (pH = 7.3) 50% BY WEIGHT DEA AQUEOUS SOLUTION AT 240°F

Total Pressure		H_2S Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb H_2S/100 lb Solution
102.95	709.62	82.28	567.14	0.7198
172.52	1189.16	151.85	1046.68	1.2519
208.81	1439.30	188.14	1296.82	1.3786
276.61	1906.63	255.94	1764.16	1.8636
277.87	1915.32	257.20	1772.84	1.7871
283.39	1953.37	262.72	1810.89	1.8328

TABLE XXXVI

SOLUBILITY OF N_2O IN WATER AT 80°F

Total Pressure		N_2O Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb N_2O/100 lb Water
92.90	640.35	92.39	636.83	0.7062
146.44	1009.39	145.93	1005.87	1.0833
193.63	1334.66	193.12	1331.15	1.3573
286.26	1973.15	285.75	1969.63	1.9534
387.27	2669.40	386.76	2665.88	2.2196
392.11	2702.76	391.60	2699.24	2.7927
500.25	3448.15	499.74	3444.64	3.3573
547.40	3773.15	546.89	3769.63	3.8042
598.77	4127.24	598.26	4123.72	3.9260
709.33	4889.31	708.82	4885.80	3.8169
843.77	5815.99	843.26	5812.37	4.9806

TABLE XXXVII

SOLUBILITY OF N_2O IN PROTONATED (pH = 7.3) 17% BY WEIGHT DEA AQUEOUS SOLUTION AT 80°F

Total Pressure		N_2O Partial Pressure		Loading
Psia	kPa	Psia	kPa	Lb N_2O/100 lb Solution
66.88	460.99	66.42	457.82	0.4407
174.42	1202.25	173.96	1199.08	0.8821
274.50	1892.09	274.04	1888.92	1.5015
406.09	2799.12	405.62	2795.88	1.7779
498.90	3438.85	498.44	3435.68	1.9898
566.49	3904.73	566.03	3901.56	2.3340
596.51	4111.66	596.05	4108.49	2.4083
763.98	5266.01	763.52	5262.83	3.0564
852.22	5874.23	852.76	5877.95	3.6403

APPENDIX B

CALIBRATION OF THE THERMOCOUPLE

A copper-constantan thermocouple was used to measure the temperature in the equilibrium cell. The thermocouple was calibrated in a constant temperature bath against an NBS calibrated platinum resistance thermometer.

The thermocouple was calibrated by reading the temperature from the platinum resistance thermometer and reading the mv of the thermocouple via a potentiometer. The data are shown in Table XXXVIII.

The data were fitted to a cubic equation by a least squares method. The equation is shown at the bottom of Table XXXVIII.

TABLE XXXVIII

CALIBRATION OF COPPER-CONSTANTAN THERMOCOUPLE DATA

Thermocouple E1 Reading (mv)	Platinum Resistance Thermometer T(°F)
0.0050	32.00
1.0050	77.54
1.2075	86.59
1.3625	93.34
1.6100	103.97
1.8525	114.44
2.1075	125.47
2.4013	137.60
2.6750	148.84
2.9800	161.38
3.2988	174.22
3.6100	186.53
3.9250	198.97
4.2550	212.08
4.5688	224.06
4.9163	237.29
5.2638	250.55

$$T = 31.75 + 46.8701(mv) - 1.2974(mv)^2 + 0.0550(mv)^3$$

APPENDIX C

CALIBRATION OF PRESSURE GAUGES

The pressure gauges were calibrated against a Ruska Model 2400 HL Dead weight tester. The data obtained for the two gauges are shown in Tables XXXIX and XXXX. The test pressure (Pt) was fitted against the gauge pressure (Pg) using a quadratic equation. The equation for each gauge is given at the bottom of the corresponding table. These equations were used to calculate the corrected gauge pressure.

TABLE XXXIX

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

Test Pressure, Psi (Pt)	Gauge Pressure, Psi (Pg)
9.99	10.00
23.97	23.70
35.95	35.60
45.94	45.40
59.92	59.20
83.89	83.00
129.83	128.70
195.75	194.80
245.69	245.60
289.63	290.45

$$P_t = -0.2181 + 1.0206(Pg) - 7.7908 \times 10^{-5}(pg)^2$$

TABLE XXXX

CALIBRATION OF (0-5000 PSI) HEISE GAUGE MODEL SOLID FRONT-C-52143

Test Pressure, Psi (Pt)	Gauge Pressure, Psi (Pg)
105.86	103.00
145.81	143.50
205.73	203.00
285.63	285.00
345.55	342.00
405.48	401.00
505.35	502.00
605.23	601.00
705.10	701.00
804.97	801.50
904.84	901.00
1008.71	1006.00

$$Pt = 2.567621 + 1.0033603\ (Pg) - 2.492185 \times 10^{-6}(Pg)^2$$

APPENDIX D

PHYSICAL PROPERTIES OF DEA SOLUTION

TABLE XXXXI

VAPOR PRESSURE OF DEA AQUEOUS SOLUTIONS (15)

Concentration Weight Percent DEA	Temperature °F	Vapor Pressure psia
20	80	0.445
	150	3.440
	240	23.680
35	80	0.397
	150	3.226
	240	22.320
50	80	0.356
	150	2.880
	240	20.670

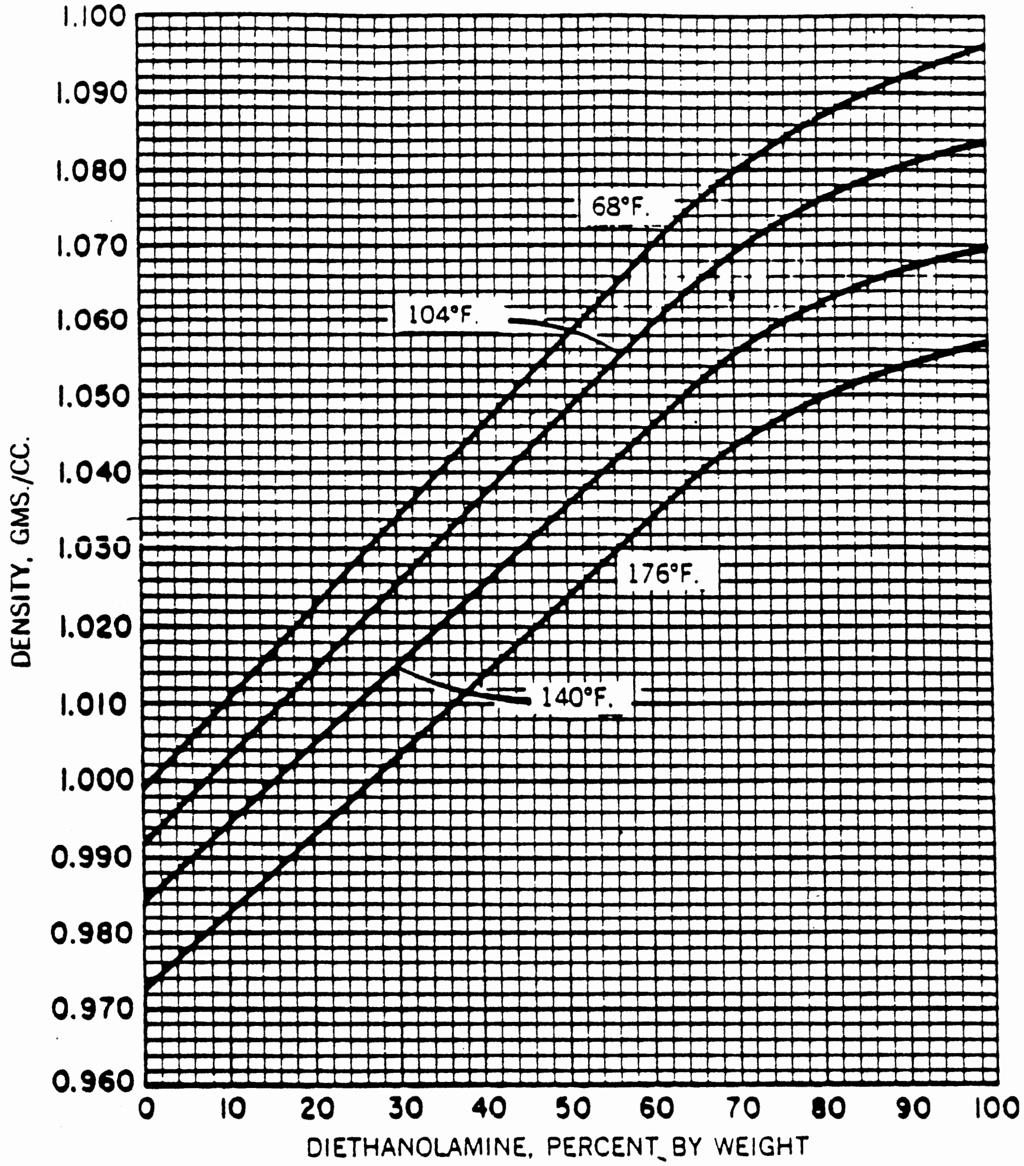


Figure 28. Density of DEA Aqueous Solutions (6).

APPENDIX E

SAMPLE CALCULATION OF SOLUBILITY

Cell volume = 1007.57 ml

Initially the cell is charged with CO_2, initial pressure = 421.48 psia

CO_2 mole fraction = 1.0

Thus, CO_2 mass fraction = 1.0

From SRK equation of state,

Density of vapor phase = 3.7984 Lb/ft^3

Initial mass of CO_2 in the cell

= 1.00757 liter x 3.5315 x 10^{-2} ft^3/liter x 1.0 Lb/Lbs vapor x 3.7984 Lb/ft^3 = 0.135155 lbs

Amount of water injected = 177.57 ml

Final cell pressure = 452.61 psia

water vapor pressure = 26.27 mm Hg

water mole fraction = 0.001123

CO_2 mole fraction = 0.998877

CO_2 mass fraction = 0.999540

From SRK the vapor density = 4.1438 Lb/ft^3

Final mass of CO_2 in the vapor phase after injecting the water =

(1.00757 - 0.17757) liter x 3.5315 x 10^{-2} x 0.999540 x 4.1438 = 0.121403 Lbs

Dissolved CO_2 = 0.135155 - 0.121403 = 0.013752 Lbs

Density of water = 0.996433 g/ml

Amount of water injected = 177.57 ml x 0.9964 g/ml x $\frac{\text{Lb}}{\text{453.6 gr}}$

= 0.390065 lbs

$$\text{Loading} = \frac{0.013752 \text{ Lbs } CO_2}{0.390065 \text{ Lbs water}} \times 100$$

$$= 3.5255 \frac{\text{Lbs } CO_2}{100 \text{ Lbs Water}}$$

APPENDIX F

ERROR ANALYSIS

The results obtained in this work are presented as the loading of the acid gas in the solution and the acid gas partial pressure. The loading is calculated from a mass balance that requires the total pressure, the temperature, and the volume of the injected solution. To calculate the maximum error in the loading, the maximum deviation in each of the above quantities is assumed. Even though, the pressure is read accurately within a subdivision via a cathetometer, still the subdivision is assumed as the maximum deviation in reading the pressure. Two gauges were used in measuring the pressure, each with a different range and subdivision as listed below.

1. 0-5000 psi gauge with 5 psi subdivisions
2. 0-300 psi gauge with 0.2 psi subdivisions

Also the maximum deviation in reading the temperature (0.04°F) and the volume of the solution (0.1 ml) are included in the calculations. Two examples are presented here, one for each gauge.

0-5000 psi gauge
5 psi subdivision

In this case, the maximum deviation is assumed as 2.5 psi in the initial reading and 2.5 psi in the final reading.

Run (P35-CO_2) - 2B

Physical Solubility of CO_2 in Protonated

26% by weight DEA Solution at 80°F

Initial Pressure, P_i = 462.32 psia

Initial Temperature, T_i = 80°F

Initial Pressure with Maximum Deviation, P_i'

= 462.32 + 2.5 = 464.82 psia

Initial temperature with maximum deviation, T_i'

= 80 - 0.04 = 79.96°F

From SRK equation of state, the initial density of the vapor phase, ρ_i' = 4.285 lb/ft^3

Final pressure P_f = 545.32 psia

Final temperature, T_f = 80°F

Final Pressure with maximum deviation, P_f' = 545.32 - 2.5

= 542.82 psia

Final temperature with maximum deviation, T_f' = 80 + 0.04 = 80.04°F

From SRK, the final density of the vapor, ρ_f' = 5.224 lb/ft^3

Solution injected = 300.8 ml at 70°F

Maximum error in measuring 50 ml = ±0.2 ml

Maximum error in the value injected = ±1.2 ml

Maximum solution injected = 302 ml

Solution injected at 80°F = 302.8 ml

Initial mass of CO_2 m_i' =

$$1.00757 \text{ liter X } 3.531466 \text{ X } 10^{-2} \frac{\text{ft}^3}{\text{liter}} \text{ X } 1.0 \frac{\text{lbs CO}_2}{\text{lbs vapor}}$$

$$\text{X } 4.285 \frac{\text{lbs vapor}}{\text{ft}^3} = 0.152469 \text{ lbs CO}_2$$

Final mass of CO_2, m_f' =

$$(1.00757 - 0.3028) \text{ X } 3.531466 \text{ X } 10^{-2} \text{ X } 0.9997 \text{ X } 5.224 \frac{\text{lbs vapor}}{\text{ft}^3}$$

$$= 0.129980 \text{ lbs CO}_2$$

Dissolved $CO_2 = m_i' - m_f' = 0.022489$ lbs.

Protonated 26% by weight DEA solution injected = 302.8 ml x

$$1.037 \frac{\text{g sol'n}}{\text{ml}} \text{ X } \frac{\text{lb}}{453.6 \text{ gr}} = 0.692258 \text{ lbs}$$

$$\text{Loading} = \frac{0.022489 \text{ lbs CO}_2}{0.692258 \text{ lbs Solution}} \text{ X } 100 = 3.2487 \frac{\text{lbs CO}_2}{100 \text{ lbs Solution}}$$

Compare to the reported value of 3.0435 lbs CO_2/100 lbs solution

Maximum % deviation = 6.74%

0-300 psi gauge
0.2 psia subdivision

For this gauge, 0.2 psi is assumed as the maximum deviation in the initial and in the final reading.

Run (P50-CO_2) - 3

Physical Solubility of CO_2 in Protonated 34% by Weight DEA Solution at 80°F

Initial Pressure, P_i = 183.98 psia

Initial Temperature, T_i = 80°F

Initial Pressure with maximum deviation, P_i' = 183.98 + 0.2

= 184.18 psia

Initial Temperature with maximum deviation, T_i'

= 80 - 0.04 = 79.96°F

From SRK, the vapor density, ρ_i' = 1.495 lb/ft^3

Final pressure, P_f = 193.55 psia

Final temperature, T_f = 80°F

Final pressure with maximum deviation, P_f'

= 193.55 - 0.2 = 193.35 psia

Final temperature with maximum deviation, T_f'

= 80 + 0.04 = 80.04°F

From SRK, the vapor density, ρ_f' = 1.574 lb/ft^3

Initial mass of CO_2, m_i' =

$1.01695 \times 3.531466 \times 10^{-2} \times 1.0 \times 1.495$

= 0.053690 lbs

Solution injected = 107.4 ml at 70°F

Maximum solution injected = 107.8 ml

Solution injected at 80°F = 108.1 ml

Final mass of CO_2, m_f' =

$$(1.01695 - 0.1081) \times 3.531466 \times 10^{-2} \times 0.9993 \times 1.574$$

$$= 0.050483 \text{ lbs}$$

Dissolved $CO_2 = m_i' - m_f' = 0.003207$ lbs

Protonated 34% by weight DEA Solution injected = 108.1 X 1.054

$$\times \frac{1}{453.6} = 0.251189 \text{ lbs}$$

$$\text{Loading} = \frac{0.003207 \text{ lbs } CO_2}{0.251189 \text{ lbs solution}} \times 100$$

$$= 1.2766 \text{ lbs } CO_2/100 \text{ lbs solution}$$

Compare to the reported value of 1.2290 lbs CO_2/100 lbs solution

Maximum % deviation = 3.87%

APPENDIX G

FREE AMINE AND CORRECTED SOLUBILITY CALCULATIONS

Calculations of CO_2 solubility on water basis from physical solubility measurements.

1. Calculation of Free Diethanolamine (DEA)

The following reactions occurred as HCl was added to the 20% by weight DEA aqueous solution;

$$RR'NH_2^+ \overset{K_1}{\rightleftarrows} H^+ + RR'NH \qquad (1)$$

$$H_2O \overset{K_2}{\rightleftarrows} H^+ + OH^- \qquad (2)$$

HCl was added until the final pH is 7.3. This gave

$$[H^+] = 4.67735 \times 10^{-8} \text{ moles/lit.}$$

Writing equations for the pseude-equilibrium constants and material balance give

$$K_1 = \frac{X_1 X_2}{X_3} \qquad (3)$$

$$K_2 = X_1 X_4 \qquad (4)$$

$$M = X_2 + X_3 \qquad (5)$$

where $X_1 = [H^+]$, $X_2 = [RR'NH]$, $X_3 = [RR'NH_2^+]$, $X_4 = [OH^-]$

After adding the HCl solution (~ 12N)

$M = 1.6622$ moles/lit. protonated and free DEA

$K_1 = 5.909 \times 10^{-10}$ moles/lit. (From Ref. 15)

$K_2 = 1.2127 \times 10^{-14}$ moles/lit. (From Ref. 19)

From (3) $$X_3 = \frac{X_1}{K_1}X_2 = 84.8176X_2 \qquad (6)$$

From (5) and (6) $X_2 = 1.9369 \times 10^{-2}$ moles/lit. free DEA

2. Calculations of Solubility on Water Basis

Assuming that the free DEA (1.9369×10^{-2} moles/lit) reacted with equivalent amount of CO_2, then

$$\alpha = 1.9369 \times 10^{-2} \frac{\text{moles}}{\text{lit.}} \times \frac{\text{lit.}}{10^3\text{ml}} \times \frac{\text{ml}}{1.02\text{ gr}} \times \frac{44.01\text{ gr } CO_2}{\text{mole } CO_2}$$

$$= 0.0836 \frac{\text{gr } CO_2}{100\text{ gr soln.}} = 0.0836 \frac{\text{Lb } CO_2}{\text{mole } CO_2}$$

In 100 lb. solution, there are 17% by weight DEA, 6% HCl and 77% water.

At P_{CO_2} = 220.29 psia, Loading (β) = $1.6589 \dfrac{\text{Lb } CO_2}{100\text{ lb. soln.}}$

$\beta' = \beta - \alpha = 1.5753 \dfrac{\text{Lb. } CO_2}{100\text{ Lb. soln.}}$ physically absorbed in the protonated 17% by weight DEA aqueous solution.

$$\beta'' = \beta' \times \frac{100\text{ Lb. water}}{77\text{ lb. water/ }100\text{ Lb. soln.}}$$

$$= 2.0458 \frac{\text{Lb. } CO_2}{100\text{ Lb. water}}$$

β'' is the solubility calculated on water basis. This was done to be able to compare CO_2 physical solubility in aqueous diethanolamine solutions to CO_2 solubility in pure water.

VITA

Mousa Khaled Abu-Arabi

Candidate for the Degree of

Doctor of Philosophy

Thesis: PHYSICAL SOLUBILITY OF HYDROGEN SULFIDE AND CARBON DIOXIDE IN ALKANOLAMINE SOLUTIONS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Om-al-dananeer, Jordan, March 8, 1961, the son of Khaled and Jamelah Abu-Arabi.

Education: Graduated from Sweleh Secondary School, Sweleh, Jordan, in June, 1978; B.S. in Chemical Engineering from Oklahoma State University, Stillwater, Oklahoma in July, 1983; M.S. in Chemical Engineering from New Mexico State University, Las Cruces, New Mexico in July, 1985; completed requirements for the Doctor of Philosophy Degree in Chemical Engineering at Oklahoma State University, Stillwater, Oklahoma in December, 1988.

Professional Experience: Graduate Teaching Assistant, Chemical Engineering Department, New Mexico State University, Las Cruces, New Mexico, January, 1984 to May, 1985. Graduate Teaching/Research Assistant, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, August, 1985 to present.

Professional Membership: American Institute of Chemical Engineers; Omega Chi Epsilon.