

**MONOETHANOLAMINE REACTIONS WITH
SELECTED ACID GASES**

By

WILLIAM THOMAS BATT

Bachelor of Science

Defiance College

Defiance, Ohio

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Thesis Approved:

R. N. M. [Signature]

Thesis Advisor

John H. [Signature]

[Signature]

Norman J. [Signature]
Dean of Graduate College

PREFACE

An anhydrous solution of monoethanolamine was reacted separately with three selected acid gases to examine the reaction mechanisms and relative rates of reaction. This was done at pressures of 10 psig and 20 psig and at room temperature. A glass reaction cell was used and pressure changes indicated the progression of the reaction.

I am truly grateful to Dr. R. N. Maddox for serving as my advisor and for his guidance and concern. I would like to thank Dr. G. J. Mains for his assistance, inspiration, and guidance - particularly in evaluation of the nmr scans. I gratefully acknowledge partial funding from the National Science Foundation in grants to the Chemistry Department to purchase the XL-100(15) NMR spectrometer (GP17641) and the TT-100PFT accessory (CHE76-05571). I also wish to thank my wife Melissa for her encouragement and support throughout this work.

TABLE OF CONTENTS

| Chapter | Page |
|--|------|
| I. INTRODUCTION | 1 |
| II. LITERATURE SURVEY | 3 |
| III. EQUIPMENT AND REAGENTS | 5 |
| Equipment | 5 |
| Reagents | 8 |
| IV. EXPERIMENTAL PROCEDURES | 9 |
| V. EXPERIMENTAL RESULTS AND DISCUSSION | 11 |
| VI. CONCLUSIONS AND RECOMMENDATIONS | 27 |
| BIBLIOGRAPHY | 28 |
| APPENDIX A - EXPERIMENTAL DATA | 30 |
| APPENDIX B - SAMPLE CALCULATION | 43 |
| APPENDIX C - NMR DATA | 46 |

LIST OF TABLES

| Table | | Page |
|-------|---|------|
| I. | 10 psig CO ₂ -MEA Pressure Data | 31 |
| II. | 10 psig H ₂ S-MEA Pressure Data | 32 |
| III. | 10 psig SO ₂ -MEA Pressure Data | 33 |
| IV. | 20 psig CO ₂ -MEA Pressure Data | 34 |
| V. | 20 psig H ₂ S-MEA Pressure Data | 35 |
| VI. | 20 psig SO ₂ -MEA Pressure Data | 36 |
| VII. | 10 psig CO ₂ -MEA Temperature Data | 37 |
| VIII. | 10 psig H ₂ S-MEA Temperature Data | 38 |
| IX. | 10 psig SO ₂ -MEA Temperature Data | 39 |
| X. | 20 psig CO ₂ -MEA Temperature Data | 40 |
| XI. | 20 psig H ₂ S-MEA Temperature Data | 41 |
| XII. | 20 psig SO ₂ -MEA Temperature Data | 42 |
| XIII. | Physical Properties of the Acid Gases | 44 |

LIST OF FIGURES

| Figure | Page |
|---|------|
| 1. Experimental Apparatus for CO ₂ and H ₂ S | 6 |
| 2. Experimental Apparatus for SO ₂ | 7 |
| 3. Experimental Results for CO ₂ , H ₂ S, and SO ₂ at 10 psig . . . | 12 |
| 4. Experimental Results for CO ₂ , H ₂ S, and SO ₂ at 20 psig . . . | 13 |
| 5. Proton Scan for Pure MEA in DCCl ₃ | 14 |
| 6. Carbon-13 Scan for Pure MEA in D ₂ O | 15 |
| 7. Proton Scan for Pure MEA in D ₂ O | 17 |
| 8. Proton Scan for CO ₂ -MEA Liquid Reaction Products in D ₂ O . . | 18 |
| 9. Carbon-13 Scan for CO ₂ -MEA Liquid Reaction Products in D ₂ O | 19 |
| 10. Carbon-13 Scan for CO ₂ -MEA Liquid Reaction Products in D ₂ O with Ammonium Bicarbonate Added | 22 |
| 11. Carbon-13 Scan for Ammonium Bicarbonate in D ₂ O | 23 |
| 12. Proton Scan for SO ₂ -MEA Reaction Liquid Phase in D ₂ O | 24 |
| 13. Proton Scan for SO ₂ -MEA Reaction Solid Phase in D ₂ O | 25 |
| 14. Spin-Spin Splittings of NMR Spectrum of Ethanol | 49 |

NOMENCLATURE

| | |
|---------------|---|
| K_2 | - reaction rate constant, cc./mole)(sec.) |
| K_L^* | - liquid phase absorption coefficient cm./sec., based on average absorption rate for penetration theory, in which no chemical reaction occurs |
| n | - number of moles, lb. mole |
| P | - pressure, psia |
| P_C | - critical pressure, psia |
| P_r | - reduced pressure |
| q | - B_0/A_1 ; ratio of the concentration of species B the nonvolatile solute, moles/cc., at the start of contact time interval to the concentration of species A the gas being absorbed, moles/cc., at the gas-liquid interface |
| R | - ideal gas constant, (psia ft ³)/(lb mole °R) |
| T | - temperature, °R |
| T_C | - critical temperature, °R |
| T_r | - reduced temperature |
| V | - volume, ft ³ |
| Z | - compressibility factor |
| Greek Letters | |
| ρ | - density gm./cc. |

CHAPTER I

INTRODUCTION

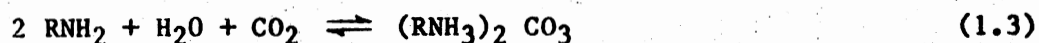
Alkanolamines have been used to remove selected impurities from natural gas for many years. The selected impurities to be removed are acidic gases and a basic reagent (ethanolamine) is therefore employed to remove them (1).

The acid gases used in this experiment were carbon dioxide (CO₂), hydrogen sulfide (H₂S), and sulfur dioxide (SO₂). The alkanolamine used in the reaction was monoethanolamine (MEA).

Even though the reaction process has been known for some time the specific CO₂ reaction mechanism is still a topic of considerable study.

There is, however, agreement in the general case that the CO₂-MEA reaction requires the presence of water while the H₂S-MEA reaction does not (1). Therefore, a comparison of reaction rates when using anhydrous MEA should show that a given reaction is faster (or more preferred) than another.

Maddox (1) gives as the primary reactions for MEA with CO₂ and H₂S as:



or



where $\text{R} = \text{C}_2\text{H}_4\text{OH}$

If water is necessary in the CO_2 reaction, the CO_2 reaction should be slower than the H_2S reaction - if the CO_2 reacts at all.

The acid gas to be reacted was charged into the glass reaction vessel followed by introduction of the MEA. The reaction was monitored by recording pressure and temperature levels within the vessel over a period of time.

The varying pressures of each reaction were used to evaluate the progression and reaction rate relative to the other acid gases.

CHAPTER II

LITERATURE SURVEY

The use of alkanolamines in reactions with CO_2 and H_2S originates with Bottoms (2) who was granted a patent covering their use in removing these acid gases from natural gas. One of the early works using amines for reaction with SO_2 was that of Korezynski and Glebocka (3) who studied some aromatic amine reactions. The solubility of CO_2 and H_2S in aqueous MEA solutions over small ranges of CO_2 and H_2S in aqueous MEA solutions over small ranges of temperature, pressure, and composition was studied by Mason and Dodge (4) and Riegger, Tarter, and Lingafelter (5).

The reactions of CO_2 and H_2S with aqueous solutions of MEA have been widely studied (6,7). However, the CO_2 -MEA reaction has had the greater amount of investigation (8) and is well summarized by Danckwerts and McNeil (9,10). Mathematical models of the reaction have been developed. Brian, Hurly, and Hasseltine compared their penetration-theory results with the film-theory solution with reasonable results (11). Their results agree well - not when the system loading is the same but when the value of q is such that the asymptote for K_2/K_L^* is the same. Emmert and Pigford (12) attempted to combine physical absorption together with chemical reaction with somewhat mixed results. They determined that the average stoichiometric factor for MEA should be between 1.0 and 1.1 in contrast to the experimentally observed value of

1.78 in the CO₂-H₂O-MEA system.

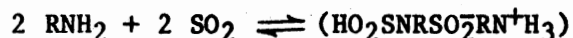
The selectivity of MEA for CO₂ and H₂S was analyzed by Vidaurri and Kahre (13). They determined that

. . . The initial quantity of CO₂ that is absorbed is primarily due to and limited by physical absorption into the water that is present. Increasing the CO₂ pressure increases the amount dissolved in the water, thereby reducing the solvent selectivity. Additional data indicate that for optimal selectivity, the partial pressure of CO₂ should be 50 psi or less (p. 335).

They employed one-to-one mixture of acid gas with MEA and used the pressure readings as the direct measurement of the amount of gas that had been absorbed.

Reactions of CO₂ or H₂S with anhydrous MEA were not found in the literature.

The earliest reference to SO₂ reactions with MEA was in the photographic industry where Henn (14) passed SO₂ into MEA to form an adduct which was subsequently used in a photographic developing emulsion. Patents were issued to Teague and Hayden (15) and Frevel and Kressley (16) for scrubbing of gases with aqueous solutions of MEA. The reaction is given by Frevel and Kressley as:



CHAPTER III

EQUIPMENT AND REAGENTS

Equipment

The experimental apparatus is shown in Figures 1 and 2. The arrangement in Figure 1 was used for CO_2 and H_2S . Figure 2 shows the set up for SO_2 use.

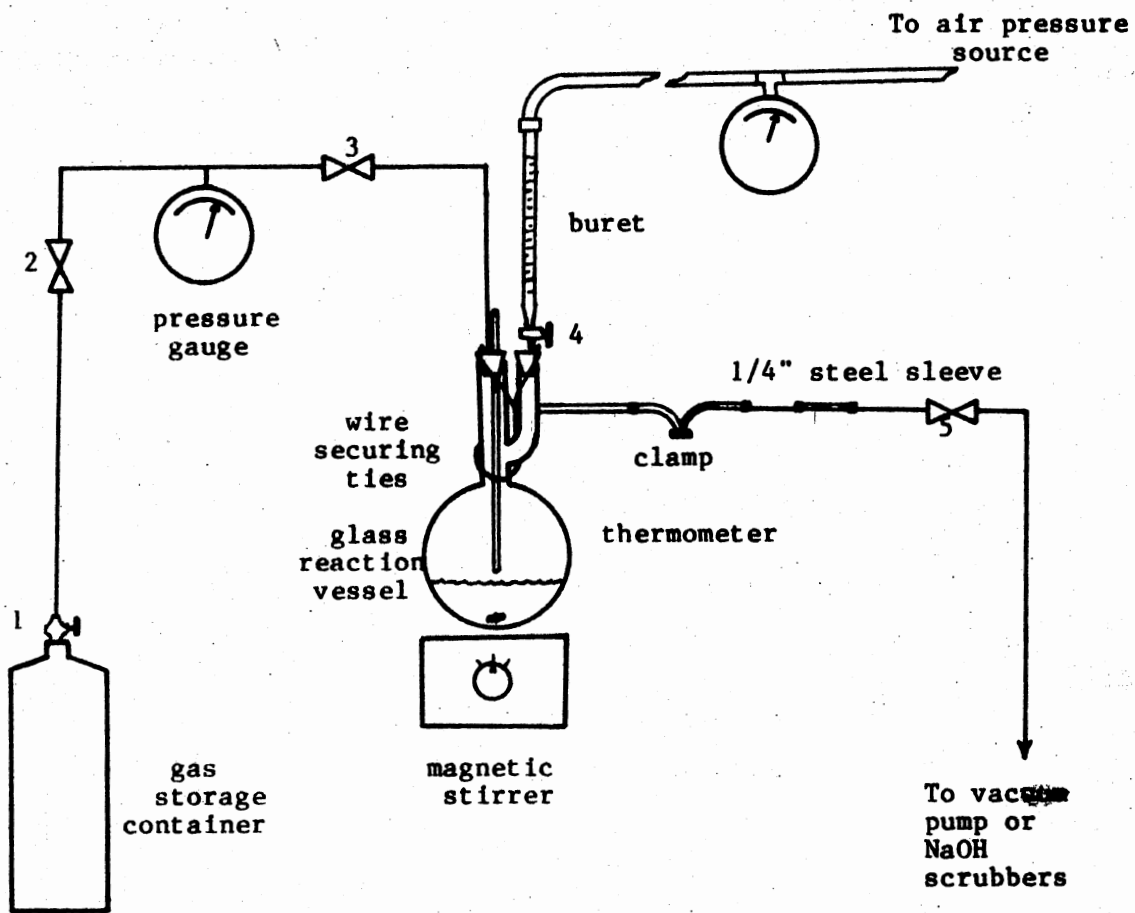
The stainless steel gas storage container was charged with either CO_2 or H_2S as desired. The container was previously cleaned and dried; 100 grams of silica gel were placed inside and the container sealed.

The reaction vessel was a glass Claisen distilling flask. The volume was determined by displacement of liquid at constant temperature with the shutoff clamp, thermometer, and stoppers in their proper positions. The volume was 600 ml.

The liquid feed system was a 25 ml buret with plastic tubing connected to an air pressure system.

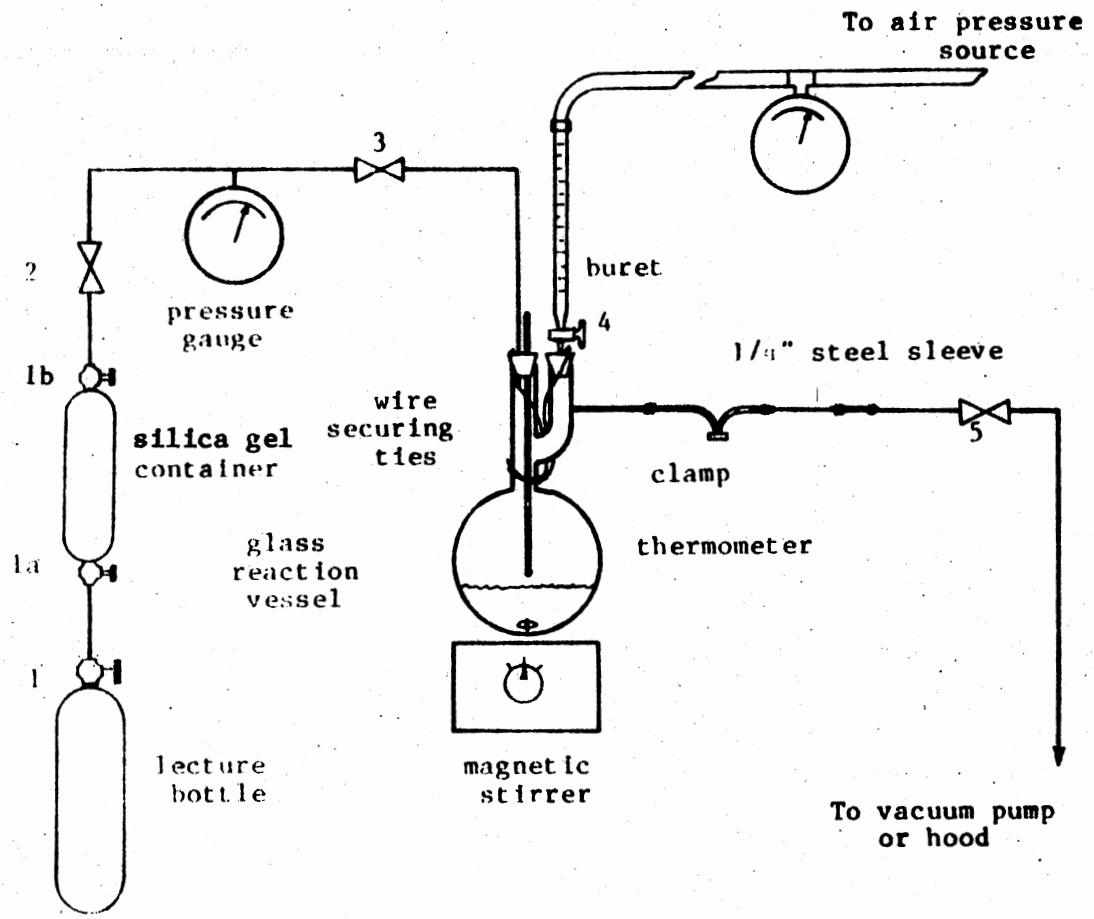
All connectors and lines from the gas storage container to the reaction vessel were 1/8 inch O.D. stainless steel. The lines from the reaction vessel to the vacuum pump (Welch Duo-seal, 1/3 horsepower) and to the H_2S scrubber system were 1/4 inch I.D. plastic tubing.

The apparatus was slightly altered for use with SO_2 . A lecture bottle of SO_2 was connected to a stainless steel cylinder with 1/4 inch I.D. plastic tubing. The stainless steel cylinder contained



Numbers refer to in-line control valves

Figure 1. Experimental Apparatus for CO_2 and H_2S



Numbers refer to in-line control valves

Figure 2. Experimental Apparatus for SO₂

115.6 grams of silica gel. Stainless steel 1/8 inch O.D. lines connect the stainless steel cylinder to the remainder of the system as previously described.

A magnetic stirrer was used to agitate the MEA after introduction to the reaction vessel.

Pressure within the system was indicated on a pressure gauge (Duraguage) that has a range of 30 inches of mercury (Hg) vacuum to 0 psig (marked off in 0.5 inch Hg increments) and 0 psig to 30 psig (marked off in 0.5 psig increments).

The temperature of the gas was measured at a point just above the liquid-gas interface. A mercury thermometer with a range of -4°F to 220°F in 2°F increments was used.

Reagents

The purified MEA was from Fisher Scientific Company. It was heated at 173.5°C for three hours to drive off any water that was present. The MEA was then kept in a sealed container.

The SO_2 and H_2S were from the Matheson Corporation with purities of 99.98% and 99.5% respectively. The CO_2 was from Linde and had a purity of 99.5%.

CHAPTER IV

EXPERIMENTAL PROCEDURES

Prior to beginning the CO₂ runs, the gas storage container (with silica gel inside) was charged, agitated, and allowed to sit for 24 hours. Instructions for operating the experimental apparatus:

1. Select the reaction vessel pressure desired. Determine the amount of gas to be introduced at that pressure. Calculate the amount of MEA necessary for a one-to-one reaction with the gas. Record the temperature.
2. Evacuate the reaction vessel and the gas feed lines to 20 in Hg vacuum. Secure polypropylene stoppers with wire ties.
3. Pressurize system to 0 psig with gas. Evacuate as before.
4. Pressurize system to 0 psig with gas. Add MEA to buret and secure its rear pressure line with a hose clamp. Bend plastic tubing and close off line on reaction vessel side arm.
5. Bring reaction vessel and MEA back pressure to desired level in a stepwise manner.
6. Wait about 10 minutes for temperature to return to original temperature and check for leaks. Start magnetic stirrer.
7. Bring MEA back pressure slightly above reaction vessel pressure.

8. Introduce MEA as quickly as possible. Begin recording temperature and pressure.
9. At end of run, vent or scrub remaining gas as required.
Clean equipment and repeat as necessary from step 1.

Results are in Appendix A. A sample calculation for amounts of gas and MEA is shown in Appendix B.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

The relative rates of reaction for 10 psig and 20 psig runs for times up to five minutes are $\text{H}_2\text{S} < \text{CO}_2 < \text{SO}_2$. For a contact time of thirty minutes at 10 psig and 20 psig the relative rates are $\text{CO}_2 < \text{H}_2\text{S} < \text{SO}_2$. Figures 3 and 4 depict the average values of all of the runs in percent of original pressure (in psia).

Since the CO_2 -MEA reaction does occur - in fact it is initially faster than the H_2S -MEA reaction - then water is not required. The quotation of Vidaurri and Kahre in Chapter II is incorrect in view of the results of this work.

The Department of Chemistry at Oklahoma State University ran nuclear magnetic resonance (nmr) scans (at about 22°C) for protons (^1H) and carbon (^{13}C) nuclei on the boiled MEA used in this experiment. Figure 5 shows a proton scan of the MEA with deuteriochloroform as the solvent. The MEA contains no detectable water - water would produce a peak in the area of 6.0 part per million (ppm). The labels α and β describe the carbon nuclei $\text{N} - \text{C} \alpha - \text{C} \beta - \text{OH}$. Peak number 1 represents the proton from the $-\text{OH}$ group. Peak number 2 represents the protons on the β carbon and peak number 3 represents the protons on the α carbon. The protons on the N are represented by peak number 4. Figure 6 shows the ^{13}C scan for the MEA. Peak numbers 2' and 3' are for the β and α carbon respectively. These peaks agree with those of Sarneski,

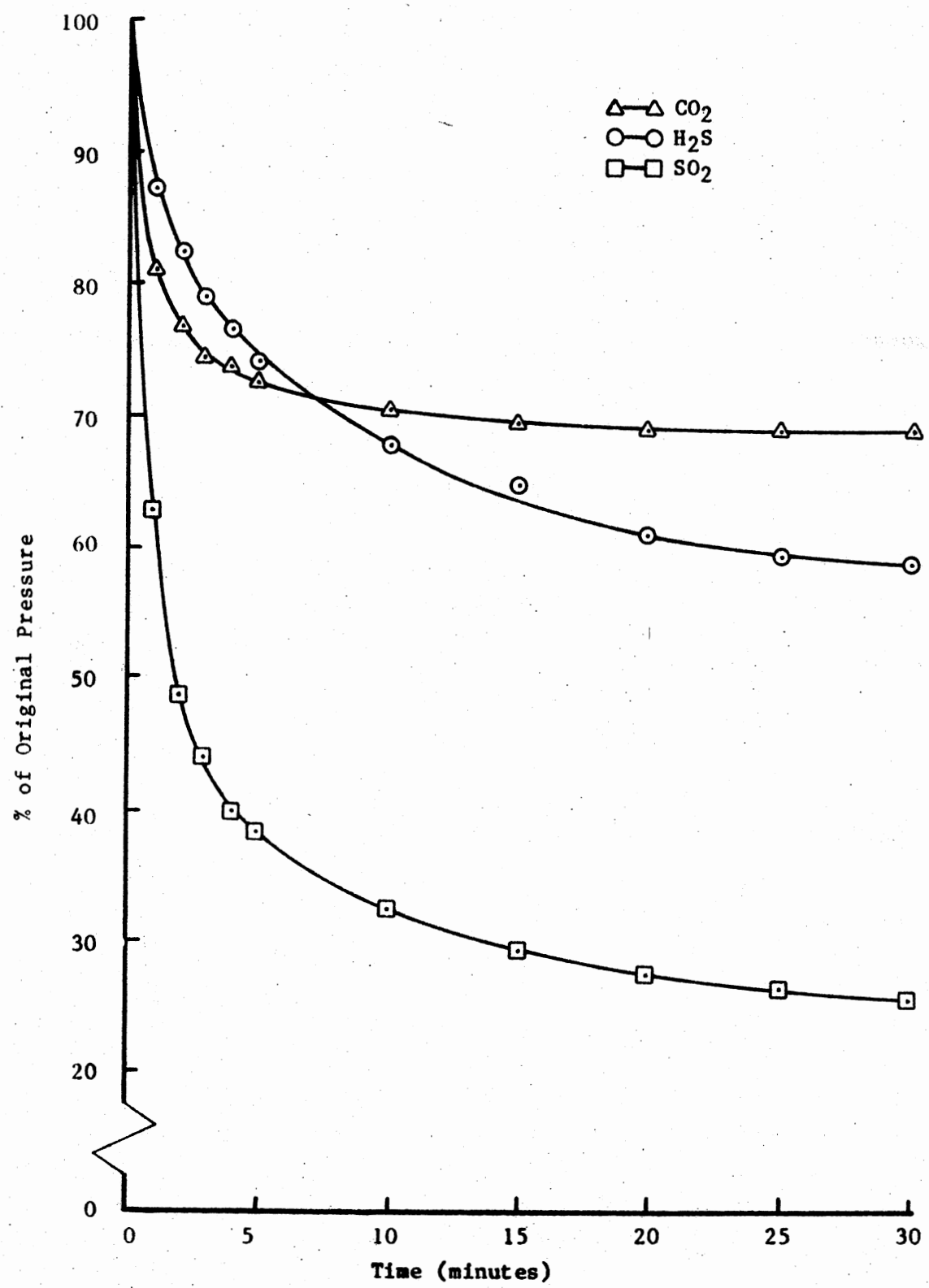


Figure 3. Experimental Results for CO₂, H₂S, and SO₂ at 10 psig

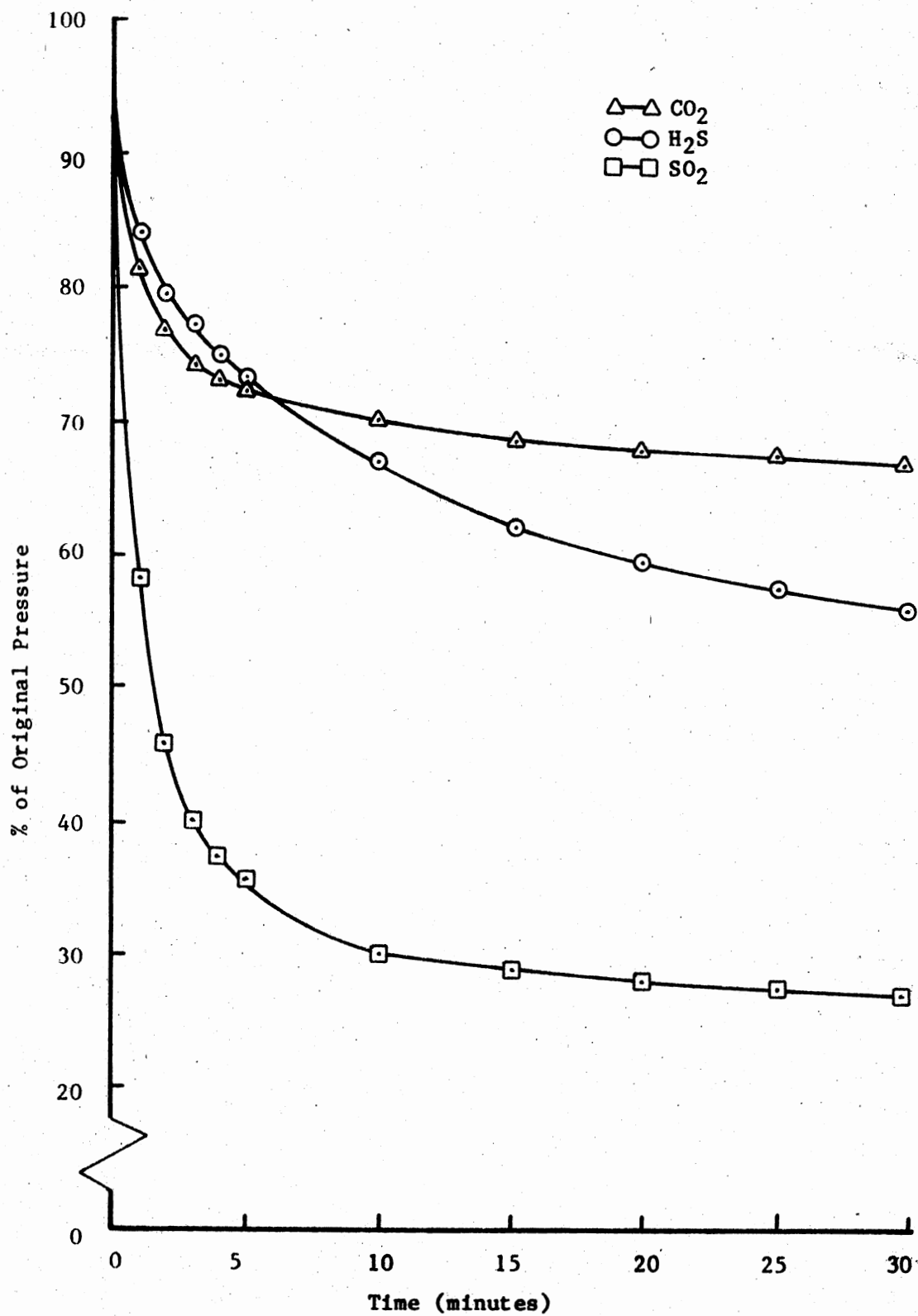


Figure 4. Experimental Results for CO₂, H₂S, and SO₂ at 20 psig

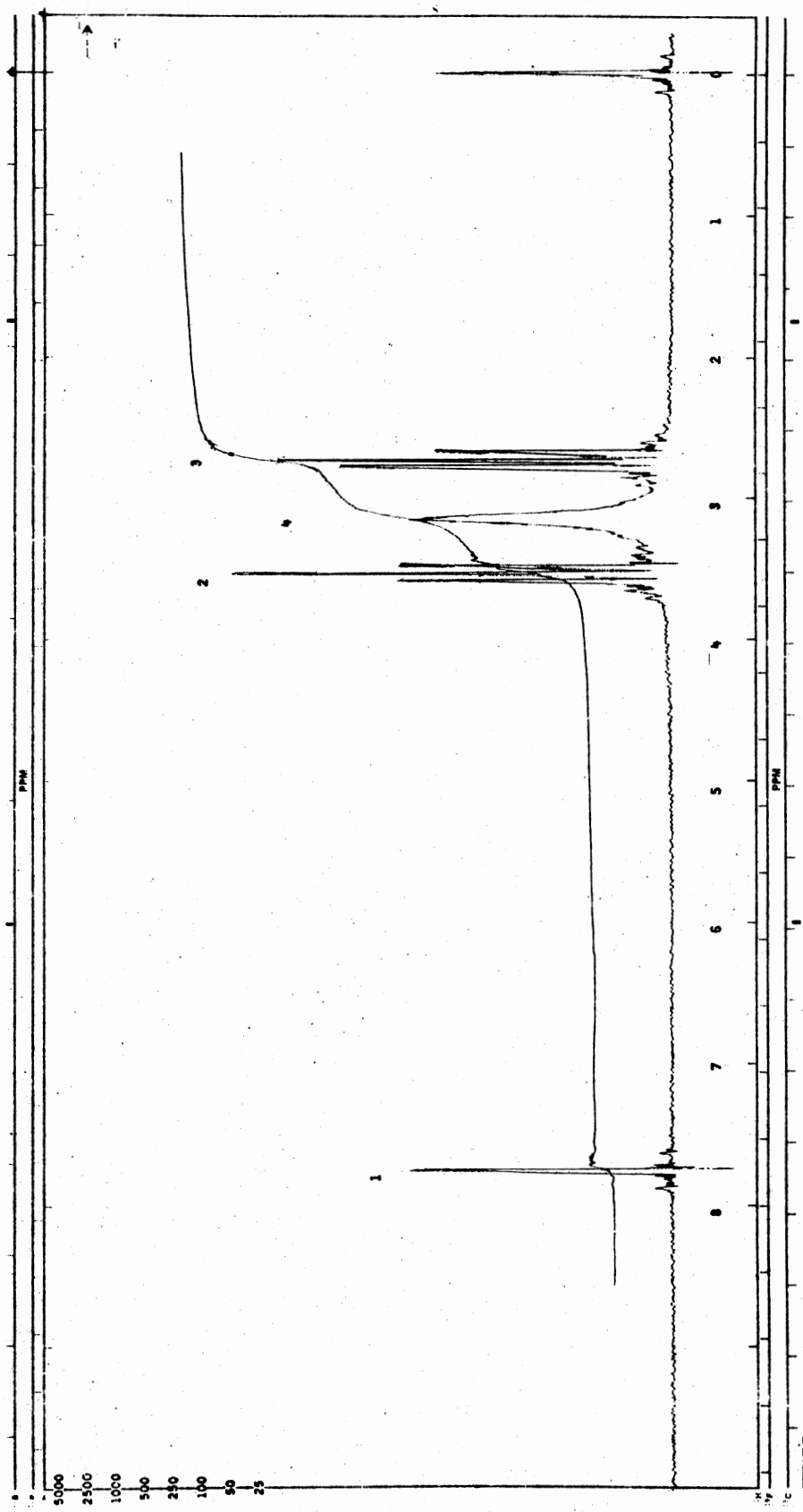


Figure 5. Proton Scan for Pure MEA in DCCl₃

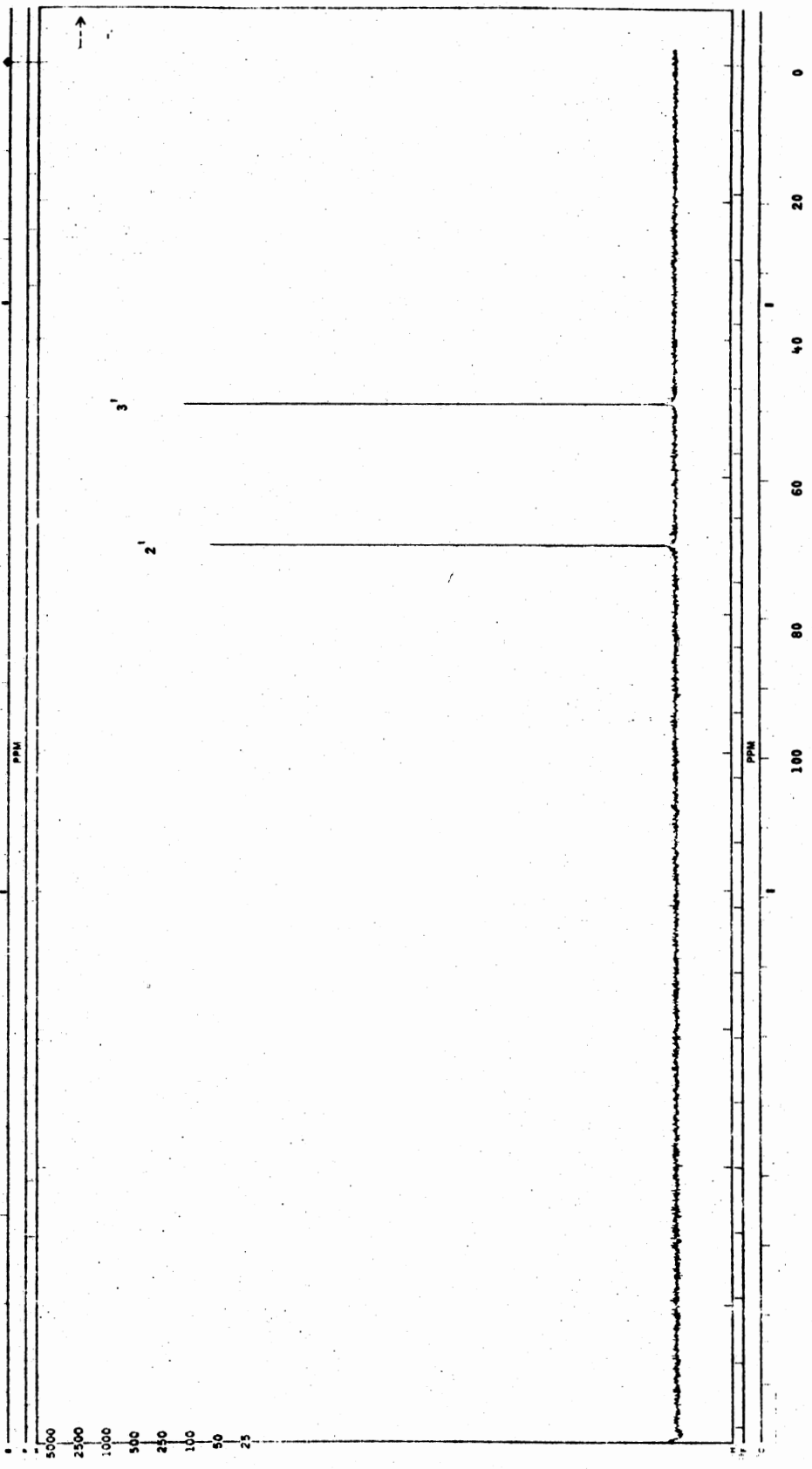


Figure 6. Carbon-13 Scan for Pure MEA in D₂O

Surprenant, Molen, and Reilley (17) considering the temperature and aqueous solution differences.

Because some of the liquid reaction products were not soluble enough in deuteriochloroform, a different solvent was required. Deuterium oxide (D_2O) was used in the remaining nmr scans. To provide a reference the MEA proton scan was rerun in D_2O (Figure 7). The D_2O undergoes a rapid exchange with the OH and N protons and peak number 5 represents these protons. Peak number 6 and 7 represent the β and α protons respectively.

The CO_2 -MEA liquid product was analyzed next. The 1H scan (Figure 8) in conjunction with the ^{13}C scan (Figure 9) shows that at least two different compounds are present. The integration line in Figure 8 provides a count of the protons scanned; appendix C provides further explanation on nmr. Peak number 8 again represents the protons from the OH and N groups. However, peaks 9 and 10 are different than before. If one adds the dotted line as in Figure 8 in peak 9 then the situation becomes clearer. Peaks 9a and 10a are different than 9b and 10b as a result of the difference in shielding of the magnetic fields at the nuclei by their electronic environments. Figure 7 also reflects the preferred conformations of the α and β CH_2 groups in the different (but similar) compounds indicated. Peaks 11 and 12 represent the β and α ^{13}C nuclei respectively. Peak 13 is the ^{13}C nucleus in the group COO^- .

Initially there was a one-to-one ratio of reactants



Since the reaction is reversible and the products remain in the system, then the reactions cannot be entirely consumed, leaving

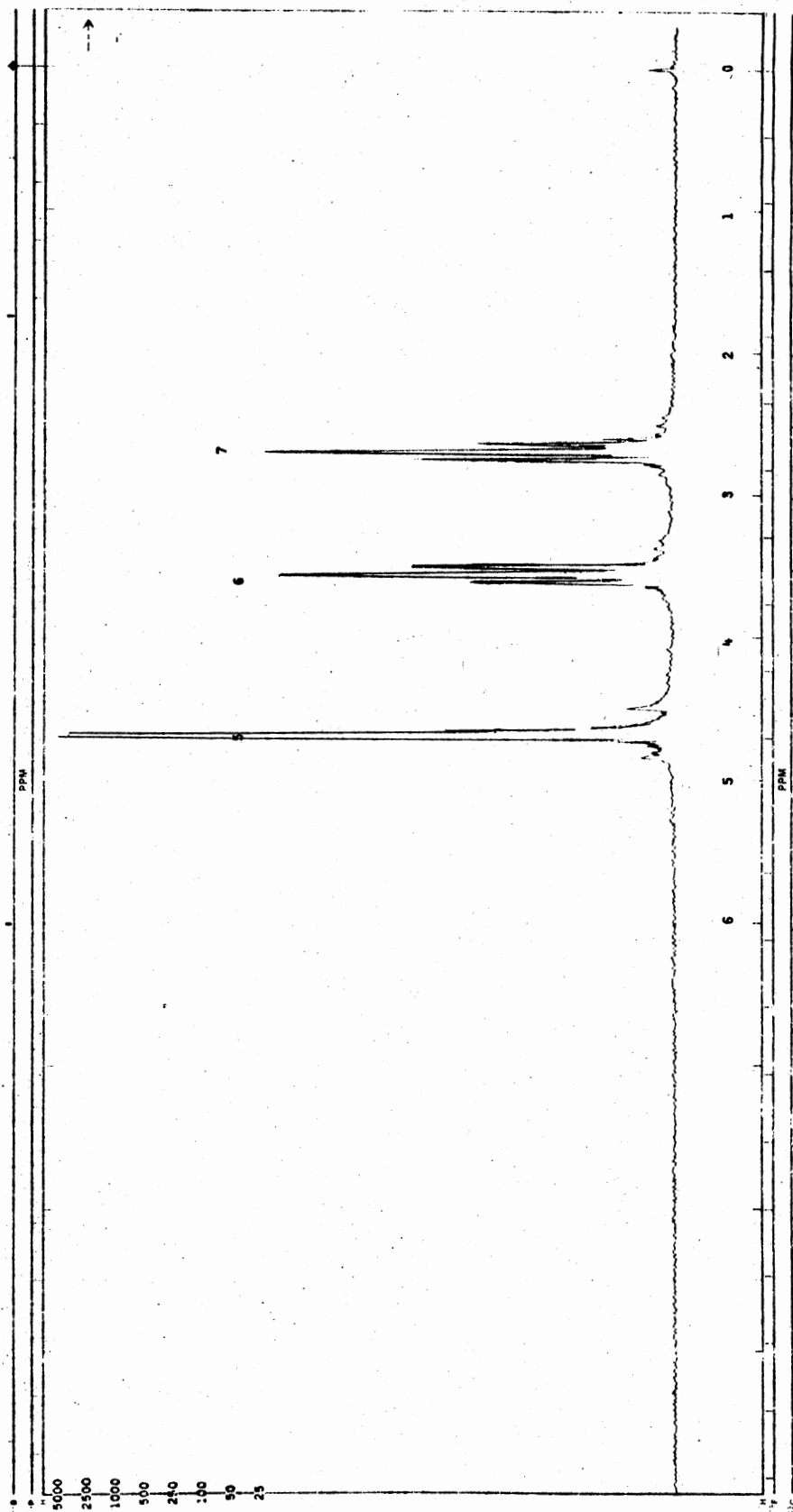


Figure 7. Proton Scan for Pure MEA in D₂O

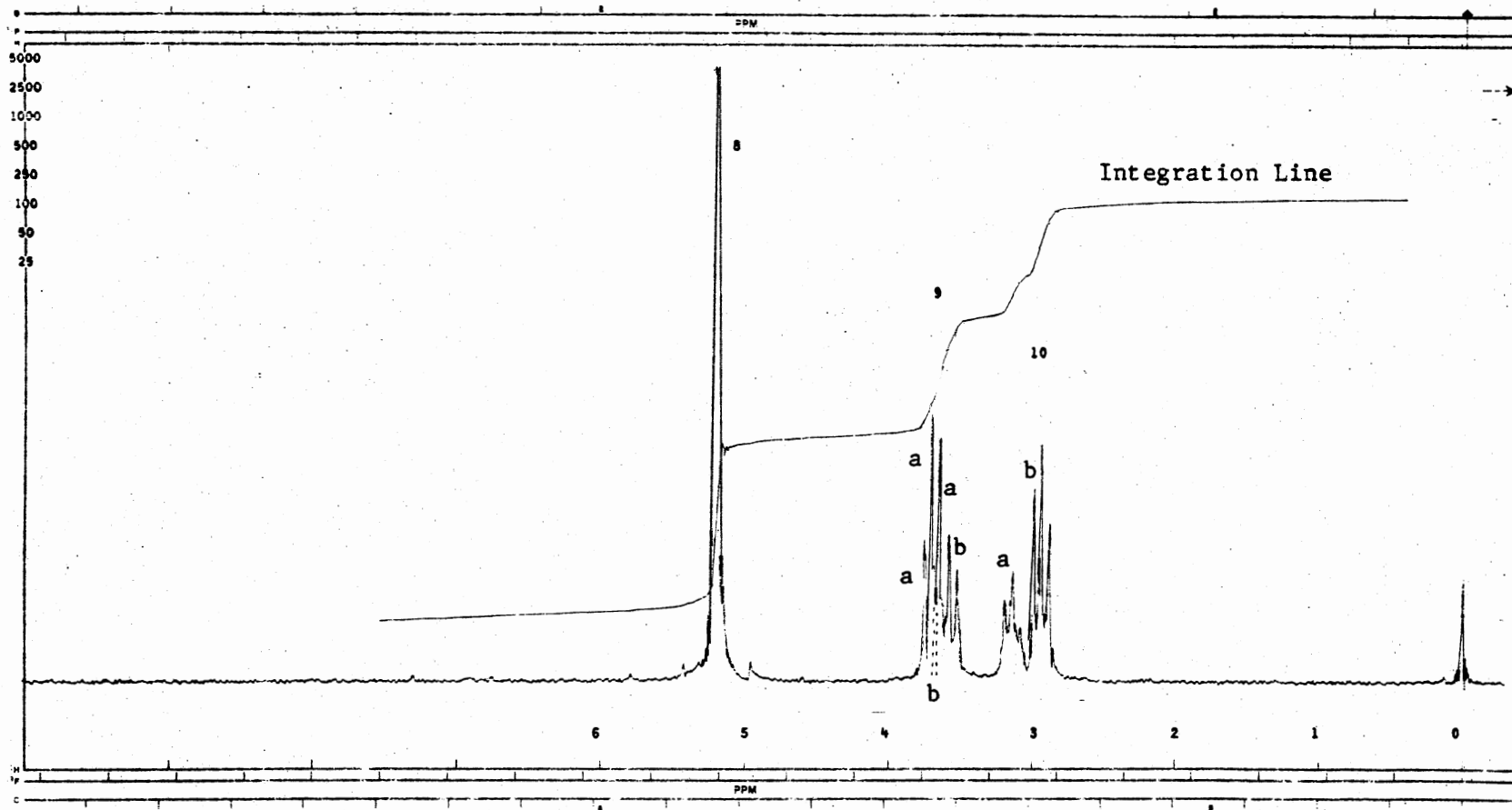


Figure 8. Proton Scan for CO₂-MEA Liquid Reaction Products in D₂O

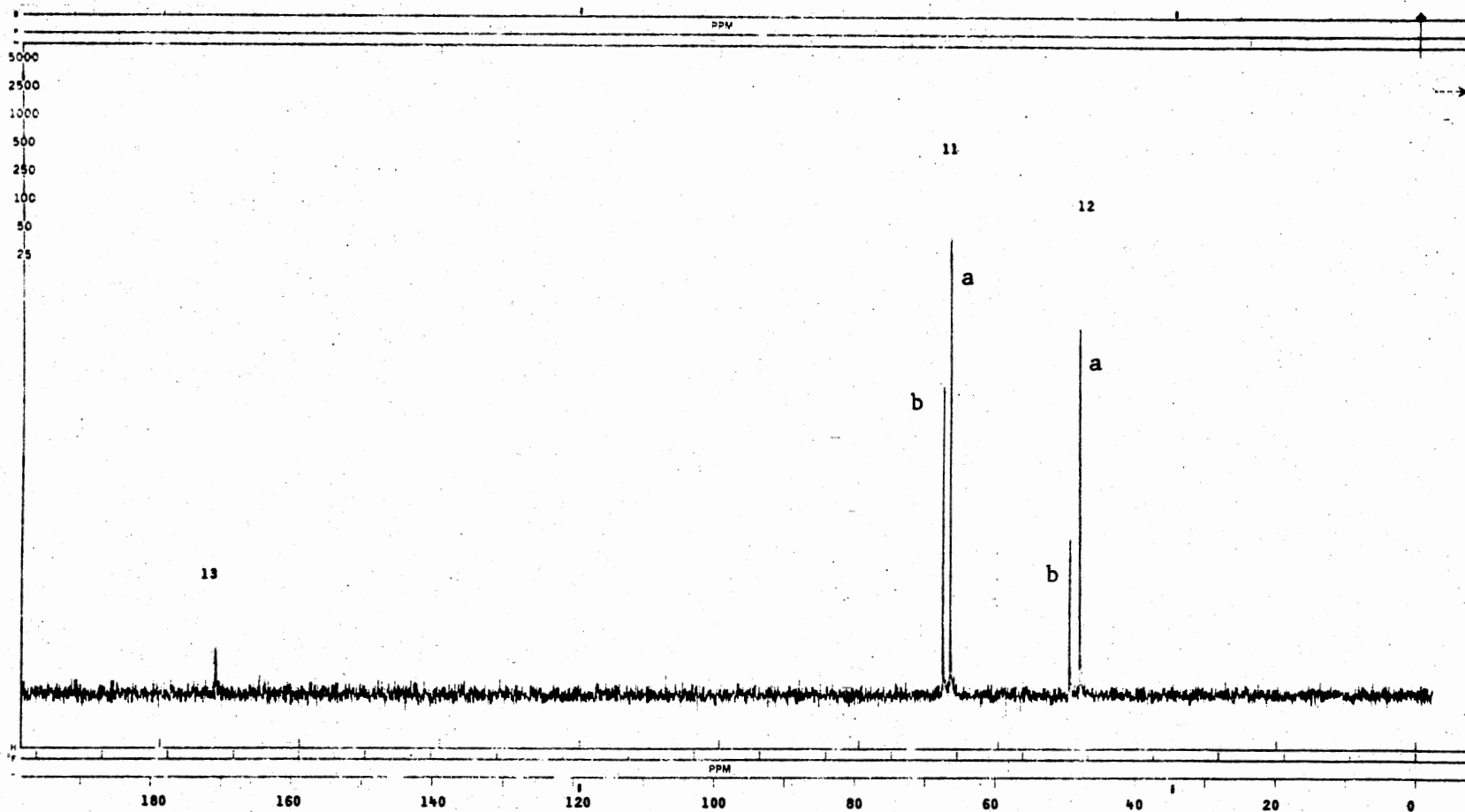
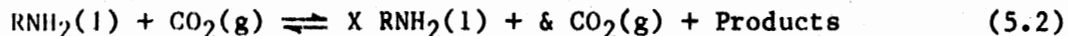
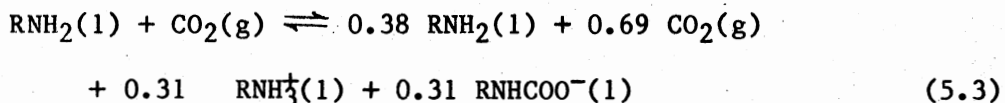


Figure 9. Carbon-13 Scan for CO₂-MEA Liquid Reaction Products in D₂O



where X and Y are between zero and one. From the pressure data on page 28, Table I, 68.7% of the CO_2 remains in the gas phase - therefore, Y is about 0.69. This leaves 0.31 moles of CO_2 in the reaction. For a one-for-one insertion reaction this means that 0.31 moles of MEA was reacted and that the protons from the insertion protonate another 0.31 moles of MEA.



Since the protons on the nitrogen in both the RNH_2 and RNH_3^+ will exchange rapidly with the D_2O , a spectrum showing MEA will be produced. Adding these mole fractions gives a total fraction of 0.69.

The carbamate formed will give a spectrum showing that the α and β protons and carbon nuclei are less shielded due to the presence of the oxygen molecules added. These peaks will be to the left of those for the combination of RNH_2 and RNH_3^+ . Figure 8 and 9 confirm this. There is more of the RNH_2 and RNH_3^+ present than the carbamate and the height of the peaks reflect this. To get an estimate of the fractions of the components in the sample one can use the heights of the peaks presented. From Figure 9

$$\text{fraction of a} = \frac{\text{height of peak a}}{\text{height of peak a} + \text{height of peak b}}$$

For peak 11 the fraction of a is 0.60 and b is 0.40. For peak 12 the fraction of a is 0.70 and b is 0.30. In peaks 11 and 12 the a represents the RNH_2 and RNH_3^+ present. The values calculated for the fraction present bracket the value of 0.69 from equation (5.3). Similar values for the fractional amounts are obtained from the proton

scan of Figure 8. From the pressure data on page 31 Table IV, 67.2% of the CO_2 remains in the gas phase - therefore, Y is about 0.67. New fractional values for 20 psig can also be calculated.

As a check for the validity of this reaction mechanism, ammonium bicarbonate (NH_4HCO_3) was added to the sample and the ^{13}C scan was repeated. The results (Figure 10) indicate the absence of bicarbonate ion (HCO_3^-) in the original sample. Peak 14 shows the response of HCO_3^- if it were in the original sample. Figure 11 is the reference ^{13}C scan for ammonium bicarbonate only in D_2O . Since there is no HCO_3^- present, this provides further proof that the reaction did not include water (9).

The H_2S -MEA reaction proceeded as expected. Since no water was required the pressure vs. time relationship followed that of Vidaurri and Kahre. Therefore, the reaction mechanism was not questioned and an nmr analysis was not performed.

The SO_2 -MEA was studied because a reaction similar to that of CO_2 and H_2S was expected. A comparison of Figures 3 and 4 shows that the SO_2 reacted much faster and more completely than either the CO_2 or H_2S . The reaction produced a reddish-brown liquid product and a bone colored powdery product that was deposited down the side of the flask where the MEA was introduced into the system. The solid would dissolve in the liquid phase and both were soluble in water.

A proton scan was made of the solid and liquid phases which are shown in Figures 12 and 13. The two phases give almost identical spectrums. Neither spectrum indicates two or more possible reaction products although the liquid spectrum does have an indication of some small amount of something in the sample. The two small peaks at the

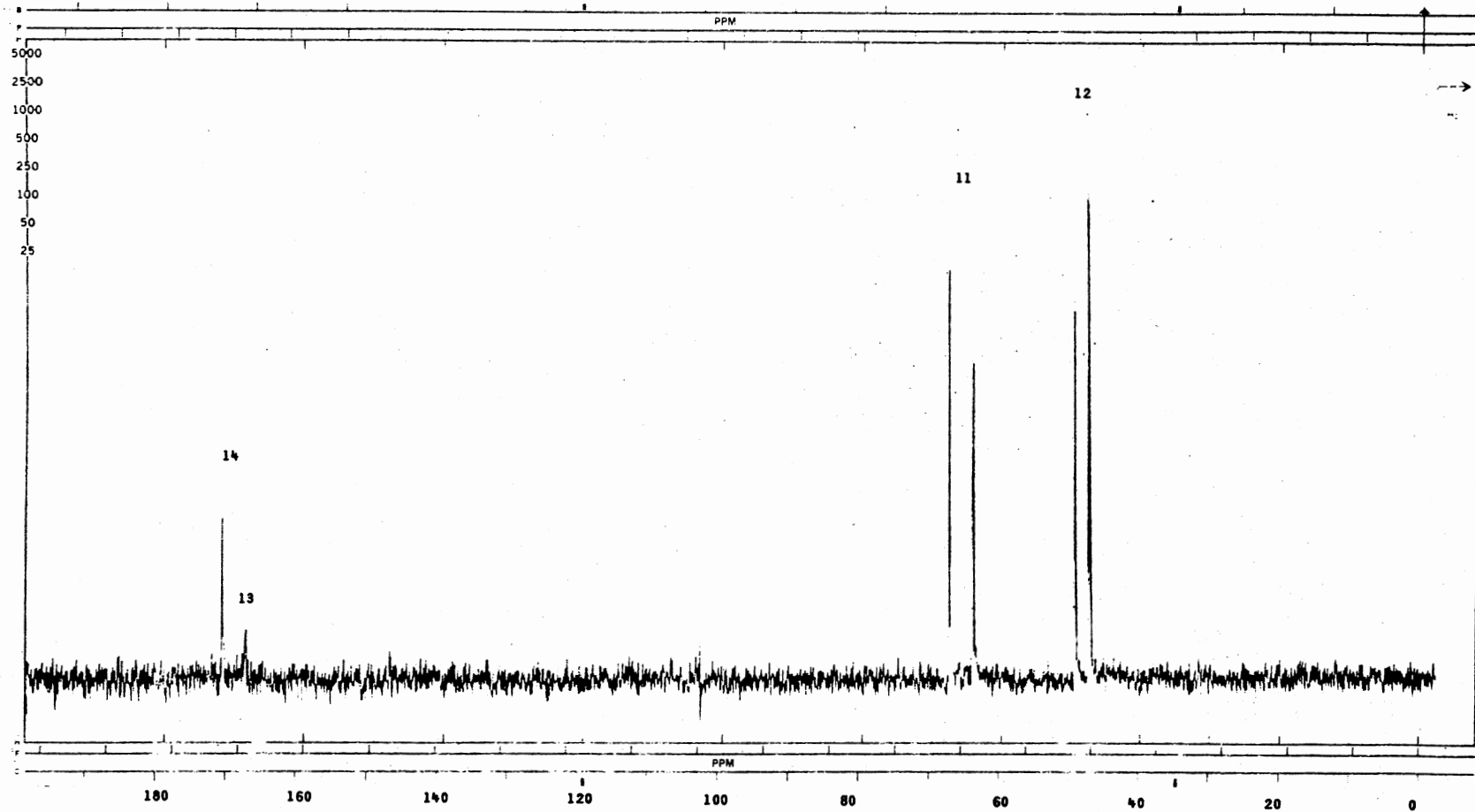


Figure 10. Carbon-13 Scan for CO₂-MEA Liquid Reaction Products in D₂O
with Ammonium Bicarbonate Added

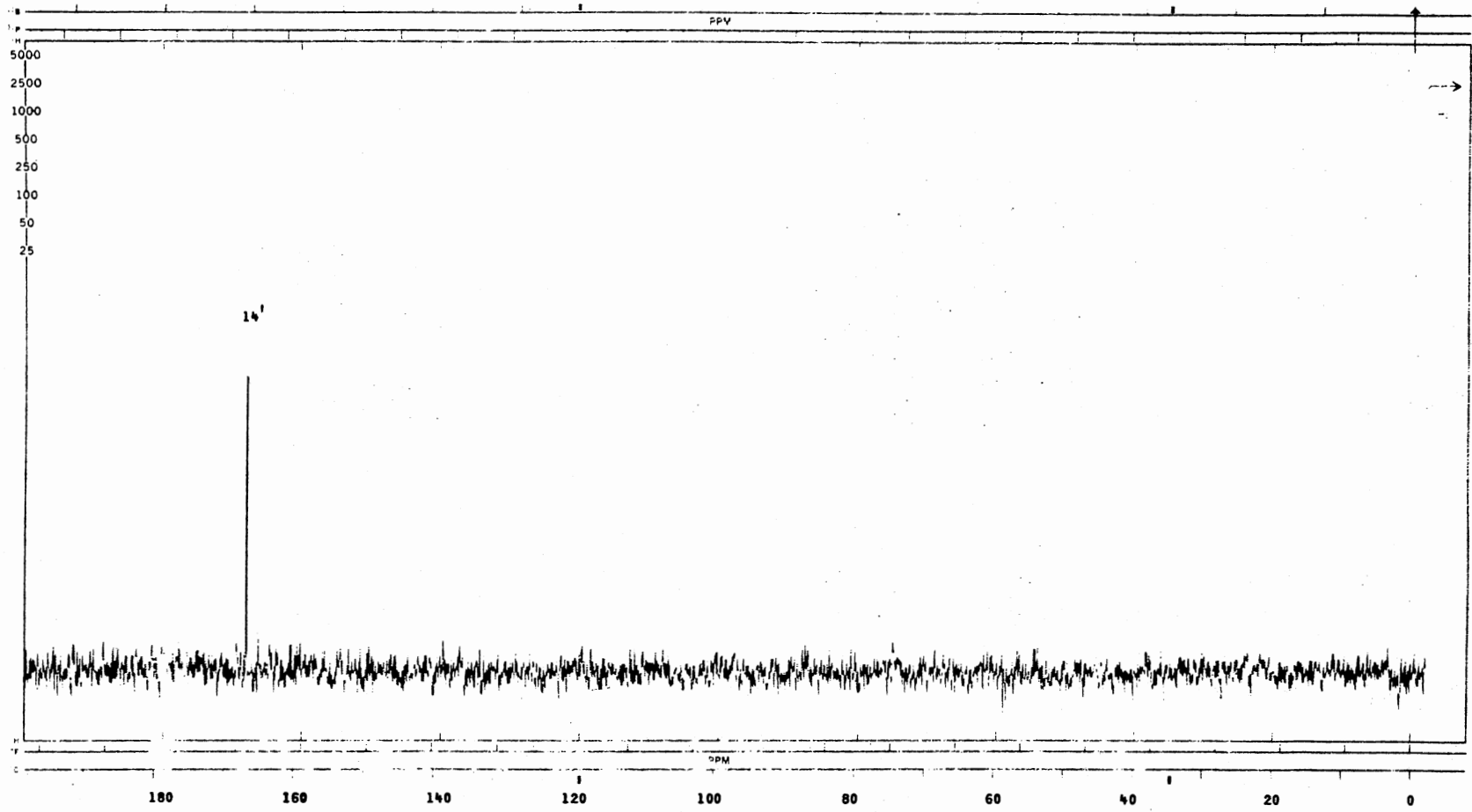


Figure 11. Carbon-13 Scan for Ammonium Bicarbonate in D₂O

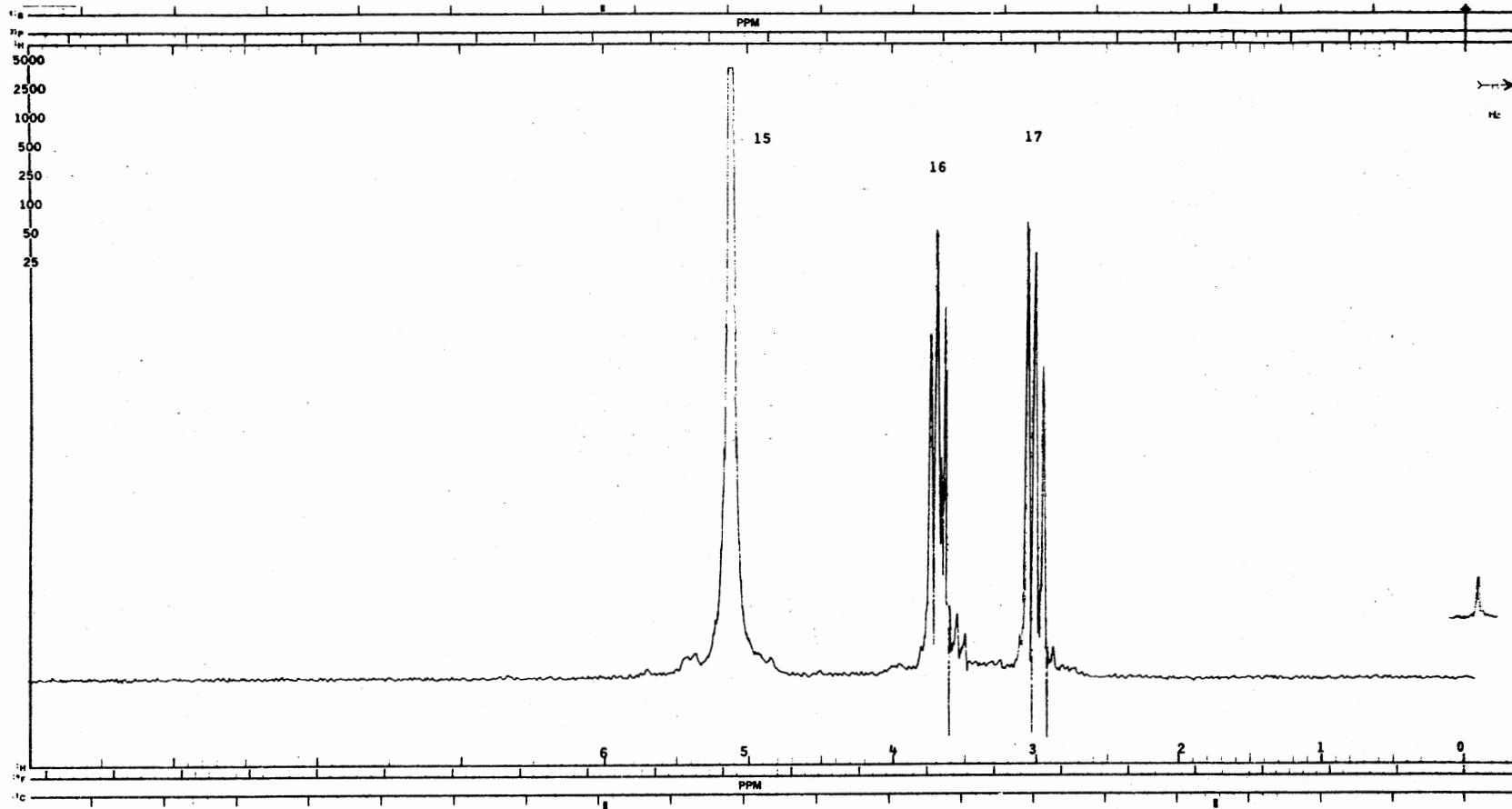


Figure 12. Proton Scan for SO₂-MEA Reaction Liquid Phase in D₂O

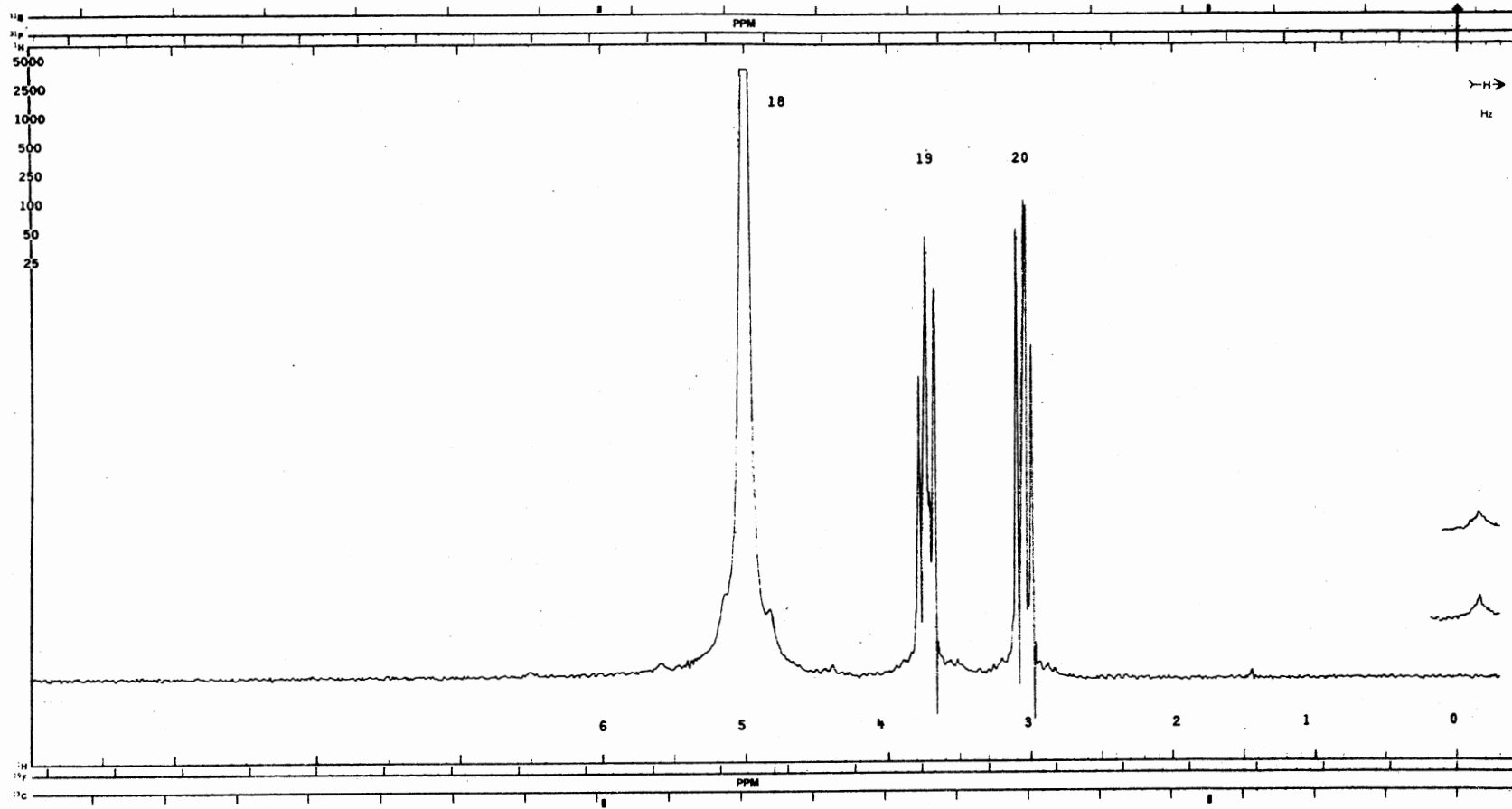


Figure 13. Proton Scan for SO_2 -MEA Reaction Solid Phase in D_2O

base of peaks 16 and 17 could be a trace of unreacted MEA remaining in the liquid. This would explain the fact that a small amount of clear yellow-tinted liquid (similar to the original MEA liquid) was noticed around the edge of the reddish-brown liquid at the conclusion of the SO₂ experimental runs.

Since the solid and liquid sample proton scans are nearly identical, and the solid dissolves in the liquid when mixed, then it is assumed that the two phases are identical.

An insertion reaction is indicated



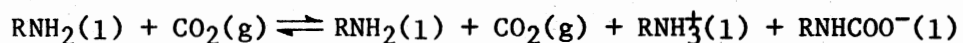
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

1. The chemical reaction of CO₂ and MEA does not require the presence of water.

2. For short contact times the reaction rates for CO₂-MEA and H₂S-MEA are of the same order of magnitude.

3. The CO₂-MEA reaction is



This reaction mechanism is not what is accepted in the literature.

Water affects the reaction but is not required.

4. The following are some recommendations for the improvement of the experiment:

a. Samples of the vapor phase could be taken to check for any vapor reaction products and to determine what fraction of the acid gas remains unreacted.

b. In conjunction with the previous recommendation, vary the amounts of MEA and acid gas to find the stoichiometric reaction ratios.

c. Proton and Carbon-13 scans for H₂S-MEA should be made and examined in light of the CO₂-MEA results.

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APPENDIX A

EXPERIMENTAL DATA

TABLE I
10 PSIG CO₂-MEA PRESSURE DATA

| Run No. → | 33 | 34 | 52 | 53 | 54 | 55 | Average |
|-------------------|-------------------------------|-------|-------|-------|-------|-------|---------|
| Time minutes ↓ | % OF ORIGINAL PRESSURE (PSIA) | | | | | | |
| 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1 | 80.7 | 79.7 | 87.4 | 79.9 | 79.5 | 76.9 | 80.7 |
| 2 | 76.1 | 75.7 | 82.8 | 76.5 | 74.5 | 72.8 | 76.4 |
| 3 | 74.1 | 73.7 | 80.7 | 74.7 | 72.4 | 71.6 | 74.5 |
| 4 | 72.8 | 72.4 | 79.7 | 73.7 | 70.8 | 70.4 | 73.3 |
| 5 | 72.0 | 71.8 | 78.1 | 73.1 | 70.4 | 69.6 | 72.5 |
| 10 | 69.8 | 69.8 | 75.7 | 71.2 | 69.2 | 68.0 | 70.6 |
| 15 | 68.8 | 69.2 | 74.1 | 70.0 | 68.4 | 67.6 | 69.7 |
| 20 | 68.0 | 68.4 | 73.5 | 69.4 | 68.2 | 67.4 | 69.1 |
| 25 | 67.8 | 68.2 | 73.3 | 69.0 | 68.2 | 67.0 | 68.9 |
| 30 | 67.6 | 68.0 | 73.3 | 68.8 | 67.8 | 66.8 | 68.7 |

TABLE II
10 PSIG H₂S-MEA PRESSURE DATA

| Run No. → | 6 | 58 | 59 | Average |
|-------------------|-------------------------------|-------|-------|---------|
| Time minutes ↓ | % OF ORIGINAL PRESSURE (PSIA) | | | |
| 0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1 | 90.3 | 84.2 | 86.0 | 86.8 |
| 2 | 85.8 | 79.9 | 81.4 | 82.3 |
| 3 | 81.8 | 77.3 | 78.1 | 79.0 |
| 4 | 78.1 | 74.9 | 75.9 | 76.3 |
| 5 | 75.4 | 73.3 | 74.1 | 74.2 |
| 10 | 68.8 | 66.4 | 67.4 | 67.5 |
| 15 | 64.8 | 64.8 | 63.5 | 64.3 |
| 20 | 62.3 | 59.7 | 61.5 | 61.1 |
| 25 | 61.1 | 58.3 | 59.5 | 59.6 |
| 30 | 60.3 | 57.1 | 58.7 | 58.7 |

TABLE III
10 PSIG SO₂-MEA PRESSURE DATA

| Run No. → | 40 | 43 | 45 | 47 | 48 | 51 | Average |
|-------------------|-------------------------------|-------|-------|-------|-------|-------|---------|
| Time minutes ↓ | % OF ORIGINAL PRESSURE (PSIA) | | | | | | |
| 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1 | 66.0 | 46.6 | 61.5 | 70.0 | 63.1 | 66.0 | 62.2 |
| 2 | 55.1 | 35.6 | 47.0 | 59.5 | 54.9 | 38.4 | 48.4 |
| 3 | 49.6 | 32.4 | 42.0 | 53.7 | 50.3 | 33.7 | 43.6 |
| 4 | 45.8 | 29.7 | 38.8 | 49.2 | 46.6 | 30.9 | 40.1 |
| 5 | 44.2 | 28.1 | 37.2 | 46.4 | 44.4 | 29.3 | 38.2 |
| 10 | 38.4 | 23.9 | 32.3 | 38.0 | 35.8 | 24.9 | 32.2 |
| 15 | 33.7 | 21.7 | 31.7 | 34.1 | 32.4 | 23.7 | 29.5 |
| 20 | 28.0 | 20.7 | 29.5 | 32.8 | 31.7 | 22.1 | 27.4 |
| 25 | 25.9 | 19.7 | 29.2 | 31.9 | 30.9 | 21.5 | 26.5 |
| 30 | 24.7 | 18.4 | 28.5 | 30.9 | 30.3 | 20.7 | 25.6 |

TABLE IV
20 PSIG CO₂-MEA PRESSURE DATA

| Run No. → | 32 | 35 | 36 | 37 | 38 | 39 | Average |
|-------------------|-------------------------------|-------|-------|-------|-------|-------|---------|
| Time minutes ↓ | % OF ORIGINAL PRESSURE (PSIA) | | | | | | |
| 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1 | 82.1 | 74.6 | 85.3 | 81.2 | 79.1 | 83.3 | 80.9 |
| 2 | 78.1 | 70.3 | 81.2 | 76.9 | 74.0 | 78.1 | 76.4 |
| 3 | 75.8 | 68.1 | 78.9 | 74.2 | 71.2 | 76.7 | 74.1 |
| 4 | 74.3 | 67.1 | 77.3 | 72.9 | 69.7 | 75.5 | 72.8 |
| 5 | 74.0 | 66.3 | 76.6 | 72.1 | 69.0 | 74.4 | 72.0 |
| 10 | 71.6 | 63.7 | 74.4 | 69.4 | 66.8 | 72.3 | 69.7 |
| 15 | 70.9 | 62.5 | 73.8 | 68.3 | 66.1 | 70.3 | 68.6 |
| 20 | 70.3 | 61.2 | 73.2 | 68.3 | 65.5 | 69.8 | 68.0 |
| 25 | 70.0 | 60.3 | 72.9 | 68.1 | 65.1 | 69.4 | 67.6 |
| 30 | 69.7 | 59.6 | 72.7 | 68.0 | 64.5 | 69.1 | 67.2 |

TABLE V
20 PSIG H₂S-MEA PRESSURE DATA

| Run No. → | 7 | 60 | Average |
|----------------|-------------------------------|-------|---------|
| Time minutes ↓ | % OF ORIGINAL PRESSURE (PSIA) | | |
| 0 | 100.0 | 100.0 | 100.0 |
| 1 | 81.8 | 85.6 | 83.7 |
| 2 | 78.6 | 80.7 | 79.6 |
| 3 | 75.8 | 77.8 | 76.8 |
| 4 | 74.0 | 75.5 | 74.7 |
| 5 | 72.3 | 73.7 | 73.0 |
| 10 | 65.4 | 68.4 | 66.9 |
| 15 | 61.9 | 62.8 | 62.3 |
| 20 | 59.4 | 59.6 | 59.5 |
| 25 | 57.9 | 57.2 | 57.5 |
| 30 | 56.7 | 56.0 | 56.3 |

TABLE VI
20 PSIG SO₂-MEA PRESSURE DATA

| Run No. → | 41 | 42 | 44 | 49 | 50 | Average |
|-------------------|-------------------------------|-------|-------|-------|-------|---------|
| Time minutes ↓ | % OF ORIGINAL PRESSURE (PSIA) | | | | | |
| 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1 | 66.5 | 52.1 | 66.5 | 53.0 | 54.7 | 58.5 |
| 2 | 54.2 | 41.6 | 56.0 | 36.7 | 39.1 | 45.5 |
| 3 | 45.2 | 37.6 | 48.8 | 32.4 | 34.7 | 39.7 |
| 4 | 42.3 | 34.7 | 45.9 | 29.6 | 32.4 | 37.0 |
| 5 | 40.7 | 33.3 | 44.4 | 28.0 | 31.0 | 35.5 |
| 10 | 34.7 | 29.5 | 38.4 | 23.7 | 26.5 | 30.5 |
| 15 | 31.2 | 28.2 | 36.3 | 22.7 | 25.8 | 28.8 |
| 20 | 30.6 | 27.2 | 36.0 | 21.7 | 25.4 | 28.2 |
| 25 | 30.2 | 26.1 | 35.7 | 21.2 | 25.2 | 27.6 |
| 30 | 29.8 | 25.3 | 35.4 | 20.7 | 24.7 | 27.2 |

TABLE VII
10 PSIG CO₂-MEA TEMPERATURE DATA

| Run No. → | 33 | 34 | 52 | 53 | 54 | 55 |
|----------------|-------------|------|------|------|------|------|
| Time minutes ↓ | TEMPERATURE | | | | | |
| 0 | 84.0 | 85.0 | 77.0 | 78.0 | 79.0 | 78.0 |
| 1 | 87.5 | 96.0 | 78.0 | 81.0 | 82.5 | 82.5 |
| 2 | 90.0 | 98.0 | 80.0 | 84.0 | 86.0 | 86.5 |
| 3 | 92.0 | 98.0 | 82.5 | 86.0 | 88.0 | 88.0 |
| 4 | 93.0 | 98.5 | 84.0 | 87.5 | 89.5 | 89.0 |
| 5 | 94.0 | 98.0 | 86.0 | 88.0 | 90.0 | 89.5 |
| 10 | 93.0 | 93.5 | 88.0 | 88.0 | 87.0 | 86.0 |
| 15 | 90.0 | 91.0 | 83.0 | 84.0 | 83.0 | 82.5 |
| 20 | 88.0 | 89.0 | 81.0 | 82.0 | 81.5 | 80.0 |
| 25 | 87.0 | 88.0 | 80.0 | 80.0 | 80.0 | 79.0 |
| 30 | 86.5 | 87.0 | 78.0 | 79.0 | 78.0 | 78.0 |

TABLE VIII
10 PSIG H₂S-MEA TEMPERATURE DATA

| Run No. → | 6 | 58 | 59 |
|----------------|-------------|------|------|
| Time minutes ↓ | TEMPERATURE | | |
| 0 | 74.0 | 80.0 | 80.0 |
| 1 | 74.0 | 81.0 | 81.0 |
| 2 | 75.0 | 83.0 | 83.0 |
| 3 | 75.5 | 84.0 | 85.0 |
| 4 | 76.0 | 85.0 | 86.0 |
| 5 | 77.0 | 85.5 | 86.5 |
| 10 | 78.0 | 85.0 | 86.0 |
| 15 | 78.0 | 84.0 | 84.5 |
| 20 | 78.0 | 83.0 | 83.5 |
| 25 | 78.0 | 82.0 | 82.0 |
| 30 | 78.0 | 81.5 | 82.0 |

TABLE IX
10 PSIG SO₂-MEA TEMPERATURE DATA

| Run No. → | 40 | 43 | 45 | 47 | 48 | 51 |
|-------------------|-------------|-------|-------|-------|-------|-------|
| Time minutes ↓ | TEMPERATURE | | | | | |
| 0 | 80.0 | 79.0 | 74.0 | 79.0 | 79.0 | 80.0 |
| 1 | 88.0 | 126.0 | 84.0 | 80.0 | 91.0 | 124.0 |
| 2 | 99.0 | 150.0 | 115.0 | 90.0 | 102.0 | 164.0 |
| 3 | 104.0 | 141.0 | 126.0 | 98.0 | 109.0 | 151.0 |
| 4 | 106.0 | 134.0 | 121.0 | 102.0 | 111.0 | 144.0 |
| 5 | 106.5 | 127.0 | 117.0 | 104.0 | 112.0 | 136.0 |
| 10 | 101.0 | 106.0 | 99.5 | 105.0 | 106.5 | 110.0 |
| 15 | 94.0 | 93.5 | 88.0 | 97.0 | 98.0 | 99.0 |
| 20 | 84.5 | 87.0 | 82.0 | 91.0 | 92.0 | 90.0 |
| 25 | 83.5 | 83.5 | 78.0 | 87.0 | 87.5 | 86.0 |
| 30 | 82.5 | 80.0 | 76.0 | 84.0 | 84.5 | 84.0 |

TABLE X
20 PSIG CO₂-MEA TEMPERATURE DATA

| Run No. → | 32 | 35 | 36 | 37 | 38 | 39 |
|-------------------|-------------|-------|------|------|------|------|
| Time minutes ↓ | TEMPERATURE | | | | | |
| 0 | 84.0 | 85.0 | 80.0 | 82.0 | 81.0 | 80.0 |
| 1 | 92.5 | 98.0 | 82.5 | 88.0 | 88.0 | 83.5 |
| 2 | 94.5 | 101.5 | 85.5 | 91.5 | 93.5 | 88.5 |
| 3 | 96.0 | 102.5 | 87.5 | 94.0 | 97.0 | 91.5 |
| 4 | 97.5 | 103.0 | 90.0 | 95.5 | 98.0 | 92.5 |
| 5 | 97.5 | 103.5 | 91.0 | 96.0 | 98.5 | 93.5 |
| 10 | 95.5 | 98.0 | 91.0 | 94.0 | 94.5 | 91.5 |
| 15 | 90.0 | 92.5 | 88.0 | 89.0 | 89.0 | 87.0 |
| 20 | 88.0 | 89.5 | 85.0 | 86.0 | 86.0 | 86.5 |
| 25 | 86.5 | 88.0 | 83.5 | 84.0 | 84.0 | 83.0 |
| 30 | 86.0 | 87.0 | 82.5 | 83.0 | 83.0 | 82.0 |

TABLE XI
20 PSIG H₂S-MEA TEMPERATURE DATA

| Run No. → | 7 | 60 |
|----------------|-------------|------|
| Time minutes ↓ | TEMPERATURE | |
| 0 | 76.0 | 82.0 |
| 1 | 82.5 | 84.0 |
| 2 | 85.5 | 86.0 |
| 3 | 87.0 | 88.0 |
| 4 | 88.0 | 89.5 |
| 5 | 88.0 | 90.5 |
| 10 | 86.0 | 90.0 |
| 15 | 83.5 | 88.0 |
| 20 | 81.5 | 86.5 |
| 25 | 80.0 | 85.0 |
| 30 | 79.5 | 84.0 |

TABLE XII
20 PSIG SO₂-MEA TEMPERATURE DATA

| Run No. → | 41 | 42 | 44 | 49 | 50 |
|-------------------|-------------|-------|-------|-------|-------|
| Time minutes ↓ | TEMPERATURE | | | | |
| 0 | 77.0 | 79.0 | 73.0 | 79.0 | 80.0 |
| 1 | 84.0 | 182.0 | 78.0 | 175.0 | 166.0 |
| 2 | 99.0 | 184.0 | 109.0 | ~195. | ~200. |
| 3 | 146.0 | 166.0 | 129.0 | 179.0 | 174.0 |
| 4 | 144.0 | 156.0 | 128.5 | 165.0 | 161.0 |
| 5 | 138.0 | 147.0 | 124.0 | 154.0 | 151.0 |
| 10 | 116.0 | 118.0 | 105.0 | 123.0 | 122.0 |
| 15 | 100.0 | 98.0 | 92.0 | 104.0 | 104.0 |
| 20 | 90.0 | 92.0 | 80.0 | 94.0 | 94.0 |
| 25 | 85.0 | 86.0 | 79.5 | 89.0 | 89.0 |
| 30 | 82.0 | 82.0 | 77.0 | 86.0 | 85.0 |

APPENDIX B

SAMPLE CALCULATION

SAMPLE CALCULATION

Run No. 29

TABLE VII
PHYSICAL PROPERTIES OF THE ACID GASES

| GAS | P _c PSIA | T _c °R |
|------------------|---------------------|-------------------|
| CO ₂ | 1071 | 547.57 |
| H ₂ S | 1306 | 672.37 |
| SO ₂ | 1145 | 775.17 |

Note: Source Reference 18

Pressure = 10 psig = 24.696 psia

Moles of CO₂ introduced

$$T_r = \frac{T}{T_c} = \frac{75 + 459.67 \text{ } ^\circ\text{R}}{547.57 \text{ } ^\circ\text{R}} = 0.9764$$

$$P_r = \frac{P}{P_c} = \frac{24.696 \text{ psia}}{1071 \text{ psia}} = 0.02306$$

From Figure 16-5, reference 18

$$Z = 0.9905$$

$$n_{\text{CO}_2} = \frac{Pv}{ZRT}$$

$$= \frac{24.696 \text{ psia} \times 600 \text{ cm}^3 \times 3.531467 \times 10^{-5} \text{ (ft}^3/\text{cm}^3)}{0.9905 \times 10.73 \text{ (psia ft}^3/\text{lb mole } ^\circ\text{R)} \times (75 + 459.67) ^\circ\text{R}}$$

$$n_{\text{CO}_2} = 9.20858 \times 10^{-5} \text{ lb mole}$$

Density of MEA

$$\rho = 1.018 \text{ gm/cm}^3 \text{ at } 68^\circ\text{F (reference 18)}$$

$$\rho = 1.0113 \text{ gm/cm}^3 \text{ at } 77^\circ\text{F (reference 1)}$$

Linear interpolation was used for other temperatures

Volume of MEA introduced for a one-to-one reaction with CO_2

$$V_{\text{MEA}} = \frac{n_{\text{CO}_2} \text{ MW}_{\text{CO}_2}}{\rho_{\text{MEA}}}$$

$$= \frac{9.20858 \times 10^{-5} \text{ lb mole} \times 61.08 \text{ (lb/lb mole)} \times 453.59 \text{ (gm/lb)}}{1.0127 \text{ (gm/cm}^3)}$$

$$= 2.519 \text{ cm}^3$$

APPENDIX C

NMR DATA

All nuclei have a positive charge, magnetic moment, and spins. The value of the spins are multiples of 1/2. When a nucleus with a spin is placed in a magnetic field, it has an energy level that can be calculated from known parameters of the nucleus. Each different nucleus has a variable number of energy levels it can occupy - the number of which can also be calculated. The difference in these energy levels is due to the difference in potential energy of the nucleus.

An nmr instrument has a radiofrequency transmitter which causes a small oscillating electromagnetic field to be applied to the sample liquid. When the frequency of the oscillating field equals the transition frequency, a resonance effect induces transitions between the energy levels. The transition frequency has the proper amount of energy for a given nucleus to change energy levels. When these transitions occur, the resultant oscillation in the field induces a voltage oscillation in a receiver coil which is then amplified and recorded.

The usefulness of nmr in studying the structure of molecules stems from the fact that the environment surrounding the nucleus has an effect on the field sensed by the nucleus. The electrons around a nucleus are moved closer to or away from a nucleus by electron density and electromagnetic effects. A nucleus is said to be deshielded by its electrons if they are drawn away from the nucleus. The difference in shielding is called "chemical shift" and is expressed relative to that of a known substance. The chemical shift parameter δ is defined as

$$\delta = \frac{A - B}{H_0}$$

where A and B are the resonance positions. B is a selected reference arbitrarily set to zero. H_0 is the strength of the applied field.

A common reference is usually tetramethylsilane (TMS). TMS is chosen because the resonance of its protons are somewhat unique and most other compounds show up as a shift from TMS in a negative direction. The amount of shift then is used to determine the functional group or the surroundings of a nucleus in question.

One other effect important here is "spin-spin splitting" of a set of protons. Consider a molecule of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) - the protons of the CH_2 group can "sense" the spins of the CH_3 group. The spin of a given proton is either in the same direction as another proton or is in the opposite direction. The possible energetically different arrangements are shown in Figure 14. The spectrum that one would expect to see from these arrangements is shown below each configuration in Figure 14.

The CH_2 group in MEA is affected by the neighboring protons of the NH_2 group and subsequently the CH_2 profile is slightly altered from that of ethanol.

Paulder (19) gives a more detailed explanation of nmr analysis and theory.

TMS was the reference for the nmr scans in this work. All samples were run at room temperature in 5 mm diameter tubes at 20 rps.

Proton scan data:

1 scan at 100.1 MHz

Spectral width of 1000 Hz

Filter of 2 Hz

Carbon-13 scan data:

Spectral width of 5000 Hz

Filter of 3KHz

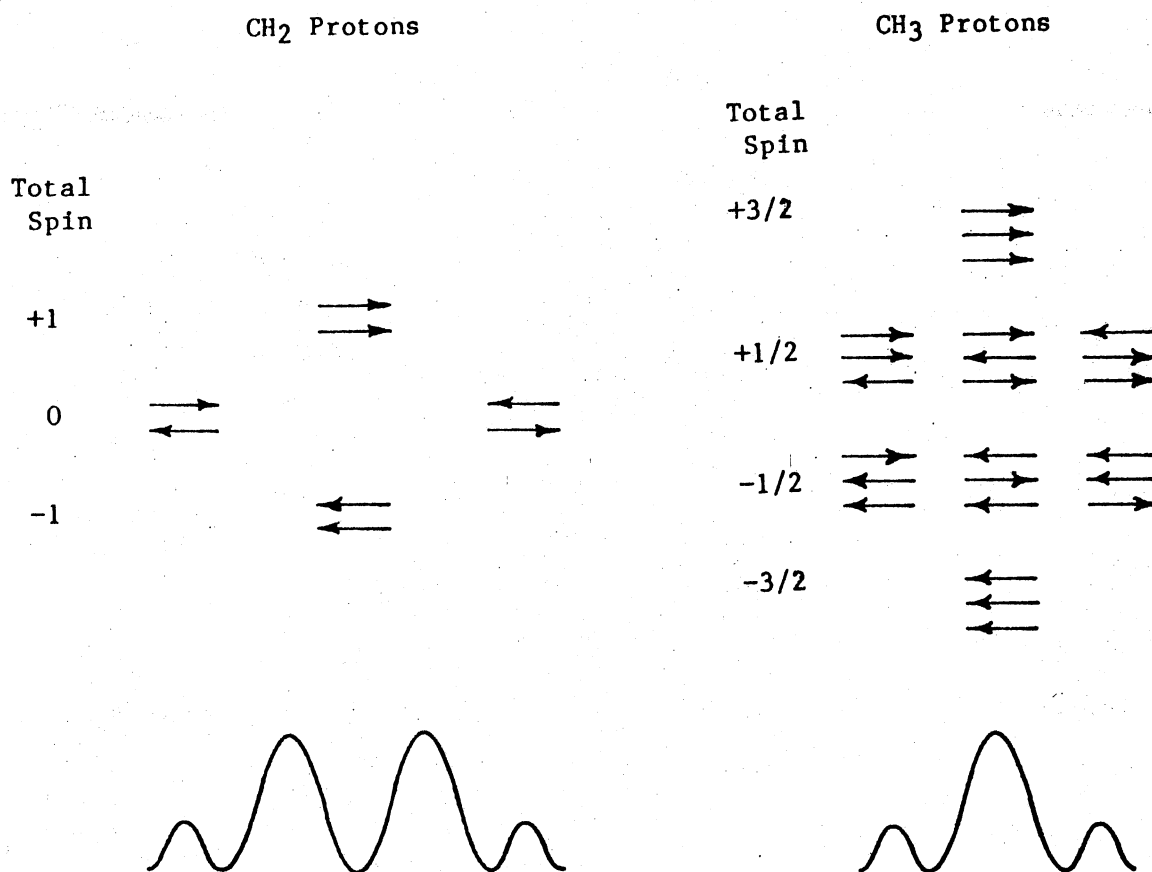


Figure 14. Spin-Spin Splittings of NMR Spectrum of Ethanol (19)

Pulse delay of 6 seconds

Decoupled from ^1H

Acquisition time of 1.3 seconds

140 acquisitions were made on the MEA and the CO_2 -MEA liquids. 240 acquisitions were made on the ammonium bicarbonate and the CO_2 -MEA-ammonium bicarbonate scans. All Carbon-13 scans were made by Fourier transform.

VITA²

William Thomas Batt

Candidate for the Degree of

Master of Science

Thesis: MONOETHANOLAMINE REACTIONS WITH SELECTED ACID GASES

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Defiance, Ohio, December 10, 1950 the son of William J. and Evelyn M. Batt.

Education: Graduated from Defiance High School, Defiance, Ohio, in June, 1968; received Bachelor of Science Degree in Chemistry from Defiance College in 1972; completed the requirements of Master of Science degree in Chemical Engineering in July, 1979.