# ABSORPTION OF CARBON DIOXIDE AND HYDROGEN SULFIDE BY STERICALLY HINDERED AMINE

by

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A THESIS

Submitted to the faculty of the Stevens Institute of
Technology in partial fulfillment of the requirements
for the degree of

MASTER OF ENGINEERING (CHEMICAL)

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# ACKNOWLEDGEMENT

I wish to express my sincere appreciation to my advisor, Professor A.P. Zioudas for his guidance, support and constant availability to me during the course of my studies.

I would also like to acknowledge the international program office for the help it provided to me and all the algerian students at Stevens Institute of Technology.

My thanks would be incomplete without recalling the love and support of my mother, my father, my sisters and brothers, without whom life would have no meaning at all.

I wish to thank especially M. Henmi for her constant encouragement during my stay in the United States.

Finally, I wish to thank all the Indian students of the Room 118 in the Chemical Engineering dept. of Stevens Institute of Technology for their help during my experiments. Dr. B. Bhave gave many valuable suggestions, the author graciously acknowledge his assistance. Rosie deserves a warm thank for her patience while typing this manuscript.

# Abstract

## Absorption of Carbon Dioxide and Hydrogen Sulfide by Sterically Hindered Amine

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The absorption of carbon dioxide, hydrogen sulfide and their mixture by two different classes of amine in an absorption cell with no agitation was investigated. The two amines used were:

-Monoethanolamine (MEA), as common amine

-2-Amino-2-Methyl-1 propanol (AMP), as sterically hindered amine

The concentration of amines was varied from 0.03M to 0.3M and the partial pressure of the gas above the liquid surface ranged from 0.75 psia to 28.7 psia.

The results show that the absorption of carbon dioxide into amine solutions was controlled by the ratio between the partial pressure of the gas and the concentration of amine solution. Three different situations were found.

* AMP absorbed 25% more $CO_2$ than MEA for pure $CO_2$ at 1 atm and 0.05M amine solution

* - MEA absorbed 14% more $CO_2$ than AMP for pure $CO_2$ at 1 atm and 0.3M amine solution

- MEA absorbed 250% more $CO_2$ than AMP for $CO_2$ at 0.75 psia and 0.05M amine solution

* - MEA and AMP absorbed the same amount of $CO_2$ at 2 atm and 0.05M

amines solution

-MEA absorbed only 17% more $CO_2$ than AMP at 1 atm and 0.03M. The curves are close to the absorption of carbon dioxide by water.

The fact that hindered amine absorbed more $CO_2$ than MEA at some special conditions can be explained by the "hindered effect" which increase the concentration of amine due to the unstable carbamates when their concentration is not negligible in the reaction zone.

The absorption of hydrogen sulfide shows no difference between the two classes of amine and the absorption of the mixture $CO_2/H_2S$ shows that for the mixture (50% $CO_2$ ; 50% $H_2S$) AMP absorbed a little more gas ($CO_2$ + $H_2S$) than MEA.

# NOMENCLATURE

a = concentration of the gas

A = concentration of the gas at Boundary conditions

b = concentration of the amine

B = concentration of the amine at Boundary condition

D = diffusivity of the gas into the liquid phase

E = enhancement factor

k = reaction constant

K = equilibrium constant

M = dimensionless group defined in equation (20)

Q = amount of gas absorbed by unit area

r = rate of reaction

R = rate of absorption

t = exposure time

x = distance in the liquid from the interface

Z = stochiometric factor

## Greek Letters

$\theta$ = ratio between the gas absorbed and the concentration of amine in the solution

## Subscripts

A = gas to be absorbed

B = amine

i = instanteneous

## Superscripts

| | |
|---|---|
| * | interface |
| o | bulk |

## Abbreviations

| | |
|---|---|
| erf | error function |
| G | pressure Gage |
| mV | millivolt |
| M | molarity |
| $N_2$ | nitrogen |
| psig | psi in the gage |
| pCV | pressure control valve |
| V | valve |

## Symbols

| | |
|---|---|
| [ ] | concentration |

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# INTRODUCTION

Over the years, the most widely used gas for the investigation on the gas absorption is carbon dioxide. Not only because of its presence in the natural gas but also its availability and its facility to handle in laboratory experiments. Carbon dioxide reacts so slowly with water that the process has little industrial importance [3]. The absorbents most often used in industry are amine solutions, which are usually 15 to 20% wt of Monoethanolamine (MEA) or 20 to 30% wt of Dietanolamine (DEA), [4].

The absorption rate of carbon dioxide with amines is controlled essentially by the chemical reactions and the stability of the carbamates formed, [10]. The stability of these carbamates presents a resistance which will limit the absorption capacity at 0.5 mole $CO_2$/mole of amine, when the stability is low, the rate of disappearance of carbon dioxide can increase to 1 mole $CO_2$/mole of amine, [10].

G. Sartori and D.W. Savage, [10], have recently used a new class of amines: sterically hindered amines that are defined as:

a) Primary amines in which the amino group ($-NH_2$) is attached to a tertiary carbon

b) Secondary amines in which the amino group ($-NH_2$) is attached to a secondary or tertiary carbon

Because of the molecular structure of the hindered amines, the carbamates formed have a lower stability than these formed by the common amines and will affect the rate of absorption of carbon dioxide when their concentration is not negligible.

In most gas purification processes, carbon dioxide is not encountered alone. All natural gases contain also hydrogen sulfide. For such a mixture, the selective removal of $H_2S$ has been extensively studied because of its industrial and economic importance and the amines usually used are tertiary amines (TEA) or methyl-diethanolamine (MDEA), [8], [9], [11]. However, less work has been done on the rate of absorption of hydrogen sulfide in amine solutions, this is essentially due to the high absorption efficiencies obtained in industry.

To understand the "hindered effect", A semi-infinite quiescent hindered amine and monoethanolamine solutions were used at different concentrations and different partial pressures of the carbon dioxide in a batch reactor. Since no data is available for the system $H_2S$-hindered amine, the author believes that it is necessary to investigate the system. The mixture of $CO_2$ and $H_2S$ was also studied in this work. A quiescent amine solutions were used because the "hindered effect" is a pure chemical reaction phenomena.

## THEORY OR ABSORPTION

Gas absorption can take place by a diffusion process alone or it may involve chemical reactions in which the absorbed gas reacts with other dissolved species. The latter process is particularly important. It provides two means of removing the absorbed gas from the interface; by diffusion and reaction, most of the industrially important gas absorption processes involve chemical reactions. The absorption rate of gases into quiescent liquids is well described in Danckwerts book,[1]. The principal situation considered in this system is that the liquid has a free surface which is exposed to the gas. The surface is plane and the liquid for practical purposes is infinitely deep this means that the bulk concentration of the amine changes only slightly. It is assumed that when the liquid surface is first brought into contact with the gas, the equilibrium concentration, $A^*$, will be achieved. This concentration is the equilibrium solubility of the gas at the partial pressure prevailing above the surface of the liquid. The equilibrium concentration will be assumed to be constant, [1].

Let's consider first the case in which no chemical reaction takes place between the dissolved gas and the liquid. Under these circumstances, the variation in time and space of the concentration a of the dissolved gas in the liquid is governed by the diffusion equation

$$D_A \frac{\partial^2 a}{\partial^2 x} = \frac{\partial a}{\partial t} \qquad (1)$$

The rate of absorption is given by [1]

$$R = \sqrt{\frac{D_A}{\pi t}}\,(A^* - A^o) \qquad (2)$$

and the total amount of gas absorbed by unit area

$$Q = \int_o^t R dt = 2\,A^* \sqrt{\frac{D_A t}{\pi}} \qquad (3)$$

When a chemical reaction is taking place in the liquid phase, a factor "E" called enhancement factor is introduced to describe the effect of chemical reaction on the rate of absorption. The enhancement factor is defined as the ratio between the amount of absorbed gas with chemical reaction and without chemical reaction at a given time, t.

$$E = \frac{Q\ (\text{with chemical reaction})}{Q\ (\text{physical absorption})} \qquad (4)$$

and the equation (1) is replaced by

$$D_A \frac{\partial^2 a}{\partial x^2} = \frac{\partial a}{\partial t} + r(x,t) \qquad (5)$$

<u>First-Order Reaction:</u>

For this case, the reaction rate expression is given by

$$r = k_1 a \qquad (6)$$

The rate of absorption is given in the literature [1] as:

$$R = A^* \sqrt{D_A k_1}\left[\text{erf}\sqrt{k_1 t} + \frac{e^{-k_1 t}}{\sqrt{\pi k_1 t}}\right] \qquad (7)$$

and the total amount of gas absorbed:

$$Q = A^* \sqrt{\frac{D_A}{k_1}} \left[ (k_1 t + \tfrac{1}{2}) \operatorname{erf} \sqrt{k_1 t} + \sqrt{\frac{k_1 t}{\pi}}\, e^{-k_1 t} \right] \qquad (8)$$

The enhancement factor is given as [7]

$$E = \sqrt{\frac{\pi}{4 k_1 t}} \left[ (k_1 t + \tfrac{1}{2}) \operatorname{erf} \sqrt{k_1 t} + \frac{e^{-k_1 t}}{2} \right] \qquad (9)$$

When $k_1 t >> 1$

$$R = A^* \sqrt{D_A k_1} \qquad (10)$$

$$Q = A^* \sqrt{D_A k_1} \left(t + \frac{1}{2k_1}\right) \qquad (11)$$

$$E = \sqrt{\frac{\pi k t}{4}} \qquad (12)$$

Applying Henry's law, the rate of absorption is proportional to the partial pressure of the gas

Instanteneous Reaction:

For this situation, the liquid phase is divided in two regions where the gas and the dissolved reactant can not co-exist. The reaction occurs on the dividing the two regions plane; called the reaction-plane. The Rate of absorption is given as

$$R = E_i\, A^* \sqrt{\frac{D_A}{\pi t}} \qquad (13)$$

and the total amount of gas absorbed:

$$Q = 2E_i A^* \sqrt{\frac{D_A t}{\pi}} \tag{14}$$

where the instantaneous enhancement factor $E_i$ can be approximated as [7]

$$E_i = \sqrt{\frac{D_A}{D_B}} + \frac{B^o}{ZA^*} \sqrt{\frac{DB}{D_A}} \tag{15}$$

Assuming $D_A = D_B$ with an error of $1/2E_i$;

$$E_i = 1 + \frac{B^o}{ZA^*} \tag{16}$$

Making this assumption we get

$$Q = 2\left(A^* + \frac{B^o}{Z}\right) \sqrt{\frac{D_A t}{\pi}} \tag{17}$$

From equation (17), the rate of Absorption is proportional to the partial pressure of the gas at large pressures of the reactive gas and low concentrations of the amine, and proportional to the bulk concentration of amine at low partial pressures of the absorbed gas and high concentrations of amine in the liquid bulk

## Second-Order Reaction:

When the dissolved gas undergoes a second-order irreversible reaction with a dissolved reactant, the reaction rate expression is:

$$r = k_2\, ab \tag{18}$$

The number of variables in this special case can be reduced by forming the dimensionless groups [1]

$$E = \frac{Q}{2A^*}\sqrt{\frac{\pi}{D_A t}} \qquad (19)$$

$$M = \frac{\pi}{4} k_2 B^o t \qquad (20)$$

"E" is known as the enhancement factor and "M" is a condensed time scale. The presentation of the results can be greatly condensed by using the observation of Brian et al [7] that the enhancement factor is approximately represented by

$$E = \sqrt{M\left(\frac{E_i - E}{E_i - 1}\right)} \Big/ \tanh \sqrt{M\left(\frac{E_i - E}{E_i - 1}\right)} \qquad (21)$$

Where "$E_i$" is the limiting value of "E" for instanteneous reactions. Equation (21) is represented in figure 1 Some special cases are also shown on this figure.

For $\sqrt{M} << 1$; "E" will approach unity, this case describes a slow reaction kinetics where physcial absorption dominates the transport process or corresponds to short contact time.

For $\sqrt{M} << E_i$; all points of "E" lie on the straight line BC. This portion represents the period when the extent of reaction is so small that the concentration of reactant B near the surface is hardly reduced which makes the reaction "Pseudo-first order". In this special case; R,Q and E are given by the equations (6) to (12) where $k_1 = k_2 B^o$.

For $\sqrt{M} \gg E_i$; the reaction is very fast or the contact time is very long. In this situation; the reaction is nearly instanteneous and "E" approaches its limiting value "$E_i$". The absorption rate in this regime is diffusion controlled and the equations (13) to (17) apply.

The kinetics and chemical reactions of carbon dioxide and hydrogen sulfide into amine solutions will be discussed in the next section.

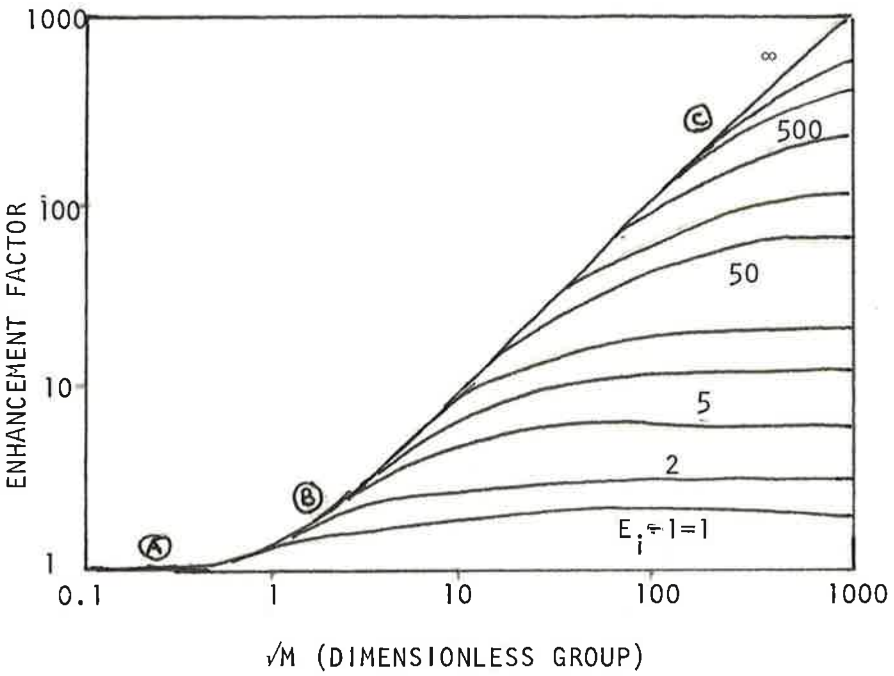

Figure 1: Enhancement Factor for 2nd order reaction
(From Reference [1])

## CHEMICAL REACTIONS AND KINETICS

### Carbon dioxide in pure water:

The absorption of carbon dioxide in water is known to be accompanied by the following chemical reactions [8]

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H^+ + HCO_3^- \qquad (22)$$

$$HCO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H^+ + CO_3^{2-} \qquad (23)$$

Neglecting the very slow reaction (23) and assuming low concentrations of ions in water; the reaction is often taken as [7].

$$CO_2 + H_2O \xrightarrow{k_1} H^+ + HCO_3^- \qquad (24)$$

The reaction is first-order with respect to carbon dioxide and the velocity constant $k_1$ was found to be temperature dependent [7].

$$\log_{10}k_1 = 329.850 - 110.541 \log_{10}T - (17265.4/T) \qquad (25)$$

### Carbon dioxide in Amine Solutions:

Due to the labely hydrogen atom in primary amines, a single $CO_2$ molecule can react directly with two amine molecules following the general reaction, [9].

type: carbamate
kinetics: fast

$$CO_2 + 2RNH_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} RNH_3^+ + RNHCOO^- \qquad (26)$$

Since the reaction is reversible, the equilibrium constant can be defined as

$$K_{CO_2} = \frac{k_3}{k_{-3}} \frac{[RNHCOO^-][RNH_3^+]}{[CO_2]\ [RNH_2]^2} \tag{27}$$

This reaction is known to be complex and it is a combination of three elementary reactions

*protonation of amine: $RNH_2 + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} RNH_3^+$ (28)

*Acid-base reaction: $RNH_2 + CO_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} RNHCOOH$ (29)

*Carbamate formation: $RNHCOOH \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} RNHCOO^- + H^+$ (30)

Because the reaction is not instanteneous, the net forward reaction rate can be calculated (see Appendix 3)

$$R_{CO_2} = k_5 \left[ [CO_2]\ [RNH_2] - \frac{1}{K_{CO_2}} \frac{[RNHCOO^-]\ [RNH_3^+]}{[RNH_2]} \right] \tag{39}$$

From equation (39), one can see how the concentration of carbamates in the soltuion represent a resistance for the absorption capacity of carbon dioxide. Recently, new hindered amines were presented in the literature [10]. The key advantage of these amines is lowering the stability of carbamates which will decrease their concentrations and then increase the rate of disappeareance of carbone dioxide.

In amine solutions, carbon dioxide is absorbed following three differents reactions. The importance of each reaction depends on the ratio of the moles of carbon dioxide absorbed by mole of amine in the solution, let's represent this ratio by $\theta$ and define these three equations, [2].

When $\theta < 0.5$:

Carbon dioxide reacts directly with amines as discussed before

$$CO_2 + 2RNH_2 \overset{k_3}{\rightleftarrows} RNH_3^+ + RNHCOO^- \qquad (26)$$

and carbamate reverses to bicarbonate

$$RNHCOO^- + H_2O \rightleftarrows HCO_3^- + RNH_2 \qquad (40)$$

When $\theta > 0.5$:

$$CO_2 + OH^- \xrightarrow{kd} HCO_3^- \qquad (41)$$

This reaction is much slower than reaction (26) and the rate of disappearance of $CO_2$ is defined as

$$R_{CO_2} = kd\,[CO_2]\,[OH^-] \qquad (42)$$

Very large values of $\theta$:

When the amine molecules are highly carbonated the reaction which will preferentially take place is the direct reaction of carbon dioxide with water

$$CO_2 + H_2O \xrightarrow{k_1} HCO_3^- + H^+ \qquad (24)$$

The rate of disappearance of carbon dioxide is then defined as:

$$R_{CO_2} = \left\{ k_1 + kd\,[OH^-] \right\} [CO_2] \qquad (43)$$

## Hydrogen Sulfide in amine Solutions:

Unlike the Carbon dioxide, hydrogen sulfide is absorbed in water with no chemical reaction and in all amines, the reactions is instanteneous, [9].

type: acid-base

kinetics: instanteneous

$$H_2S + RNH_2 \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} HS^- + RNH_3^+ \quad (44)$$

Where the equilibrium constant is

$$K_{H_2S} = \frac{k_7}{k_{-7}} \quad \frac{[HS^-]\ [RNH_3^+]}{[H_2S]\ [RNH_2]} \quad (45)$$

This reaction is a result of two elementary reactions

*protonation of amine: $RNH_2 + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} RNH_3^+$ (46)

*Decomposition of $H_2S$: $H_2S \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} H^+ + HS^-$ (47)

Since the reaction is instanteneous, the rate of reaction can not be defined:

## Carnone dioxide/Hydrogen Sulfide mixture in amine solutions:

When a mixture $CO_2/H_2S$ is absorbed in amine solutions, besides the reactions of each gas with the solution, another reaction known as the "Shift-reaction" can take place when the concentration of amine is low [11].

$$2H_2S + RNHCOO^- \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} 2HS^- + RNH_3^+ + CO_2 \quad (48)$$

with the following equilibrium constant

$$K_9 = \frac{K^2_{H_2S}}{K_{CO_2}} \tag{49}$$

At this point, one can see how $H_2S$ and $CO_2$ affect each other and that unstable carbamates have an important role in the selective absorption of hydrogen sulfide

The description of the apparatus and operating procedure are given in the next chapter.

# DESCRIPTION OF THE APPARATUS AND OPERATING PROCEDURE

## Description of the Apparatus:

The apparatus consists of an absorption cell and a gas-storage cylinder separated by different valves which will be used depending on the rate of Absorption. The pressure in the cell is maintained constant by bleeding in gas through the valves and from the gas-cylinder. The rate of absorption is then measured indirectly (see Appendix 2) by measuring the pressure change in the gas cylinder used as the source of gas. The pressure in the cell was measured by a pressure transducer related to a recorder and the valves were operated to maintain a steady line in the recorder. The interfacial temperature was also recorded to measure any thermal effects at the interphase.

## Operating Procedure:

### Test of the 10 DC excitation source:

After testing each electrical equipment by itself, connect them and plug "ON". Initially the rheostat is in position "OFF", then increase the tension slowly to 10 volts and check on the voltmeter the stability of the tension for at least one hour.

### Calibration of the pressure transducer and Recorder A:

Before the calibration, the electrical side of the pressure transducer should be checked, this will give us a line in the moving chart for any pressure between 0 and 15 psig. For this purpose, let the electrical equipments warm-up during 10 minutes before to put the recorder "ON". The pressure transducer gives an output electrical signal from 0 to 40 mV when the pressure differential across it vary between 0 to 15 psig. The reference pressure is the atmospheric pressure and the pressure to measure is the pressure in the cell. The input signal is then 10 volts and the output is 4 mV/Volt input. For our purpose the full scale range of 0.1 volt was chosen. (See figure 3)

## Calibration of the thermocouple and Recorder B:

Millivolts outputs of chromel/constantan Thermocouple are given in OMEGA catalog. (See figure 4).

| Temperature($^{o}$C) | Readings (mV) |
|---|---|
| 20 | 1.19 |
| 30 | 1.80 |
| 40 | 2.41 |
| 50 | 3.04 |

The battery of te cold-function should be tested before each experiment.

## LEAK Test:

Due to the nature of the experiments, leak tests were an integral part of the experimental procedure. The first step of the leak test is to evacuate the whole system. This can be done as follows: All the valves initially closed.

1) Open: $V_1$, $V_2$, $V_3$, $V_4$, $V_5$, $V_6$, $V_7$, $V_{10}$, $V_{15}$, PCV
2) Start the vaccum pump and open $V_{16}$ at the same time
3) When almost full vaccum is achieved in the system, close $V_{16}$

and stop the pump.

4) Read the pressure of the system in the vaccum gage G1. After at least one hour if any change is observed, use nitrogen pressure to locate the leaks.

For this purpose, the system was divided in three sections

- cell absorption section: $V_{14}$, to $V_1$, $V_2$, $V_4$.
- upstream section: $V_1$, $V_2$, $V_4$ to $V_{13}$ ($V_5$, $V_7$ closed)
- storage tank section: tank to $V_{19}$ ($V_6$, $V_{13}$ closed)

The detection of leaks was done in the following procedure:

1. through valve $V_{14}$, full the cell with nitrogen pressure at 15 psig. at the gage G1, if any leak is observed at on hour time, use the leak solution and then correct the leaks until the pressure at G1 stays constant.

2. Open: $V_1$, $V_2$, $V_4$, $V_6$, PCV ($V_5$, $V_7$ closed) and add nitrogen until the system is filled at 15 psig and using the same procedure as before, the leaks should be corrected.

3. Open now $V_5$, $V_7$, $V_9$, $V_{10}$ and correct the leaks of this section

4. Do again the first step and check that the whole system stays under vaccum for at least one hour otherwise the procedure should be repeated

Experimental procedure:

1. put the whole system under vaccum

2. fill the cell with a distillated water after being boiled

3. start the vaccum pump until no bubbles will appear at the interface then close $V_{16}$ and shut-off the pump

4. push the degased water out of the cell and into the Erlenmeyer flask using nitrogen pressure

5. add the necessary amount of amine in the water to achieve a predecided concentration. Take a sample in a small bottle

6. evaculate the system and draw slowly the solution in the cell. Observe the liquid from the window fill in enough liquid so that the liquid surface almost touches the tip of the thermocouple

7. keep the pump running to eliminate all dissolved gases from the solution

8. now adjust the tip of the thermocouple with the help of the screw. The surface tension effects causes the formation of a drop at the tip

9. close valves $V_1$, $V_2$, $V_3$ $V_{14}$ so that the cell side stays under vaccum in the next step

10. through $V_{13}$, fill the cylinder A at 15 psig with the gas to be absorbed

11. open $V_{14}$ and fill the cell, with the gas to be used, at atmospheric pressure wait until the pressure is stabilized, then

12. start the recorders A and B and open one of the valves $V_1$, $V_2$, PCV to keep the pressure of the cell constant during the experiment, a steady line should be obtained in recorder A

13. at the end of the experiment, stop the electrical equipments, push the amine solution in the flask where a sample was taken to determine the final concentration using HCl titration

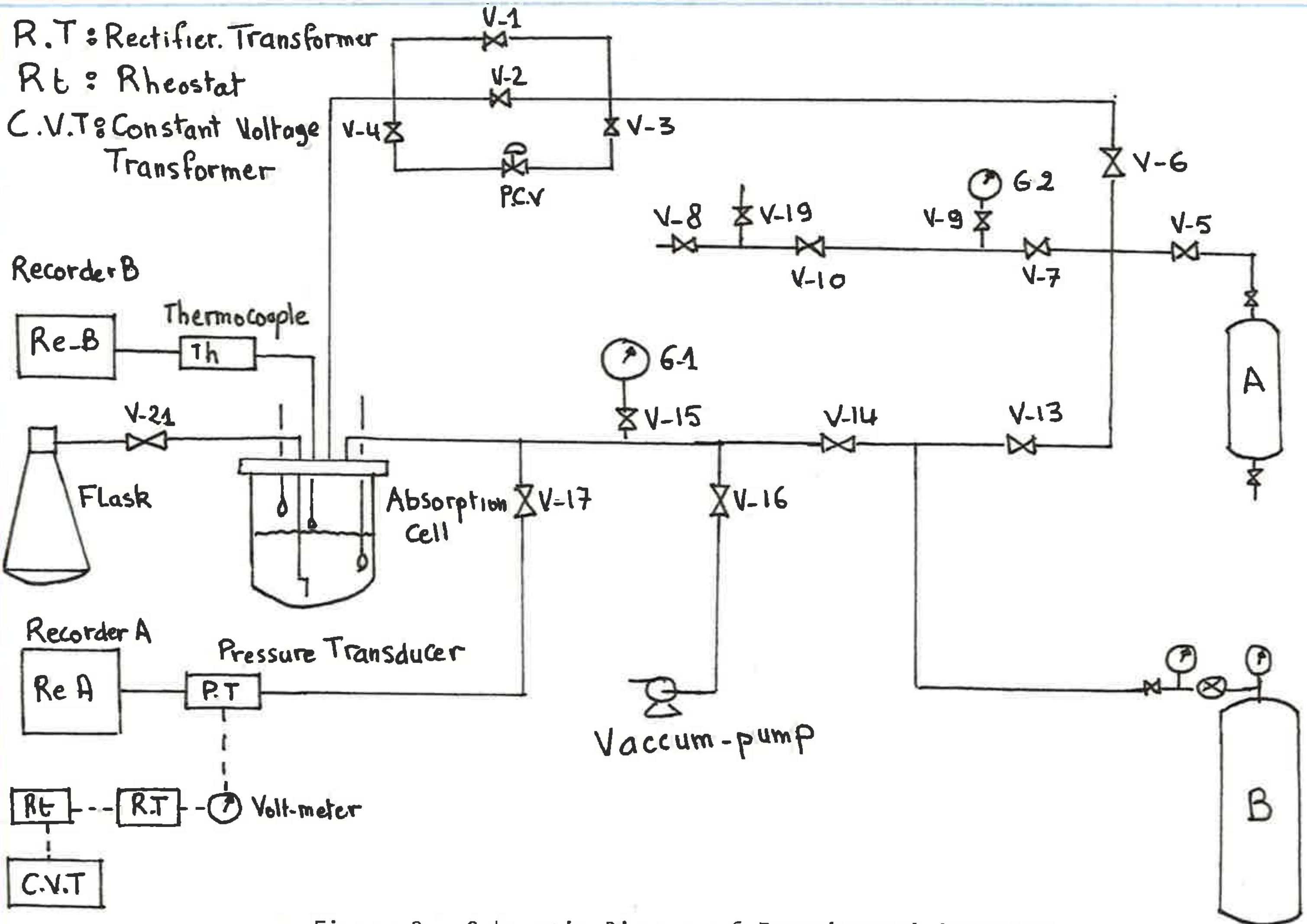

Figure 2: Schematic Diagram of Experimental Apparatus

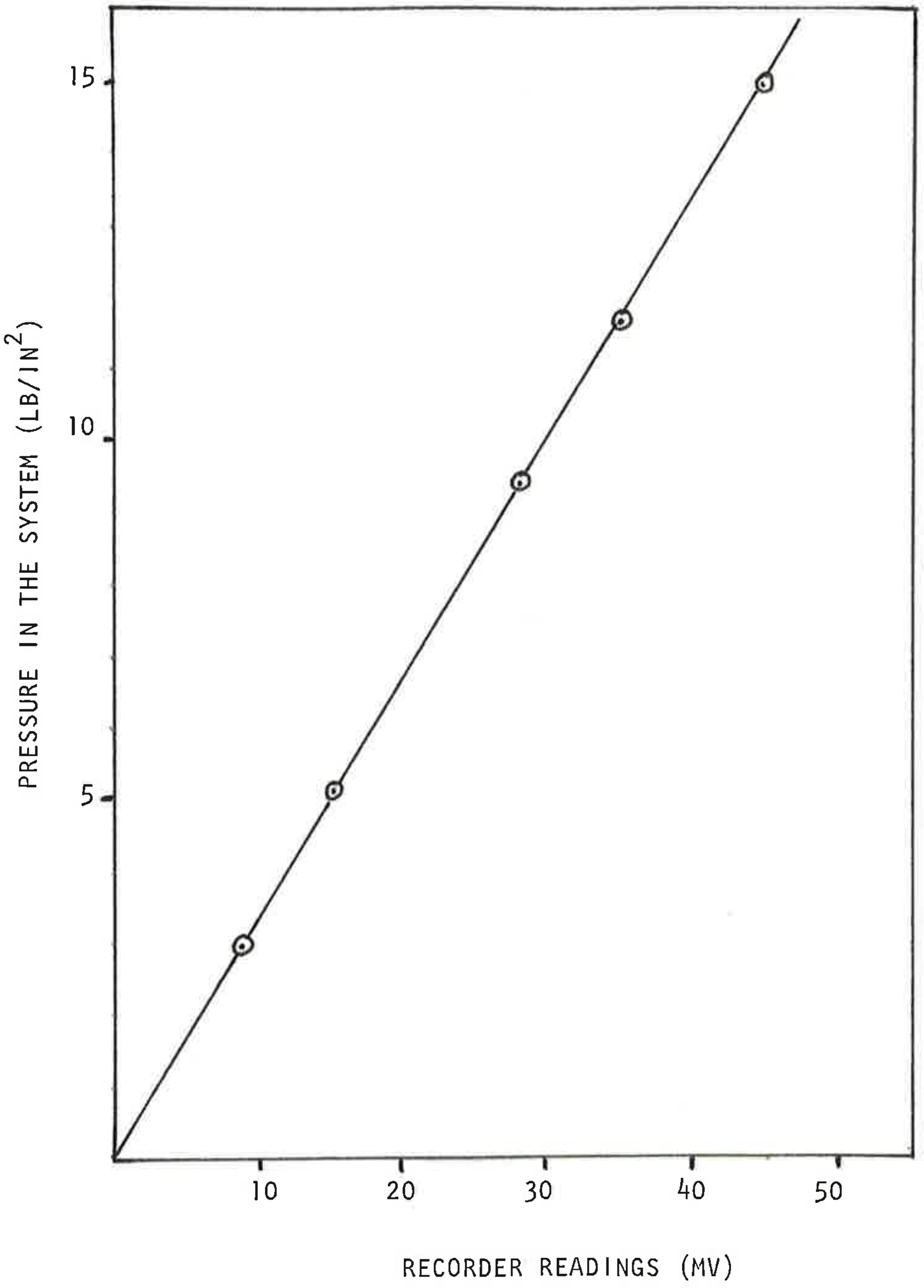

Figure 3: Calibration of the Pressure Transducer and Recorder A

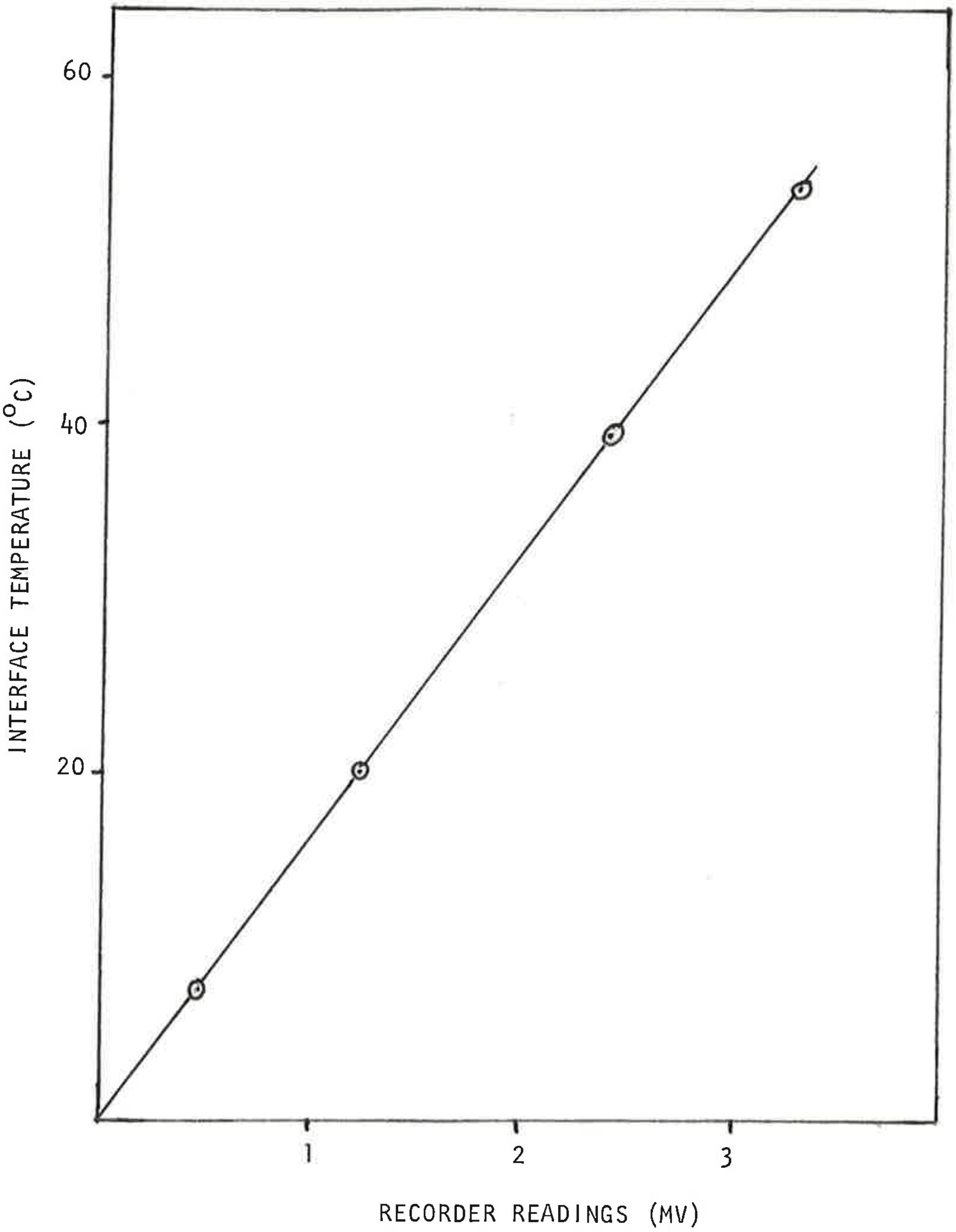

Figure 4: Calibration of the thermocouple and the Recorder B

## EXPERIMENTAL TEST:

The absorption of carbon dioxide in pure water was used as a test of the apparatus. The theory of this absorption is given in the literature, [1] and [7]. The kinetics are described by equations (22) to (25) and the rate of absorption is given by equations (6) to (12). The diffusivity of carbon dioxide in water was described by Wilke and Chang relation, [1], while its solubility was taken from the data of Morgaw and Naass [3]. The results in figure 5 show that at short contact time, less than 500 sec; the experimental values of Q nearly coincide with the theoretical values. However at longer time, the two curves diverge; for example for 1 600 sec the difference is 15%, considering the difficulty of controlling a low absorption and the errors of the values taken for the diffusivity, solubility and the velocity constant, the results are good and the apparatus is reproducible. The results are given in table 1 and figure 5.

Table 1: Experimental and Theoretical results of Carbon dioxide Absorbed into water at 18°C and 1.16 atm

| Time (sec) | Pressure in cylinder A(kPa) | Q x $10^5$(EXP) gmoles/$cm^2$ | Q x $10^5$(THEO) gmoles/$cm^2$ | Error % |
|---|---|---|---|---|
| 0 | 200 | 0 | 0 | 0 |
| 110 | 198 | 0.26 | 0.30 | 13 |
| 210 | 196 | 0.53 | 0.51 | 4 |
| 360 | 194 | 0.79 | 0.82 | 4 |
| 500 | 192 | 1.05 | 1.11 | 5 |
| 670 | 190 | 1.32 | 1.46 | 10 |
| 820 | 188 | 1.58 | 1.77 | 11 |
| 980 | 186 | 1.84 | 2.10 | 12 |
| 1150 | 184 | 2.10 | 2.45 | 14 |
| 1300 | 182 | 2.37 | 2.77 | 14 |
| 1450 | 180 | 2.63 | 3.07 | 14 |
| 1600 | 178 | 2.89 | 3.40 | 15 |

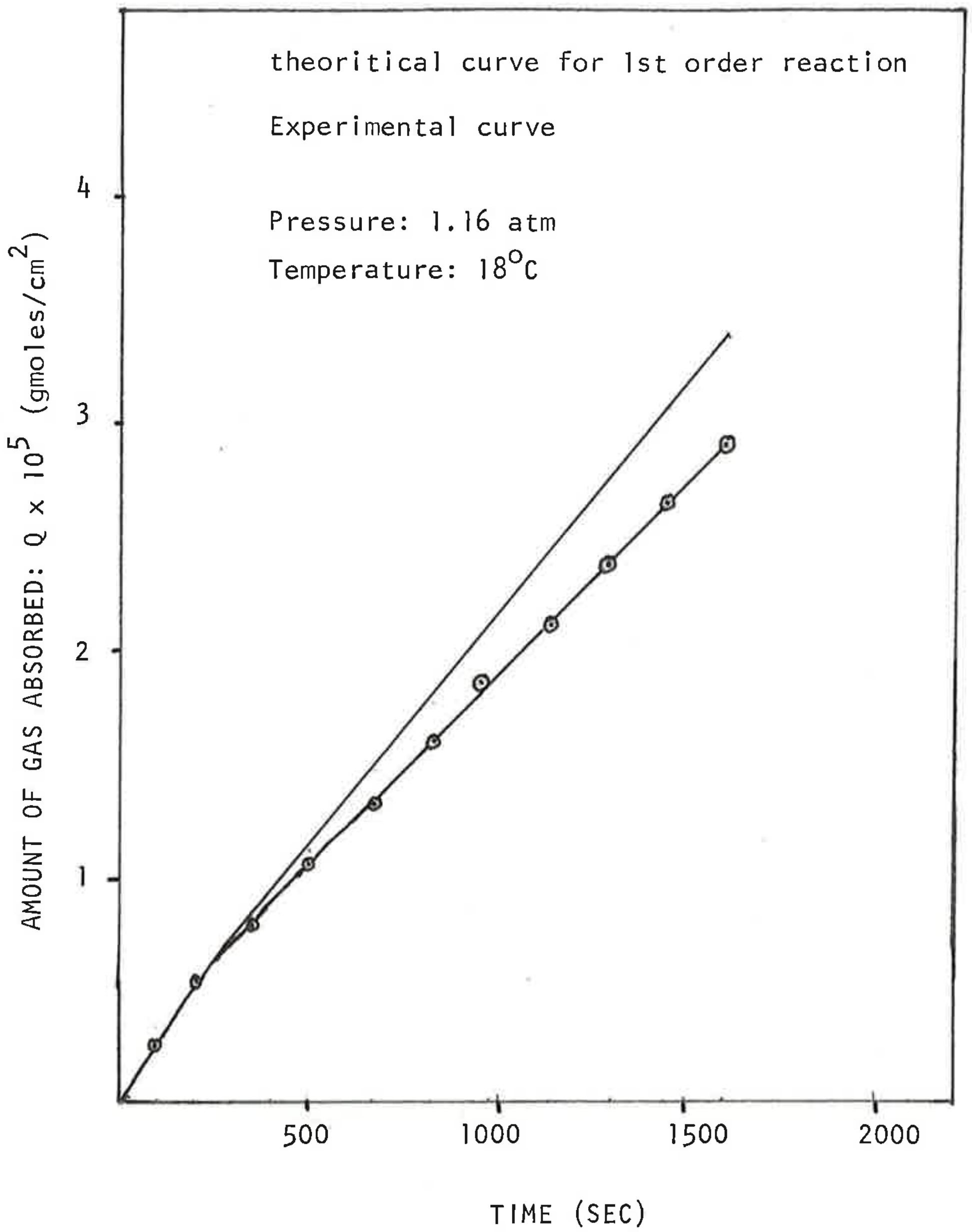

Figure 5: Carbon dioxide water system

# EXPERIMENTAL RESULTS

The experimental results are divided in three different sections:

- *Absorption of carbon dioxide into amine solutions
- *Absorption of hydrogen sulfide into amine solutions
- *Absorption of the mixture $CO_2/H_2S$ into amine solutions

## Absorption of carbon dioxide into amine solutions:

The hindered amine 2-amino-2-methyl-1-propanol (AMP) was first used at 0.1M and 0.05M for different partial pressures of carbon dioxide varying from 0.75 psia to 23.7. Then pure carbon dioxide at atmospheric pressure was absorbed into the hindered amine solutions at different concentrations (0.03M to 0.3M). The results are represented in tables 2-11.

The same experiments were done for the common monoethanolamine solution (MEA), the results are represented in tables 12-20.

## Absorption of hydrogen sulfide into amine solutions:

Pure hydrogen sulfide at atmospheric pressure was first absorbed into pure water and then at different concentrations of hindered amine (Tables 21-24), then the parital pressure of hydrogen sulfide was changed from 0.75 psia to 14.7 psia and absorbed into 0.1M of hindered amine solution (tables 25 and 26). The last part of this section is the absorption of pure hydrogen sulfide at atmospheric pressure into monoethanolamine solutions at different concentrations varying from 0.05M to 0.3M. The results are found in tables 27-29.

## Absorption of the mixture $CO_2/H_2S$ into amine solutions:

The mixture of 5% $CO_2$, 5% $H_2S$ and 90% $N_2$ (Nitrogene) was absorbed at 15 psig into the two classes of amines at the same concentration of 0.1M. The results are represented in tables 30-31. Then a mixture of 50% $CO_2$; 50% $H_2S$ was asborbed at 15 psig into the same amine solutions. The results are in tables 32-33.

# TABLES AND EXPERIMENTAL CURVES

Table 2: Experimental results of pure carbon dioxide absorbed into 0.1M hindered amine (AMP) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1070 | 9 | 5.34 |
| 180 | 14 | 0.89 | 1230 | 8 | 6.23 |
| 360 | 13 | 1.78 | 1410 | 7 | 7.12 |
| 510 | 12 | 2.67 | 1560 | 6 | 8.02 |
| 710 | 11 | 3.56 | 1770 | 5 | 8.92 |
| 900 | 10 | 4.45 | | | |

Table 3: Experimental results of carbon dioxide absorbed into 0.1M hindered amine (AMP) solution at 24°C and 1 atm (50% $CO_2$, 50% $N_2$)

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1210 | 11 | 3.56 |
| 330 | 14 | 0.89 | 1460 | 10 | 4.45 |
| 610 | 13 | 1.78 | 1740 | 9 | 5.34 |
| 930 | 12 | 2.67 | | | |

Table 4 Experimental results of carbon dioxide absorbed into 0.1M hindered amine (AMP) solution at 24°C and 1 atm (5% $CO_2$; 95% $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 3900 | 14 | 0.89 |
| 1200 | 14.5 | 0.44 | | | |

Table 5 Experimental results of pure carbon-dioxide absorbed into 0.05M hindered amine (AMP) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 845 | 11 | 3.56 |
| 200 | 14 | 0.89 | 1075 | 10 | 4.45 |
| 420 | 13 | 1.78 | 1315 | 9 | 5.34 |
| 600 | 12 | 2.67 | 1550 | 8 | 6.23 |

Table 6: Experimental results of carbon dioxide absorbed into 0.05M hindered amine (AMP) solution at 24°C and 1 atm (50% $CO_2$; 50% $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1300 | 12 | 2.67 |
| 390 | 14 | 0.89 | 1700 | 11 | 3.56 |
| 870 | 13 | 1.78 | | | |

Table 7: Experimental results of carbon dioxide absorbed into 0.05M hindered amine (AMP) solution at 24°C and 1 atm (5% $CO_2$, 95% $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 2200 | 1415 | 0.44 |

Table 8: Experimental results of pure carbon dioxide absorbed into 0.05M hindered amine (AMP) solution at 24°C and 2 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 625 | 13 | 4.75 |
| 275 | 14 | 2.37 | 980 | 12 | 7.13 |

Table 9: Experimental results of pure carbon dioxide absorbed into 0.3M hindered amine (AMP) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 800 | 7 | 7.12 |
| 90 | 14 | 0.89 | 900 | 6 | 8.02 |
| 170 | 13 | 1.78 | 1000 | 5 | 8.92 |
| 280 | 12 | 2.67 | 1080 | 4 | 9.80 |
| 380 | 11 | 3.56 | 1180 | 3 | 10.70 |
| 490 | 10 | 4.45 | 1290 | 2 | 11.60 |
| 600 | 9 | 5.34 | 1400 | 1 | 12.40 |
| 690 | 8 | 6.23 | 1480 | 0 | 13.31 |

Table 10: Experimental results of pure carbon dioxide absorbed into 0.2M hindered amine (AMP) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 775 | 8 | 6.23 |
| 90 | 14 | 0.89 | 885 | 7 | 7.12 |
| 180 | 13 | 1.78 | 1000 | 6 | 8.02 |
| 300 | 12 | 2.67 | 1130 | 5 | 8.92 |
| 420 | 11 | 3.56 | 1250 | 4 | 9.63 |
| 545 | 10 | 4.45 | 1370 | 3 | 10.50 |
| 660 | 9 | 5.34 | 1490 | 2 | 11.40 |
|  |  |  | 1610 | 1 | 12.50 |

Table 11: Experimental results of pure carbon dioxide absorbed into 0.03M hindered amine (AMP) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1220 | 11 | 3.56 |
| 230 | 14 | 0.89 | 1510 | 10 | 4.45 |
| 540 | 13 | 1.78 | 1840 | 9 | 5.34 |
| 870 | 12 | 2.67 | | | |

Table 12: Experimental results of pure carbon dioxide absorbed into 0.1M Monoethanolamine (MEA) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 920 | 10 | 4.45 |
| 180 | 14 | 0.89 | 1090 | 9 | 5.34 |
| 360 | 13 | 1.78 | 1280 | 8 | 6.23 |
| 550 | 12 | 2.67 | 1480 | 7 | 7.12 |
| 730 | 11 | 3.56 | 1720 | 6 | 8.02 |

Table 13: Experimental results of carbon dixoide absorbed into 0.1M Monoethanolamine (MEA) solution at 25°C and 1 atm (50% $CO_2$, 50% $N_2$)

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 790 | 12 | 2.67 |
| 240 | 14 | 0.89 | 1140 | 11 | 3.56 |
| 480 | 13 | 1.78 | 1480 | 10 | 4.45 |

Table 14: Experimental results of carbon dioxide absorbed into 0.1M Monoethanolamine (MEA) solution at 25°C and 1 atm (5% $CO_2$, 95% $N_2$)

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1030 | 13 | 1.78 |
| 510 | 14 | 0.89 | 1610 | 12 | 2.67 |

Table 15: Experimental results of pure carbon dioxide absorbed into 0.05M Monoethanolamine (MEA) solution at 24.5°C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1070 | 11 | 3.56 |
| 270 | 14 | 0.89 | 1340 | 10 | 4.45 |
| 550 | 13 | 1.78 | 1650 | 9 | 5.34 |
| 800 | 12 | 2.67 | | | |

Table 16: Experimental results of pure carbon dioxide absorbed into 0.05M Monoethanolamine (MEA) solution at 24°C and 2 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 600 | 13 | 4.75 |
| 275 | 14 | 2.37 | 965 | 12 | 7.13 |

Table 17: Experimental results of carbon dioxide absorbed into 0.05M Monoethanolamine (MEA) solution at 25°C and 1 atm (5% $CO_2$, 95% $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1200 | 14 | 0.89 |
| 600 | 14 | 0.44 | 1800 | 13.5 | 1.30 |

Table 18: Experimental results of pure carbon dioxide absorbed into 0.2M Monoethanolamine (MEA) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 950 | 7 | 7.12 |
| 110 | 14 | 0.89 | 1070 | 6 | 8.02 |
| 230 | 13 | 1.78 | 1190 | 5 | 8.92 |
| 350 | 12 | 2.67 | 1310 | 4 | 9.80 |
| 470 | 11 | 3.56 | 1430 | 3 | 10.70 |
| 590 | 10 | 4.45 | 1550 | 2 | 11.60 |
| 710 | 9 | 5.34 | 1670 | 1 | 12.40 |
| 830 | 8 | 6.23 | 1790 | 0 | 13.31 |

Table 19: Experimental results of pure carbon dioxide absorbed into 0.3M Monoethanolamine (MEA) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 620 | 7 | 7.12 |
| 70 | 14 | 0.89 | 720 | 6 | 8.02 |
| 130 | 13 | 1.78 | 810 | 5 | 8.92 |
| 200 | 12 | 2.67 | 880 | 4 | 9.80 |
| 290 | 11 | 3.56 | 960 | 3 | 10.70 |
| 380 | 10 | 4.45 | 1050 | 2 | 11.60 |
| 440 | 9 | 5.34 | 1140 | 1 | 12.40 |
| 530 | 8 | 6.23 | 1240 | 0 | 13.31 |

Table 20: Experimental results of pure carbon dixoide absorbed into 0.03M Monoethanolamine (MEA) solution at 24°C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1070 | 12 | 2.67 |
| 360 | 14 | 0.89 | 1440 | 11 | 3.56 |
| 700 | 13 | 1.78 | 1800 | 10 | 4.45 |

Table 21: Experimental results fo pure hydrogen sulfide absorbed into water at 27°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 595 | 12 | 2.61 |
| 150 | 14 | 0.87 | 1394 | 11 | 3.47 |
| 255 | 13 | 1.74 | | | |

Table 22: Experimental results of pure hydrogen sulfide absorbed into 0.05M hindered amine (AMP) solution at 27°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 850 | 7 | 6.95 |
| 100 | 14 | 0.87 | 995 | 6 | 7.82 |
| 160 | 13 | 1.74 | 1135 | 5 | 8.69 |
| 255 | 12 | 2.61 | 1285 | 4 | 9.55 |
| 360 | 11 | 3.47 | 1395 | 3 | 10.42 |
| 475 | 10 | 4.34 | 1600 | 2 | 11.36 |
| 595 | 9 | 5.21 | 1800 | 1 | 12.16 |
| 710 | 8 | 6.08 | | | |

Table 23: Experimental results of pure hydrogen sulfide absorbed into 0.1M hindered amine (AMP) solution at 27$^{o}$C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 555 | 8 | 6.08 |
| 65 | 14 | 0.87 | 635 | 7 | 6.95 |
| 140 | 13 | 1.74 | 720 | 6 | 7.82 |
| 220 | 12 | 2.61 | 825 | 5 | 8.69 |
| 305 | 11 | 3.47 | 940 | 4 | 9.55 |
| 385 | 10 | 4.34 | 1045 | 3 | 10.42 |
| 465 | 9 | 5.21 | 1145 | 2 | 11.30 |

Table 24: Experimental results of pure hydrogen sulfide absorbed into 0.3M hindered amine (AMP) solution at 27$^{o}$C and 1 atm

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 215 | 9 | 5.21 |
| 25 | 14 | 0.87 | 255 | 8 | 6.08 |
| 60 | 13 | 1.74 | 295 | 7 | 6.95 |
| 95 | 12 | 2.61 | 340 | 6 | 7.82 |
| 135 | 11 | 3.47 | 385 | 5 | 8.69 |
| 170 | 10 | 4.34 | 430 | 4 | 9.55 |
|  |  |  | 475 | 3 | 10.42 |
|  |  |  | 525 | 2 | 11.30 |

Table 25: Experimental results of hydrogen sulfide absorbed into 0.1M hindered amine (AMP) solution at 27°C and 1 atm ($50\%$ $H_2S$; $50\%$ $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 765 | 9 | 5.21 |
| 75 | 14 | 0.87 | 925 | 8 | 6.08 |
| 200 | 13 | 1.74 | 1085 | 7 | 6.95 |
| 340 | 12 | 2.61 | 1250 | 6 | 7.82 |
| 465 | 11 | 3.47 | 1440 | 5 | 8.69 |
| 615 | 10 | 4.34 | 1625 | 4 | 9.55 |
| | | | 1815 | 3 | 10.44 |

Table 26: Experimental results of hydrogen sulfide absorbed into 0.1M hindered amine (AMP) solution at 27°C and 1 atm ($5\%$ $H_2S$, $95\%$ $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 1110 | 12 | 2.61 |
| 290 | 14 | 0.87 | 1555 | 11 | 3.47 |
| 680 | 13 | 1.74 | | | |

Table 27: Experimental results of pure hydrogen sulfide absorbed into 0.3M Monoethanolamine (MEA) solution at 27$^oC$ and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 210 | 8 | 6.08 |
| 20 | 14 | 0.87 | 245 | 7 | 6.95 |
| 50 | 13 | 1.74 | 285 | 6 | 7.82 |
| 80 | 12 | 2.61 | 310 | 5 | 8.69 |
| 110 | 11 | 3.47 | 345 | 4 | 9.55 |
| 1140 | 10 | 4.34 | 380 | 3 | 10.42 |
| 170 | 9 | 5.21 | 420 | 2 | 11.30 |

Table 28: Experimental results of pure hydrogen sulfide absorbed into 0.1M Monoethanolamine (MEA) solution at 27$^oC$ and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 450 | 8 | 6.08 |
| 35 | 14 | 0.87 | 525 | 7 | 6.95 |
| 95 | 13 | 1.74 | 610 | 6 | 7.82 |
| 160 | 12 | 2.61 | 685 | 5 | 8.69 |
| 235 | 11 | 3.47 | 765 | 4 | 9.55 |
| 300 | 10 | 4.34 | 850 | 3 | 10.42 |
| 370 | 9 | 5.21 | 940 | 2 | 11.30 |
|  |  |  | 1015 | 1 | 12.16 |

Table 29: Experimental results of pure hydrogen sulfide absorbed into 0.05M Monoethanolamine (MEA) solution at 27°C and 1 atm

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 15 | 0 | 720 | 8 | 6.08 |
| 55 | 14 | 0.87 | 845 | 7 | 6.95 |
|  | 13 | 1.74 | 960 | 6 | 7.82 |
| 265 | 12 | 2.61 | 1085 | 5 | 8.69 |
| 370 | 11 | 3.47 | 1215 | 4 | 9.55 |
| 485 | 10 | 4.34 | 1325 | 3 | 10.42 |
| 605 | 9 | 5.21 | 1445 | 2 | 11.30 |
|  |  |  | 1565 | 1 | 12.16 |

Table 30: Experimental results of the mixture of carbon dioxide and hydrogen sulfide absorbed into 0.1M hindered amine (AMP) solution at 27°C and 1 atm (5% $CO_2$, 5% $H_2S$, 90% $N_2$)

| time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ | time (sec) | Pressure (psig) | $Q \times 10^5$ gmoles/cm$^2$ |
|---|---|---|---|---|---|
| 0 | 1 | 0 | 1180 | -1 | 2.20 |
| 620 | 0 | 1.24 | - | - | - |

Table 31: Experimental results of the mixture of carbon dioxide and hydrogen sulfide absorbed into 0.1M MEA solution at 27°C and 1 atm

| time (sec) | Pressure (spig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 1 | 0 | 10000 | -1 | 2.20 |
| 530 | 0 | 1.24 | | | |

Table 32: Experimental results of the mixture carbon dioxide and hydrogen sulfide absorbed into 0.1M hindered amine (AMP) solution at 27°C and 1 atm (50% $CO_2$, 50% $H_2S$)

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 3 | 0 | 660 | 0 | 7 |
| 190 | 2 | 2.35 | | | |
| 420 | 1 | 5.10 | 1180 | -1 | 10.5 |

Table 33: Experimental results of the mixture carbon dioxide and hydrogen sulfide absorbed into 0.1M hindered amine (AMP) solution at 27°C and 1 atm (50% $CO_2$ , 50% $H_2S$)

| time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ | time (sec) | Pressure (psig) | Q x $10^5$ gmoles/$cm^2$ |
|---|---|---|---|---|---|
| 0 | 3 | 0 | 760 | 0 | 7 |
| 240 | 2 | 2.35 | | | |
| 500 | 1 | 5.10 | 1300 | -1 | 10.5 |

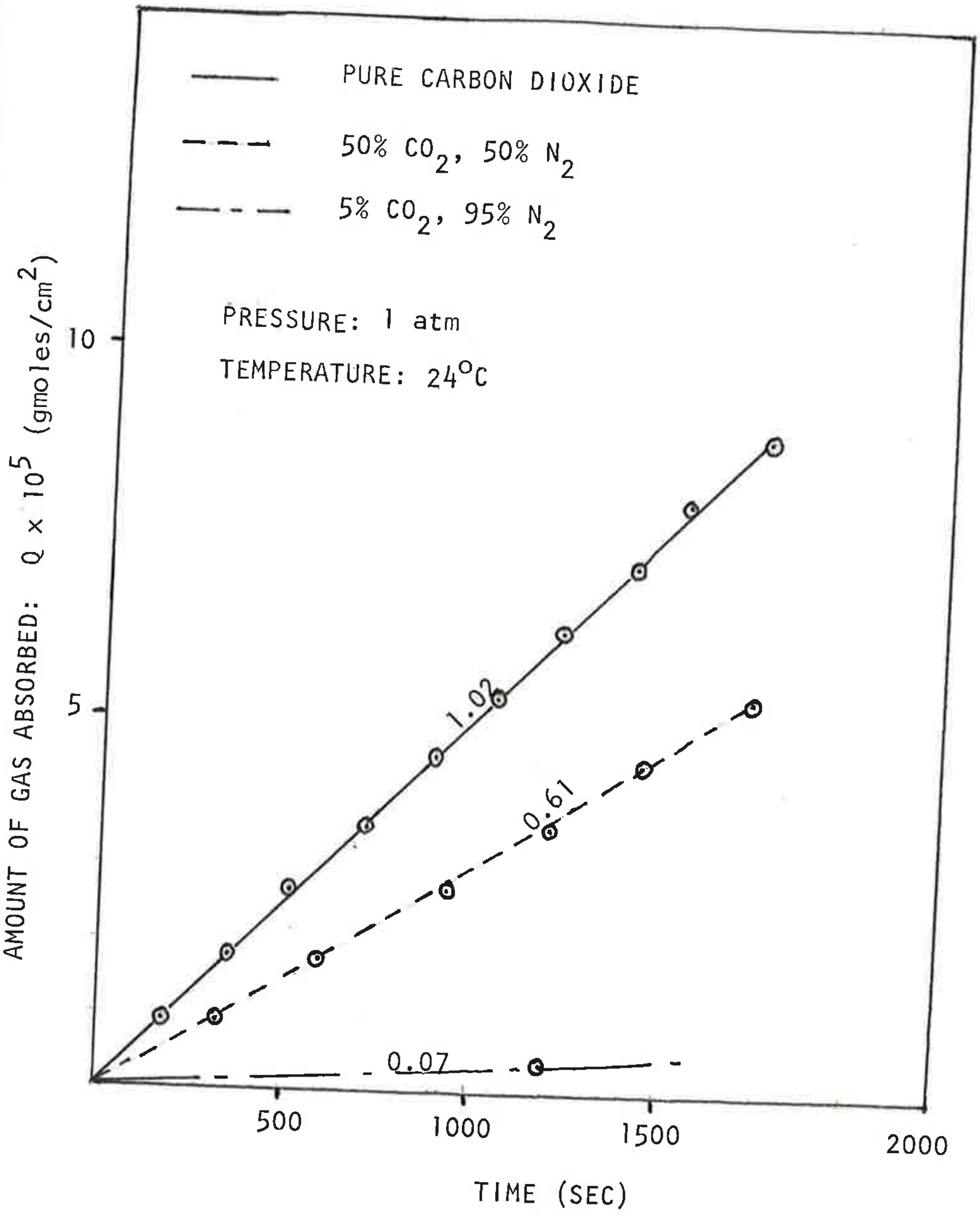

Figure 6: Absorption of carbon dioxide at different parital pressure into 0.1M hindered amine solution

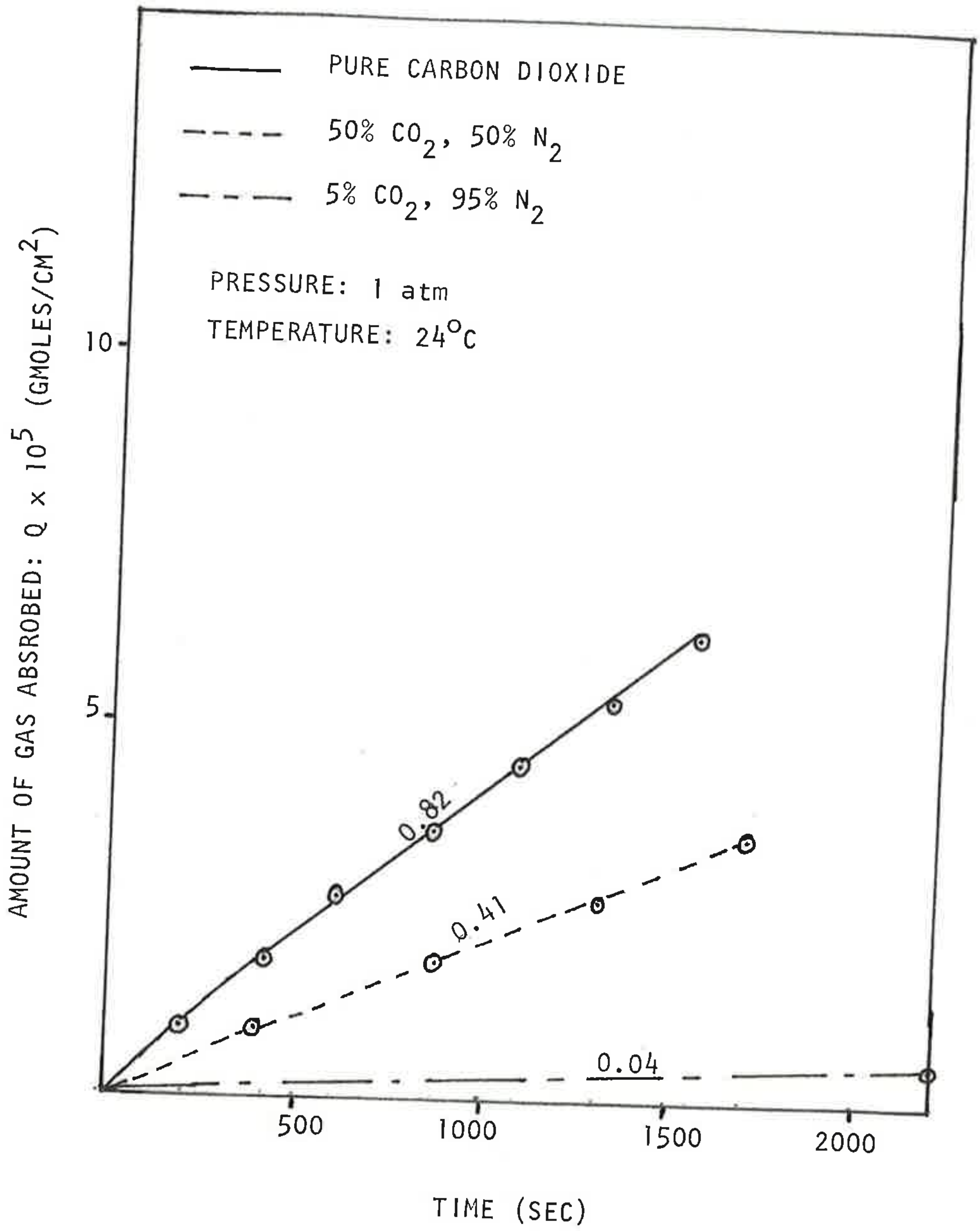

Figure 7: Absorption of carbon dioxide at different parital pressures into 0.05M hindered amine solution

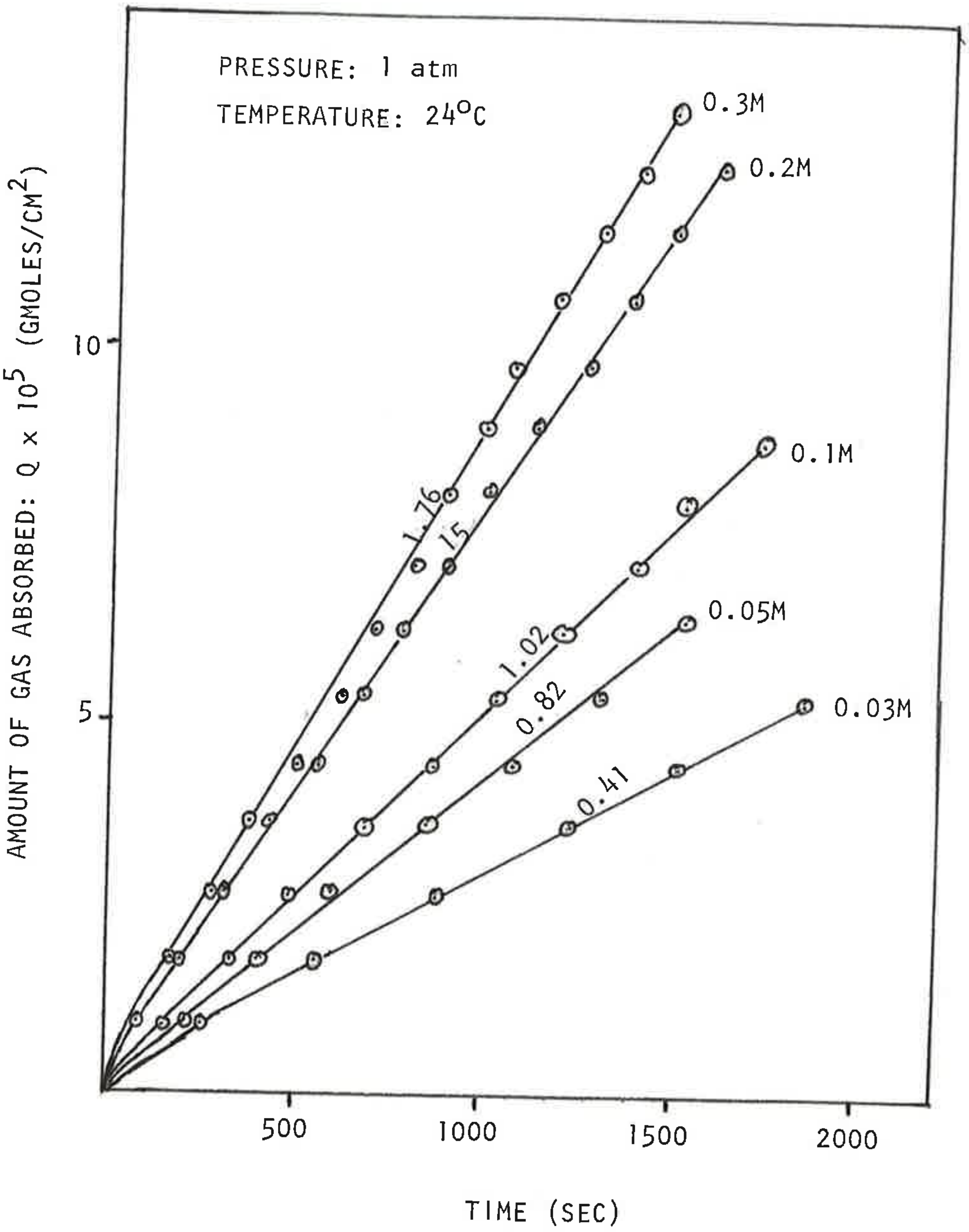

Figure 8: Absorption of pure carbon dioxide into hindered amine solutions at different concentrations

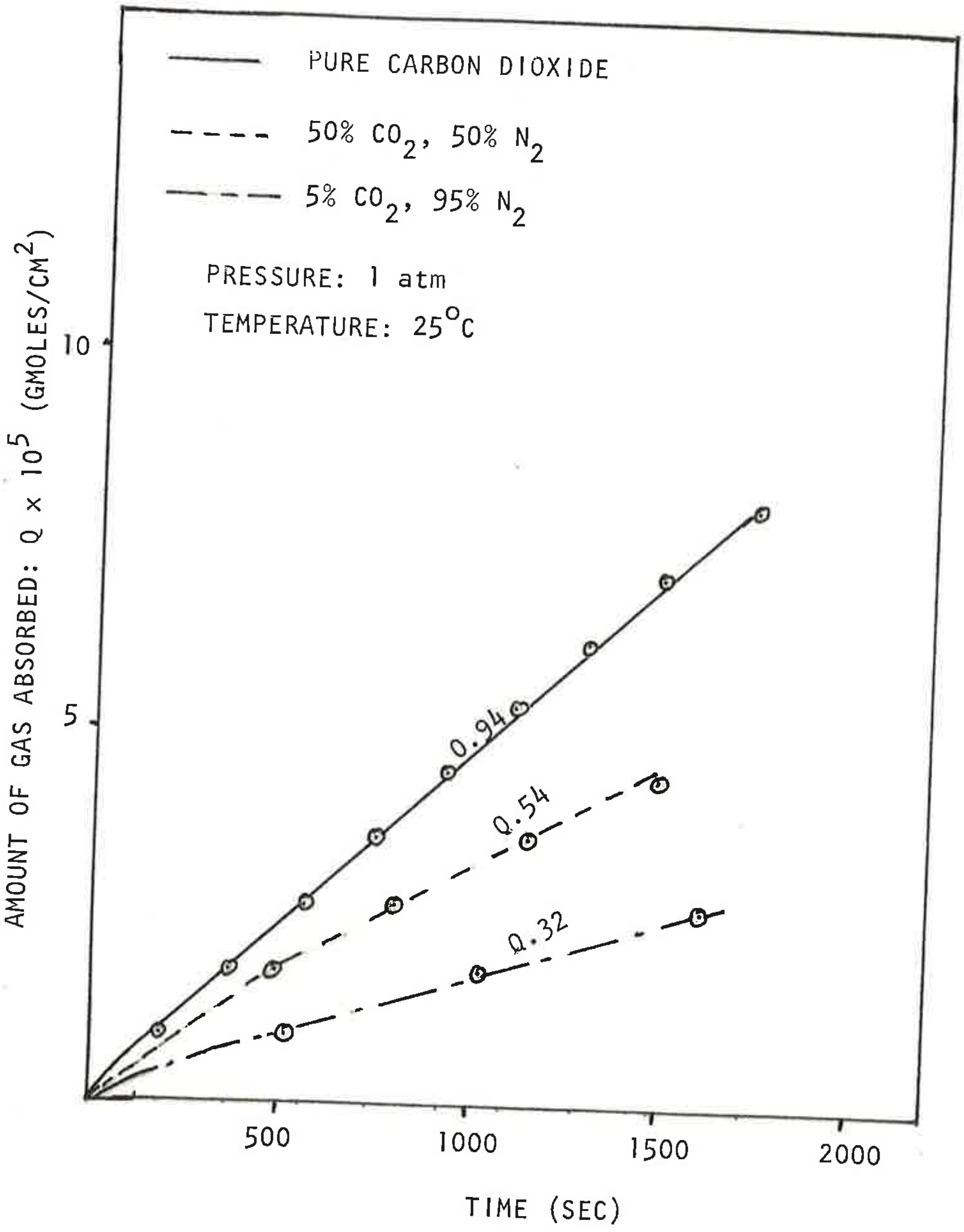

Figure 9: Absorption of carbon dioxide at different partial pressures into 0.1M MEA solution

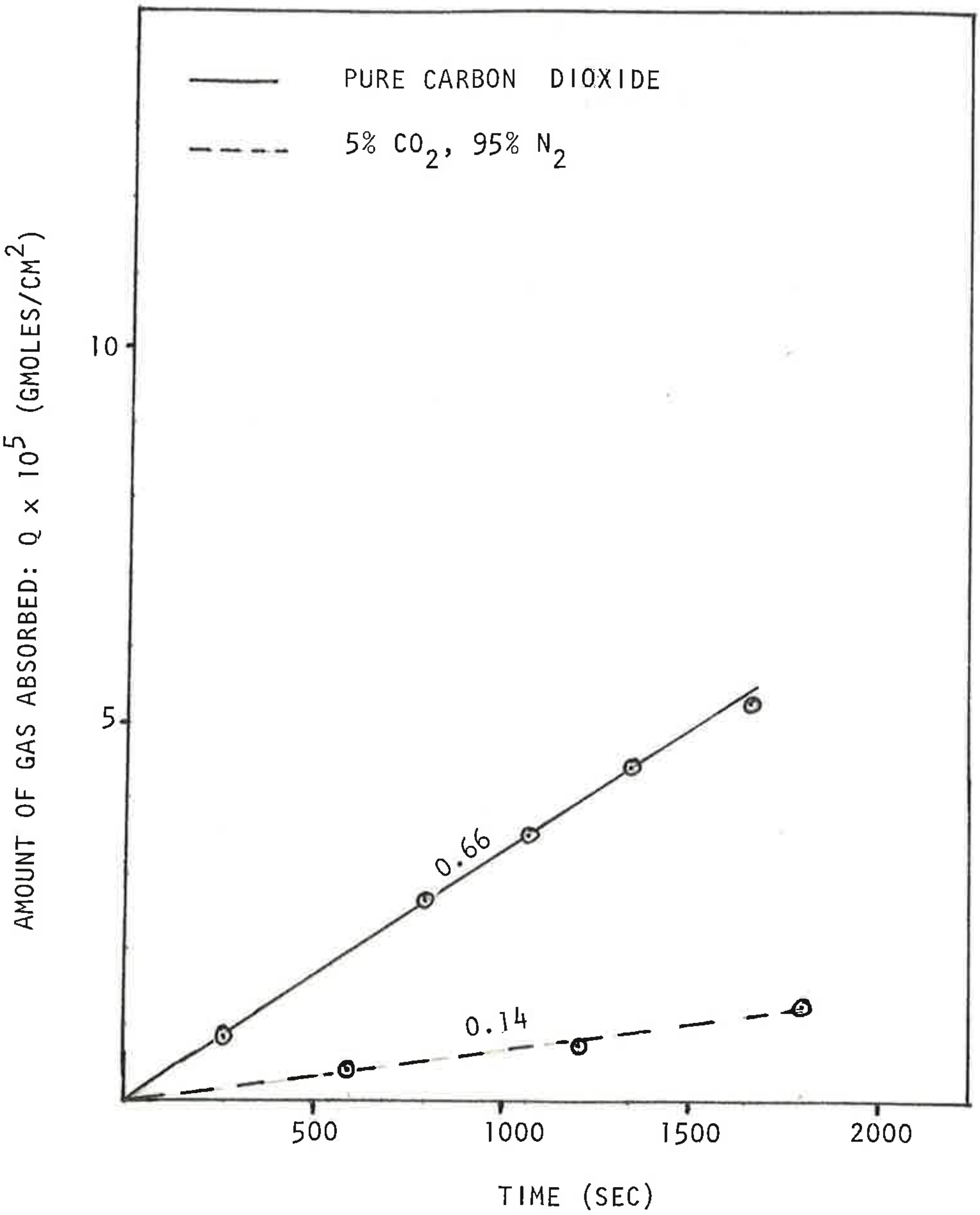

Figure 10: Absorption of carbon dioxide at different partial pressures into 0.05M MEA solution

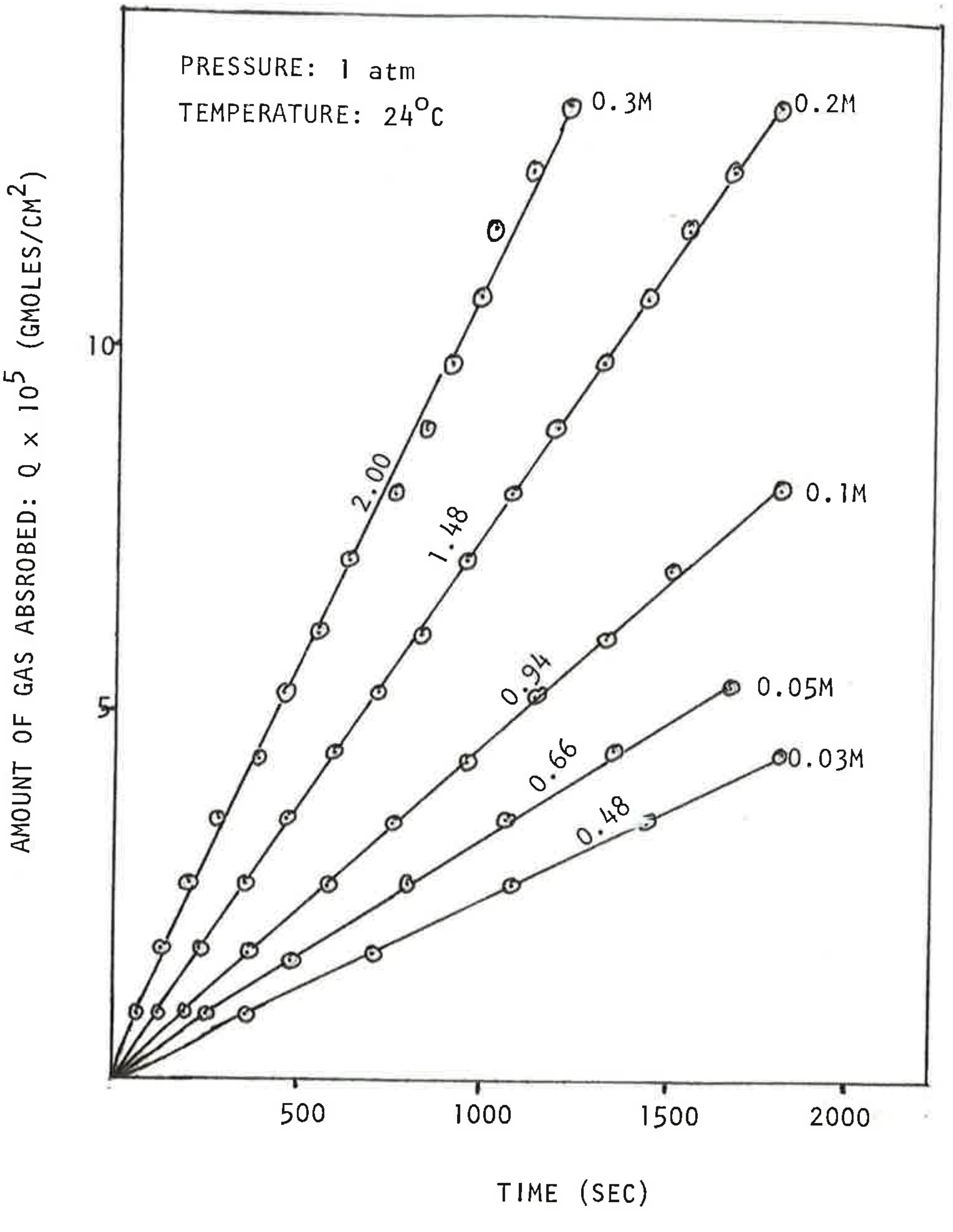

Figure 11: Absorption of pure carbon dioxide into MEA solutions at different concentrations

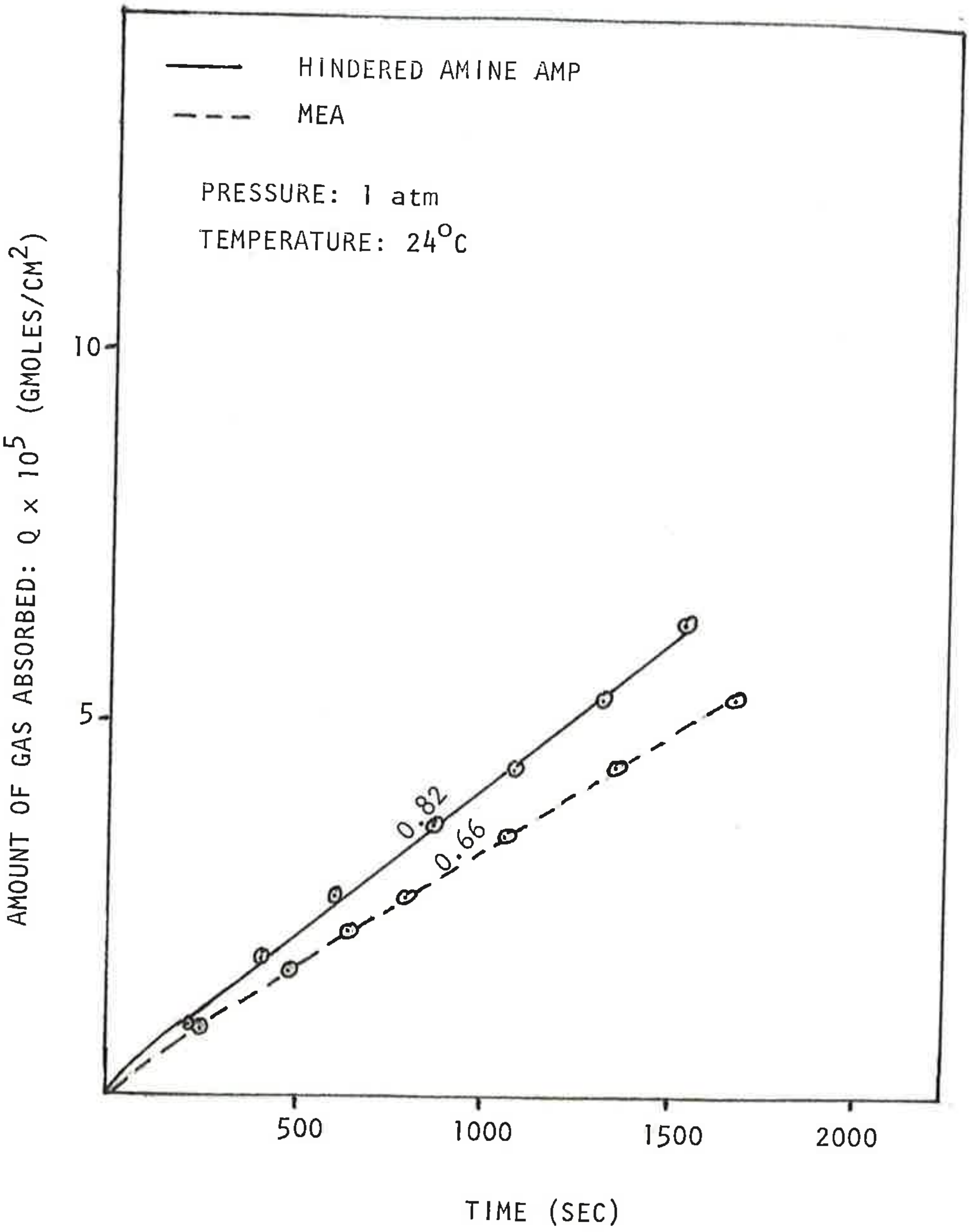

Figure 12: Absorption of pure carbon dioxide into the two different classes of amines at 0.05M solutions

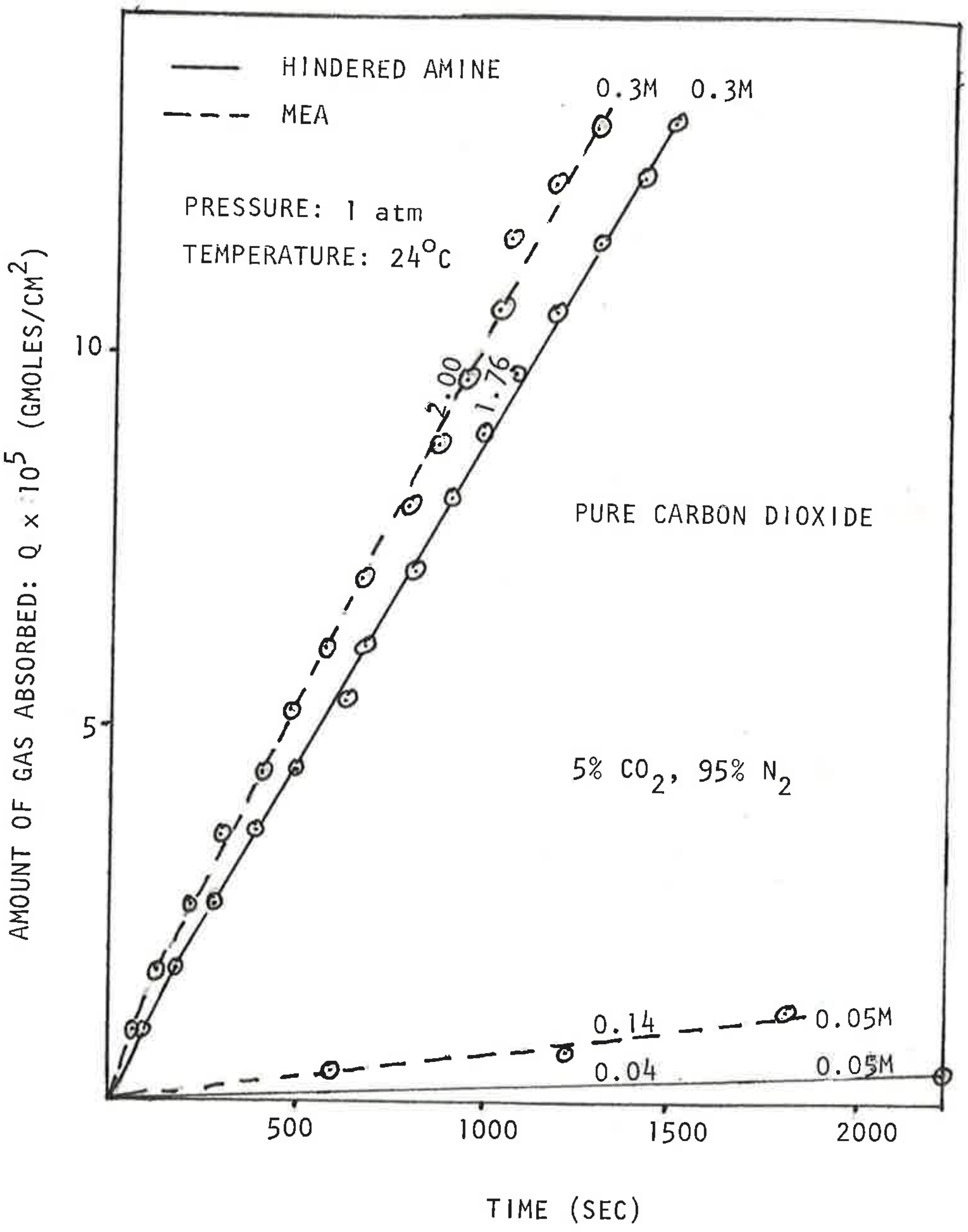

Figure 13: Effect of the decrease of the partial pressure of $CO_2$ and increase of the molarity of the solutions on the absorption

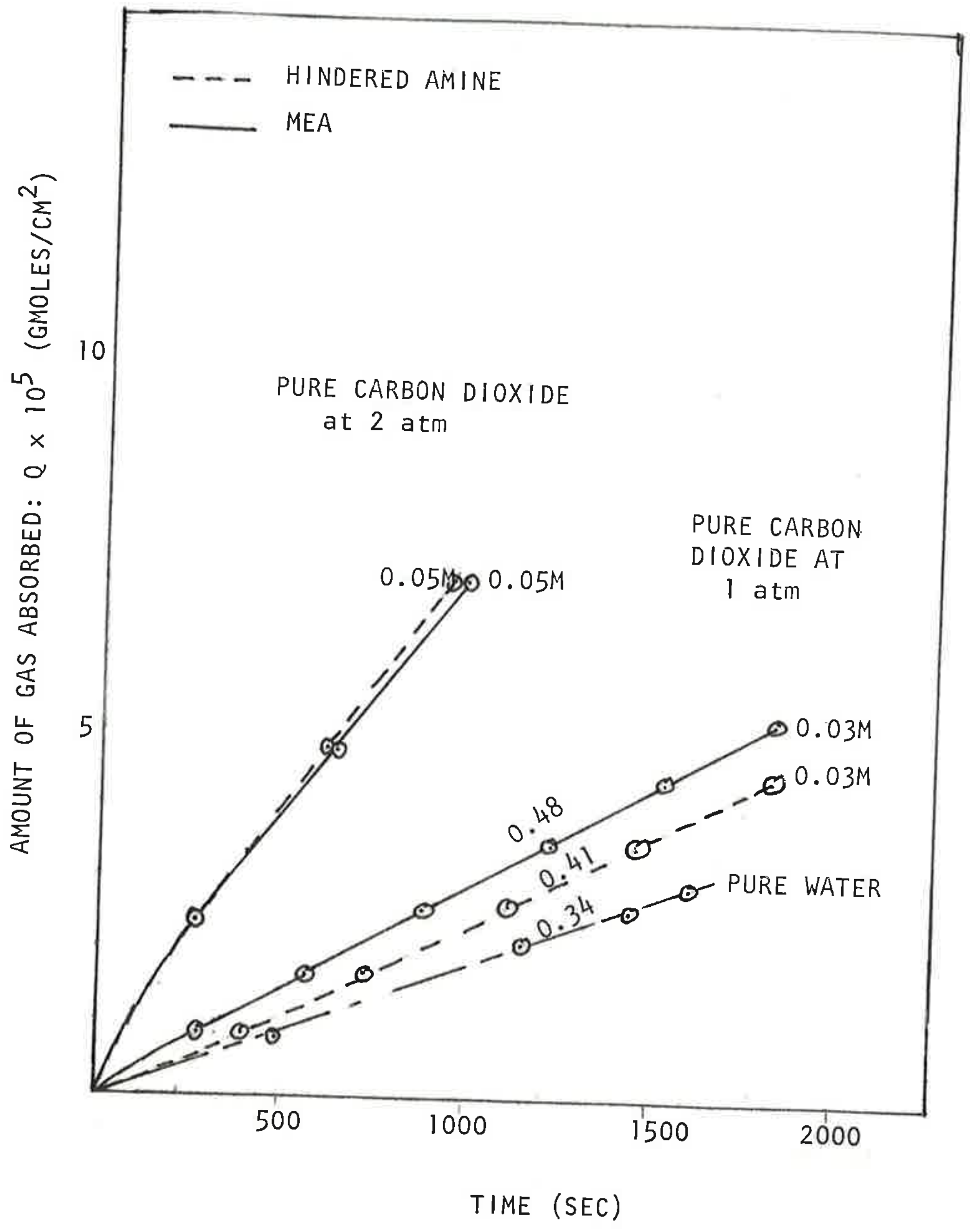

Figure 14: Effect of the decrease of the molarity of amines and increase of the $CO_2$ partial pressure on the absorption

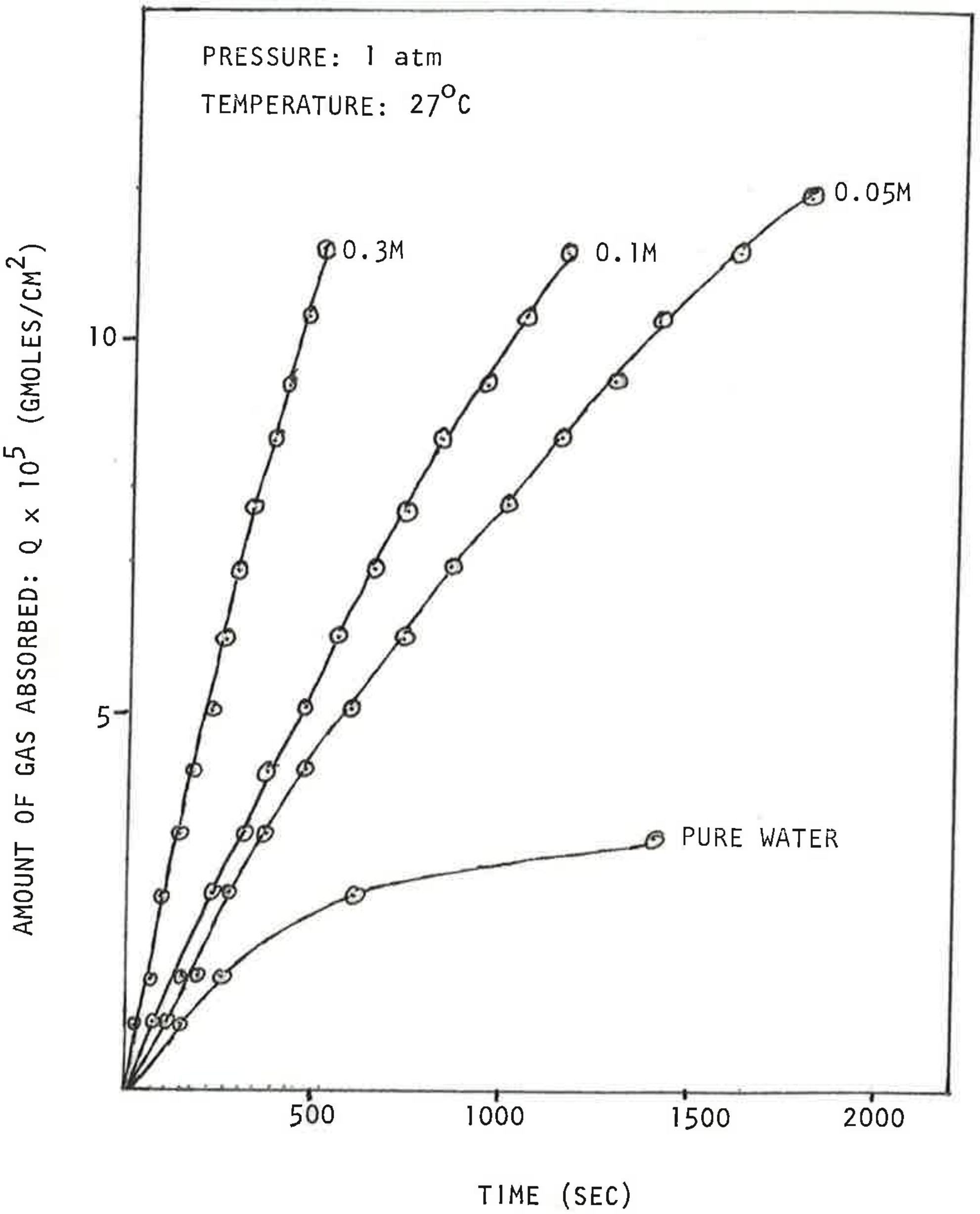

Figure 15: Absorption of pure hydrogen sulfide into hindered amine solutions at different concentrations

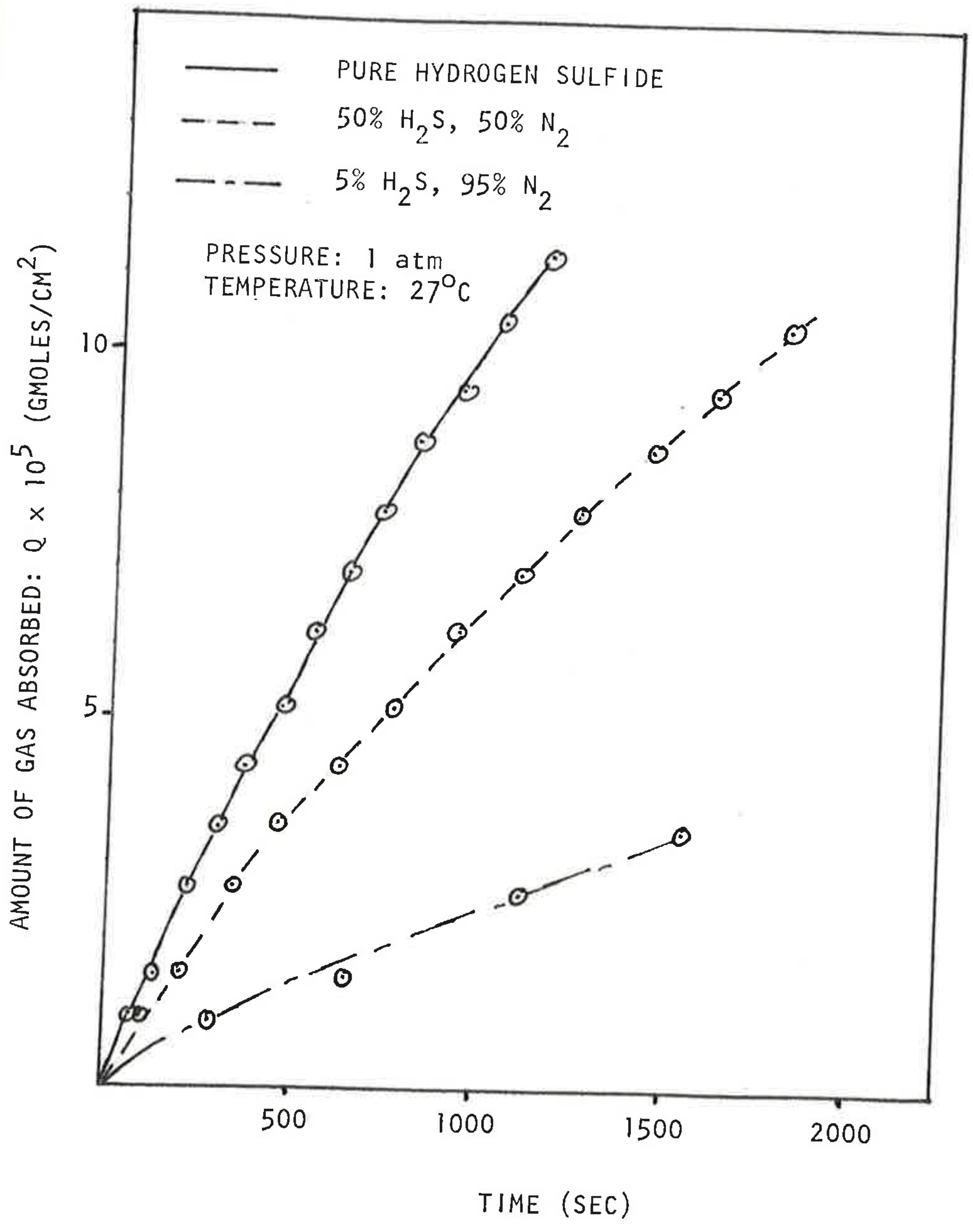

Figure 16: Absorption of hydrogen sulfide at different partial pressures into 0.1M hindered amine solution

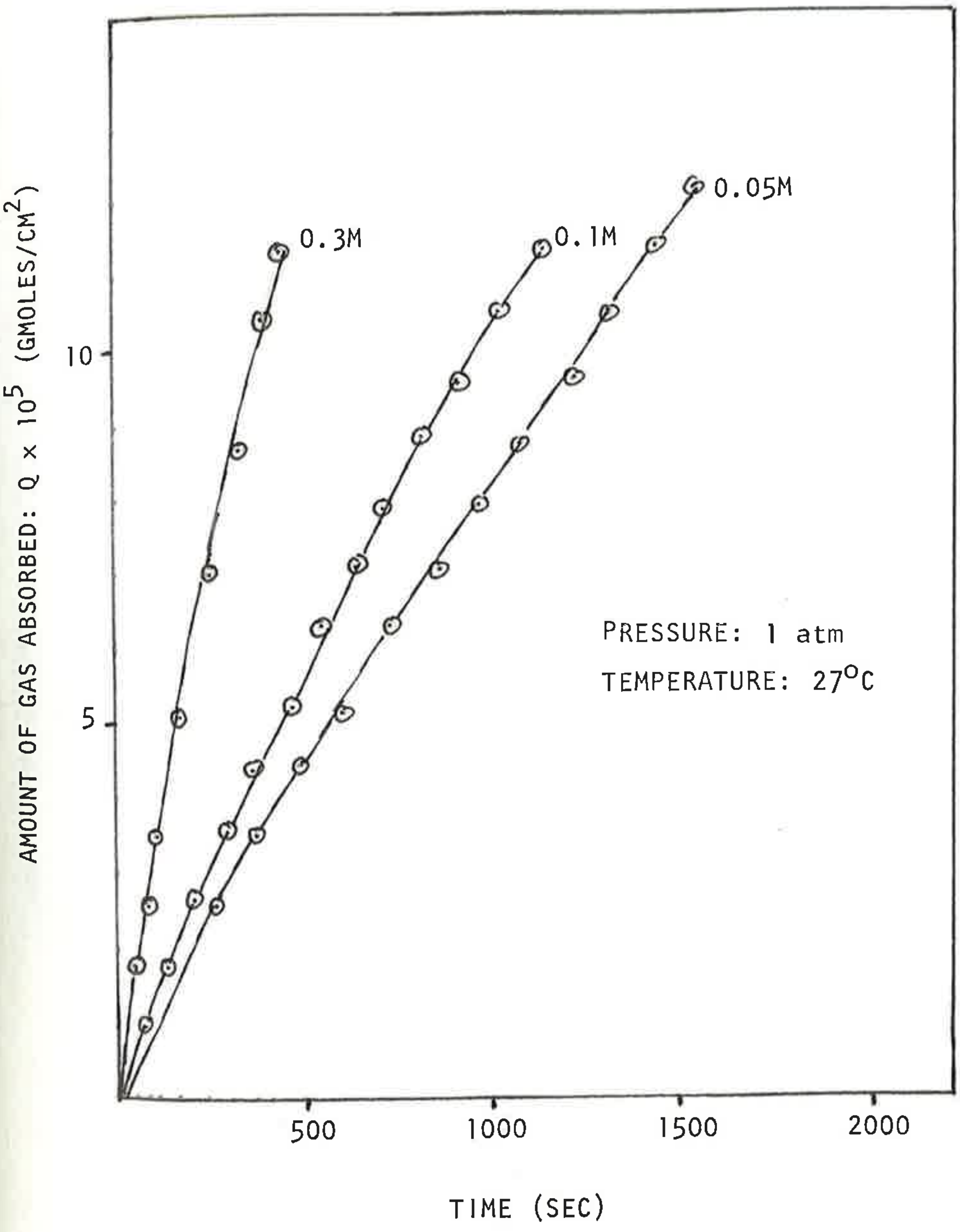

Figure 17: Absorption of pure hydrogen sulfide into MEA solutions at different concentrations

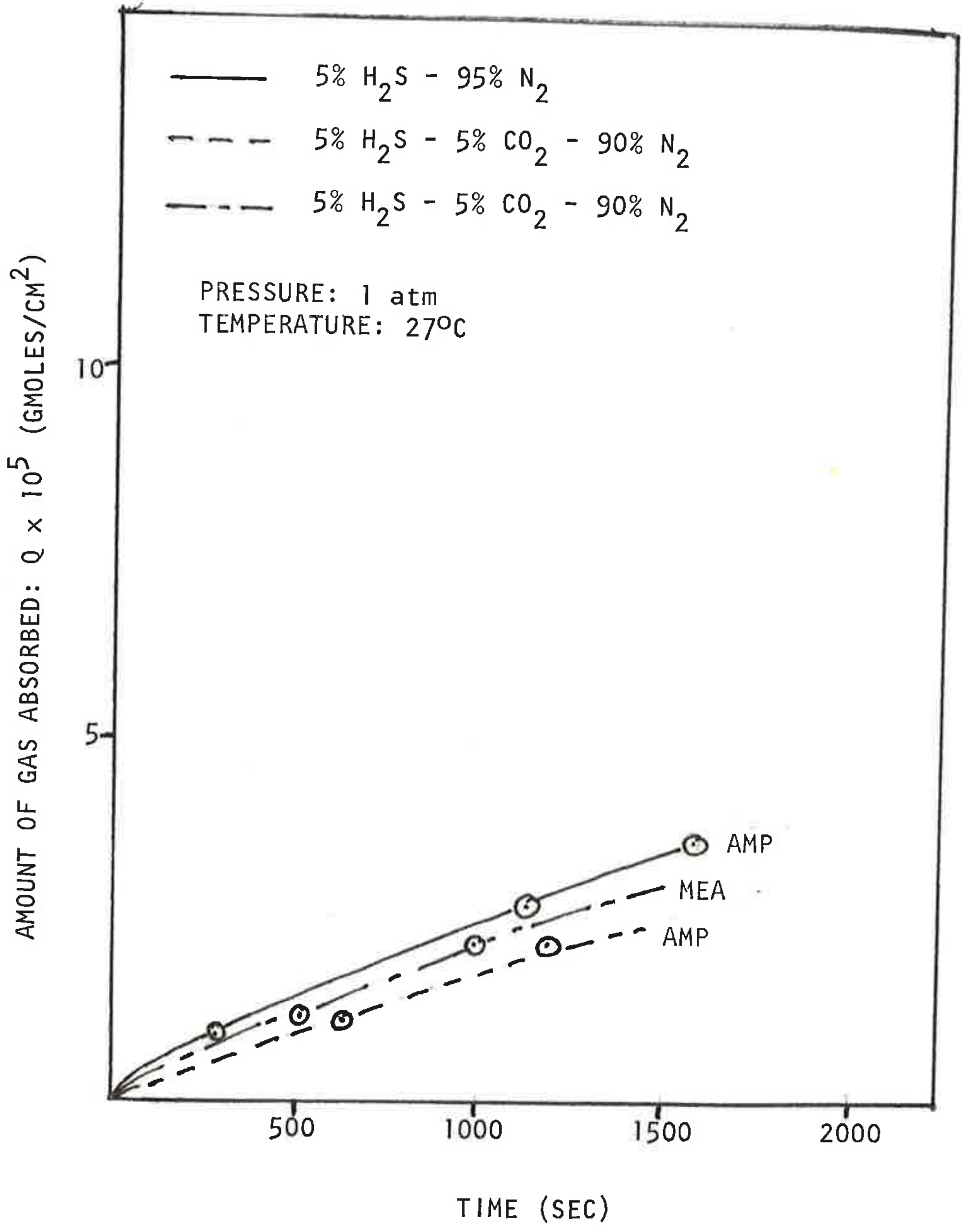

Figure 18: Comparison between the absorption of $H_2S$ alone and the mixture $CO_2/H_2S$ into 0.1M amine solutions

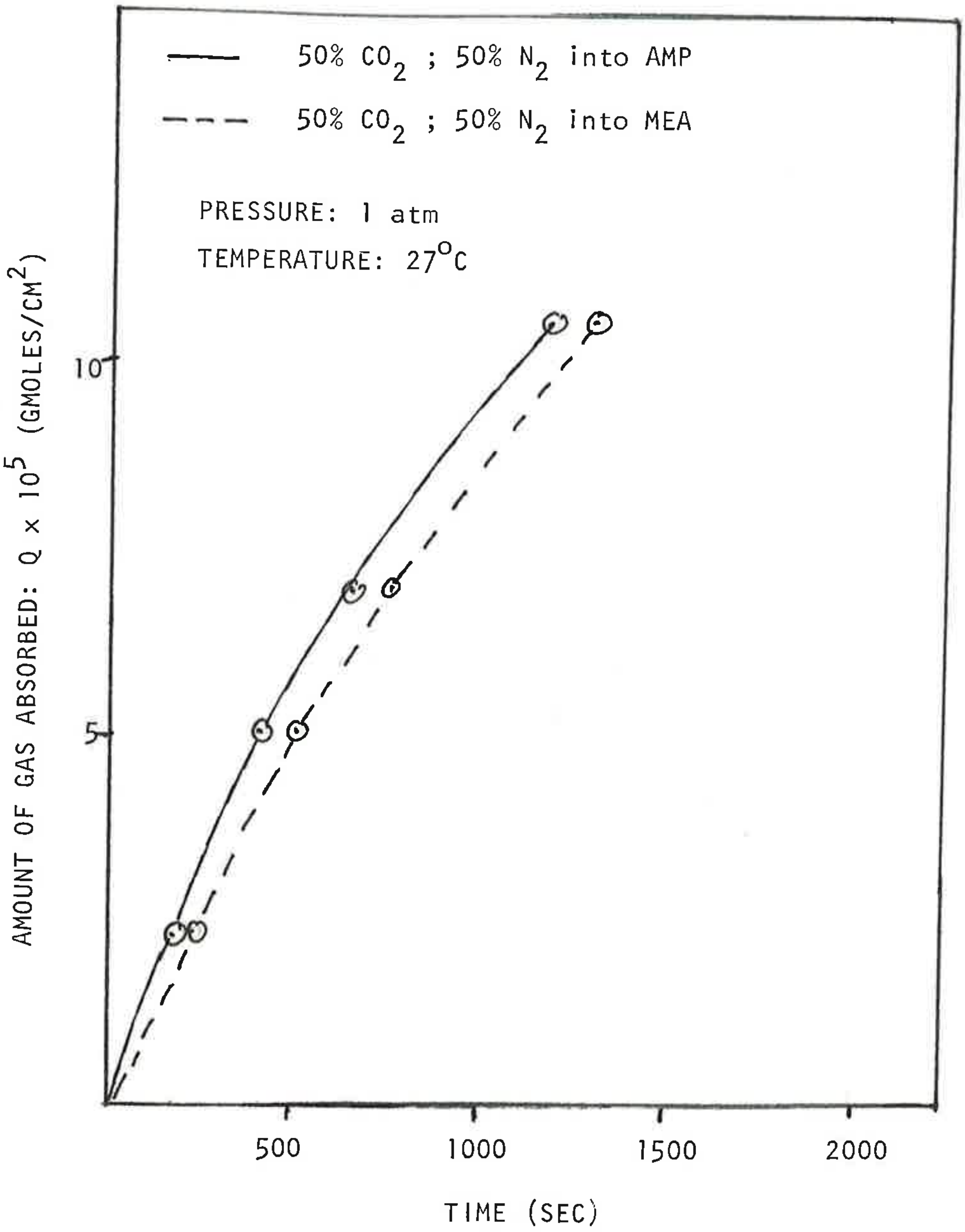

Figure 19: Comparison between the absorption of the mixture into the two classes of amine at 0.1M

# DISCUSSION

According to the mathematical model developed in Dauckwert's book [1], the absorption of a gas accompanied by a first order reaction into a liquid solution is proportional to the partial pressure of the gas prevailing over the surface and proportional to the exposure time when $k_1 t >> 1$. The slope of the curve representing the amount of a gas absorbed as function of exposure time is $A^* \sqrt{D_A k_1}$ and for a pseudo-first order reaction, the slope become $A^* \sqrt{D_A k_2 B^o}$ where the total amount of gas absorbed is proportional to the square root of the liquid reactant concentration $B^o$.

In our experiment, all curves representing the amount of carbon dioxide absorbed by amine solution were proportional to the exposure time at time $t > 200$ s. The proportionality between the amount of $CO_2$ absorbed, its partial pressure and the square root of the amine concentration was also found in the most cases, which means that we are dealing with a pseudo first order reaction between carbon dioxide and amine solutions.

However in some cases, the amount of carbon dioxide absorbed was not proportional to its partial pressure or to the square root of the amine concentration $B^o$. This can be explained by the fact that during the absorption of carbon dioxide into amine solutions, three chemical reactions take place and the importance of each one will depends on the value of $\theta$, [2]. The direct reaction (26) between $CO_2$ molecules and amine molecules is important only at low values of $\theta (\theta < 0.5)$. The carbamates formed in this reaction will affect the rate of absorption only when their concentration in the reaction zone is large, or when the value of $\theta$ is around 0.5. Since hindered amines give unstable carbamates which can react easily with water to regenerate amine, when $\theta$ is around 0.5, the "hindered effect" can increase the rate of absorption by increasing the amine concentration, this could explain our result for pure carbon dioxide at 1 atm absorbed into 0.05M amine. The hindered amine AMP absorbed 25% $CO_2$ more than MEA even that the velocity constant $k_2$ of MEA is higher than AMP velocity constant, (See figure 12).

The value of $\theta$ can be decreased by increasing the concentration of amine or decreasing the partial pressure of carbon dioxide. In this special case, the concentration of carbamates is too low that one can not observe the "hindered effect" and the amine with higher reaction velocity will absorb more carbon dioxide. These experiments were done. The concentration of amine was increased from 0.05M to 0.3M for pure carbon dioxide at 1 atm and in this situation MEA absorbed 14% more than the hindered amine AMP. The partial pressure of carbon dioxide were decreased to 0.75 psia for 0.05M amine solution and MEA absorbed 250% more than AMP. (See figure 13).

The reaction (26) has a lower role in the absorption of carbon dioxide into amine solutions at very large values of $\theta (\theta > 0.5)$, since in the reactions (41) and (21) the amine does not react directly with carbon dioxide, one can expect a small difference between the two classes of amine. To increase the value of $\theta$ in our experiment, the partial pressure of carbon dioxide was increased to 2 atm for 0.05M amine solution, the two classes of amine absorbed almost the same amount of $CO_2$ decreasing the concentration of amine at 0.03M for pure carnone dioxide at 2 atm will also increase the value of θ and MEA absorbed only 17% more than AMP. Some experiments were done at 0.01M amine solutions and the two classes of amine absorbed the same amount of $CO_2$ which was close to the absorption of carbon dioxide in pure water. (See figure 14).

All the curves found for hydrogen sulfide absorption into amine solutions were proportional to square root of time. Only a small difference of amount of hydrogen sulfide absorbed was found when the concentration fo amine was changed from 0.05M to 0.3M and almost no difference was observed between the two classes of amine at the same operating conditions. Figures 15-17. For 0.1M hindered amine solution, the amount of gas absorbed was proportional to the partial pressure only at high pressure, (figure 16). According to the equations (14) and (17), the reaction between the hydrogen sulfide and the two classes of amine is instanteneous as described before.

Some experiments were done for the mixture of carbon dioxide and hdyrogen sulfide into the two classes of amine. First a mixture of 5% $CO_2$, 5% $H_2S$ and 90% $N_2$ was absorbed into 0.1M amine solutions. For both amine, the amount total of gas absorbed was less than the amount of hydrogen sulfide absorbed from 5% $H_2S$, 95% $N_2$ at the same operating conditions. This could be the result of the competition between $CO_2$ and $H_2S$ during the reactions into the liquid phase. However MEA absorbed a little more gas than the hindered amine AMP.

Another experiment was done for a mixture of 50% $CO_2$ and 50% $H_2S$ and in this case, the hindered amine absorbed more than MEA. This phenomena can be due to the "hindered effect", but to have a real information on the selectivity of $H_2S$, the gas mixture should be analyzed at different times during the absorption.

# CONCLUSIONS

The following conclusions were drawn from the investigations:

1) The apparatus used in these experiments give reproducible results and it can be utilized for slow and fast absorption.

2) The reaction of carbon dioxide with hindered amine AMP is a pseudo-first order as for the monethanolamine.

3) For the comparison of the two classes of amine, three different situations were observed

a) MEA absorbed more $CO_2$ than AMP

b) AMP absorbed more $CO_2$ than MEA

c) both amines absorbed the same amount of $CO_2$

These three situations were found to depend on the value of $\theta$ and the concentration of the carbamates in the reaction zone. The "hindered effect" was observed only in situation b) Where $\theta$ is around 0.5

4) The reaction of hydrogen sulfide into amine solutions is instanteneous for the two classes of amine and no difference was observed between AMP and MEA at the same operating conditions.

5) For the mixture of carbon dioxide and hydrogen sulfide, the hindered amine AMP absorbed more gases than MEA for the mixture 50% $CO_2$; 50% $H_2S$

6) The temperature change at the liquid surface due to the heat of reaction and absorption were measured. The change was too small and was neglected during our experiment time of 30 minutes.

# FUTURE WORK

The results of this work justify some recommendations for future.

1) The apparatus can be used for any gas-liquid, however the pressure used in the pyrex-absorption-cell should not exceed 2 atm.

2) The capacity of the cylinder A should be changed depending on the rate of absorption to get better results. Small cylinder A will be used for low absorption and larger cylinder for fast absorption.

3) A magnetic stirring could be used to describe the effect of mixing the liquid on the rate of absorption.

4) A mixture of absorbed gases can be used and the selective removal of one of them can be measured by a Gas-Chromatograph at different time of the experiment.

5) An exothermic gas-liquid reaction can be used in this apparatus. The effect of the heat of reaction on the rate of absorption can be described.

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# APPENDIX

## Appendix A: Diffusivity and Solubility of gases in solutions:

### DIFFUSIVITY:

Different theoretical approaches to the description of diffusion in liquids have be developed depending if the solution is electrolyte or nonelectrolyte. Semi-empirical and empirical relations are also available in the literature. For estimating the diffusivity $D_A$, the well-known method of Wilke and change based on the Stokes-Einstein equation is still widely used, [1].

$$D_A = 7.4 \times 10^{-8}\, T(xM_B)^{0.5}/\mu_B\, V_{mA}{}^{0.6}$$

where:

$M_B$ = molecular weight of the solvent

VmB = molar volume of the solute at the normal boiling point

x = association parameter (2.26 for water)

$\mu B$ = viscosity of the solvent

T = temperature

### SOLUBILITY:

It was observed that the solubility of a gas in a liquid is often proportional to its partial pressure when the partial pressure is not large. The equation which describes this phenomena is known as "Henry's Law"

$$P_i = H_e A^*$$

However when the partial pressure of the gas become large, the previous equation is replaced by a more general are

$$f_i = H_e A^*$$

where $f_i$ is the fugacity of the gas

The solubility in electrolyte solutions can be estimated by the empirical method of Van Krevelen and Hoftizer; [1] that relates the solubility in solution to that in pure solvent at the same temperature by

$$\log_{10} \frac{He}{He_B} = hI$$

where:

$H_{eB}$ = henry's constant in pure solvent

$I$ = ionic strength of the solution

$$I = \tfrac{1}{2} \Sigma \, Ci \; Z_i^2$$

where:

Ci = concentration of ions

Zi = valency of ions

and

h = sum of contribution refering to the specis of gas ha and to the species of positive and negative ions present in the solution

$$h = h_g + h_+ + h_-$$

the values of $h_g$, $H_+$, $h_-$ are given in the literature, [1].

## Appendix B: Relation between Pressure decrease in cylinder A and Rate of Absorption

Since the cylinder A is isolated from the outside gas supply, as soon as the absorption started, the pressure change in the storage tank A could only be due to the absorption of the gas in the liquid. Assuming that the gas follows Ideal gas law, the amount of gas absbored can be determined as follows. Initially, we know the total amount number of gas $N_o$ in the cylinder and at any time, it the amount of gas in the cylinder $N_i$, is related to its partial pressure

$$\text{at} \quad t = o \rightarrow No = \frac{P_o V}{RT}$$

$$\text{at} \quad \text{time } t \rightarrow N_i = \frac{P_i V}{RT}$$

The total amount $\Delta N$ of gas absorbed at any time t is:

$$\Delta N = N_o - N_i = \frac{P_o V}{RT} - \frac{P_i V}{RT} = \frac{P_o}{RT} (1 - \frac{P_i}{P_o})$$

$$\Delta N = N_o [1 - \frac{P_i}{P_o}]$$

the total amount of gas absorbed by unit surface at any time is defined as

$$Q = \frac{\Delta N}{A} = \frac{N_o}{A} [1 - \frac{P_i}{P_o}]$$

Appendix C: Rate of disappearance of $CO_2$ in the system $CO_2$-$RNH_2$

Using equations (28) and (29), we get respectively

$$R_{H+} = k_4 \; [RNH_2] \; [H^+] - k_{-4} \; [RNH_3{}^+] \qquad (31)$$

$$R_{RNHCOOH} = k_6 \; [RNHCOOH] - k_{-6} \; [RNHCOO^-] \; [H^+] \qquad (32)$$

Because of the non appearance of RNHCOOH and $H^+$ in the general reaction on can conclude

$$R_{RNCOOH} = R_{H}{}^+ = 0 \qquad (33)$$

Using now the equations (31), (32) and (33), the concentrations of $[H^+]$ and [RNHCCOO] are found as

$$[H^+] = \frac{k_{-4}[RNH_3{}^+]}{k_4[RNH_2]} \qquad (34)$$

$$[RNHCOOH] = \frac{k_{-6}}{k_6} \; [RNHCOO^-][H^+] \qquad (35)$$

Combining now (34) and (35), one can get:

$$[RNHCOOH] = \frac{k_{-6} \; k_{-4}}{k_6 \; k_4} \; \frac{[RNHCOO^-][RNH_3{}^+]}{[RNH_2]} \qquad (36)$$

From equation (24), the rate of disappearance of $CO_2$ is:

$$R_{CO_2} = k_5 \; [CO_2][RNH_2] - k_{-5}[RNHCOOH] \qquad (37)$$

Replacing equation (36) in (37):

$$R_{CO_2} = k_5[CO_2][RNH_2] - k_{-5}\,\frac{k_{-6}\;k_{-4}}{k_6\;k_4}\;\frac{[RNHCOO^-][RNH_2^+]}{[RNH_2]} \qquad (38)$$

Using the equilibrium constant, the rate of disappearance of carbon dioxide will be:

$$RCO_2 = k_5\left\{[CO_2][RNH_2] - \frac{1}{KCO_2}\;\frac{[RNHCOO^-][RNH_3^+]}{[RNH_2]}\right\} \qquad (39)$$

## Appendix D: Preparation of Gas Mixture

When a gas mixture is used, a second sampling cylinder should be used and connected in the system taking cylinder A place. This cylinder should be large enough to fill the cell of absorption. Then the next procedure is followed:

1. Make a vaccum in the system
2. Fill the cylinder with a predecided pressure of the gas to be absorbed. Since we know the total pressure in the cylinder (15 psig), the partial pressure of the gas is ($P_T$ $Y_i$)
3. Read the pressure at manometer G1
4. Fill the cylinder until the total pressure is achieved by nitrogen
5. Read the pressure at manometer G1
6. Close the valve of the cylinder and connected to the cell

# VITA

Zin-Eddine Dadach was born in Beni-Saf, Algeria, on June 5, 1957. As a high school student in tlemcen, Algeria; he received his pre-University certificate (Baccalaureat Technique Mathematique) in 1975. After four years at the Institut Algerien du petrole, Algeria and one year of industrial training at the SONATRACH LPG Center, Arzew, Algeria, he received the "diplome d'ingenieur" (option: Raffinage et petrochimie) in June 1980. He was then awarded a scholarship from the Institute Algerien du Petrole and joined Stevens Institute of Techonology, Hoboken, New Jersey, in January 1981 to pursue graduate studies. He is expected to receive his M.Eng. (chemical degree)in August, 1983).