

EQUILIBRIUM CONSTANTS FOR PHYSICAL
SOLVENTS IN NATURAL GAS

BY

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DEDICATION

Dedicated to my parents and my son, Adeleke, who brought so much that is worthwhile into my life.

PREFACE

This dissertation is concerned with the measurements of vaporization equilibrium ratios (K-values) for hydrogen sulfide and carbon dioxide in physical solvents. The primary objective is to develop a simple procedure for measuring K-values and measure K-values for materials frequently used as physical solvents for natural gas sweetening. Measurements were made on tetra-ethylene-glycol dimethyl-ether, tetra-methylene-sulfone and propylene carbonate to pressures up to 1000 psia and temperatures from 50°F to 150°F.

So many people have helped me throughout my academic career that I hardly know where to begin. I take this opportunity to express my sincere appreciation to my major adviser, Dr. Robert N. Maddox for his untiring help and direction in the preparation of this work. He has proven too much more than a professorial adviser, for he has been a friend and confidant. I cannot begin to express how much assistance he has given me for the time we have been together.

I am grateful to my advisory committee which consisted of Drs. Gilbert J. Mains, Jan Wagner, and John H. Erber, for their assistance, helpful criticisms and suggestions. I am particularly indebted to Dr. G. J. Mains for the time

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NOMENCLATURE

B	- mole fraction of H ₂ S in the sour gas
C.P	- commercial purity
DGA	- diglycolamine
ft ³	- cubic feet
G.C	- gas chromatograph
gmmole	- gram mole
gm.	- weight in gram
lbmole	- pound mole
K	- equilibrium ratio, Y/X
kp	- pressure unit in kilo pascal
MEA	- mono ethanolamine
ml.	- milliliter
N	- total moles of gas mixture, lbmole
n	- number of moles of component gas, lbmole
O.D	- outside diameter
P _c	- critical pressure, psia
P _{pc}	- pseudo critical pressure, psia
P _{pc} '	- corrected pseudo critical pressure, psia
psi	- pounds per square inch
psia	- pounds per square inch absolute
P-V-T	- pressure-volume-temperature

P_r	- reduced pressure, P/P_c , P/P_{pc}'
P_{Total}	- total pressure, psia
R	- ideal gas constant, $10.73 \frac{\text{psia} \cdot \text{ft}^3}{\text{lbmole} \cdot ^\circ\text{R}}$
T	- temperature, $^\circ\text{R}$
T_c	- critical temperature, $^\circ\text{R}$
T_{pc}	- pseudo critical temperature, $^\circ\text{R}$
T_{pc}'	- corrected pseudo critical temperature, $^\circ\text{R}$
T_r	- reduced temperature, T/T_c , T/T_{pc}'
VLE	- vapor-liquid-equilibrium
V	- volume, liter
X	- liquid mole fraction
Y	- vapor mole fraction
Z	- compressibility factor

Greek Letters

ϵ	- pseudo critical temperature adjustment factor, $^\circ\text{R}$
α	- mole ratio in liquid
Δ	- difference

Subscripts

i	- component, initial condition
j	- component

k - component
f - final condition
CO₂ - carbon dioxide
CH₄ - methane
H₂S - hydrogen sulfide

Other

> - greater than
< - less than

CHAPTER I

INTRODUCTION

Many natural and refinery gases contain hydrogen sulfide (H_2S), carbon dioxide (CO_2) and water vapor. Gases containing hydrogen sulfide are classified as "sour" and gases free from hydrogen sulfide are called "sweet". Natural gas that is transported to the fuel market must meet legal requirements which specify a maximum hydrogen sulfide content. The need for this specification is due to a number of reasons: the desire to ~~to~~ reduce corrosion in natural gas pipelines; for health and safety considerations because hydrogen sulfide is toxic and the combustion products result in sulfur dioxide and trioxide which are also toxic.

In the past, natural gas containing 25 to 30% by volume acid gases was considered to be the maximum treated for sale but nowadays serious consideration is given to treating almost any natural gas.

The removal of the acid gases (H_2S and CO_2) from natural and refinery gases is commonly accomplished by absorption in a suitable solvent. Many processes employ an aqueous alkanolamine solution and are classed as "chemical" processes because alkanolamine has the ability to react with the acid gases. They have the advantage of being able to reduce the

concentration of H_2S and CO_2 to low levels even at low total pressures of the gas stream. However, the alkanolamine solutions do not remove mercaptans and other sulfur compounds readily and require the application of large quantities of heat for regeneration. For these reasons the main trend in improving the process of acid gases removal has led to the development of "physical" processes which employ physical solvents to remove the H_2S , CO_2 , and other sulfur compounds. These physical solvents require minimum expenditure of energy for regeneration, as most of the absorbed gases come out of the solution upon reduction of the pressure.

The removal of carbon dioxide from natural gas is not necessarily compulsory if the heating value of the natural gas is sufficiently high with carbon dioxide. But the removal of hydrogen sulfide is accompanied by the removal of carbon dioxide because: (1) carbon dioxide has similar acid characteristics; (2) the chemical solvent that reacts with H_2S will also react with CO_2 ; (3) the physical solvent that absorbs H_2S will also absorb CO_2 . The real problem is the level at which hydrogen sulfide is being removed. Typical contract specification in the United States is one quarter of a grain per one hundred standard cubic feet. This translates into 4×10^{-6} mole fraction which is a very low concentration.

The ultimate objectives of this research are: (1) develop a simple procedure for measuring vapor liquid equilibrium (VLE) ratios (K-values); (2) measure the

equilibrium ratios for materials frequently and widely used as physical solvents for natural gas sweetening.

The primary application of equilibrium ratios (K_i) is in the design of separation processes. It is a thermodynamic vapor-liquid equilibrium measure of a component to concentrate in the vapor phase. If K_i is less than unity, component i concentrates in the liquid phase and is regarded as a heavy component.

The physical solvents employed in this work are used to remove hydrogen sulfide and carbon dioxide when they appear in high concentrations in natural gas. Only limited data are available in the literature for any of the materials investigated and for most, there are no data. The reason the data did not exist is the expense of collecting the data. Developing and improving the technique used in this study will simplify the cost tremendously. But the work was done because the data are needed and collection of the data could be accomplished.

The proving of the technique used in this study for measuring equilibrium ratios is discussed in detail in Chapter IV.

Analysis of the H_2S - CO_2 - methane system by chromatography is very difficult and for this reason the analytical expertise of Dr. G. J. Mains of the Oklahoma State University Department of Chemistry was used in this study.

The systems studied were:

1. CO_2 - CH_4 - propylene carbonate

2. CO_2 - CH_4 - Tetra-ethylene-glycol-dimethyl-ether
3. CO_2 - CH_4 - Tetra-hydrothiophene-1-1-dioxide
4. H_2S - CH_4 - Propylene carbonate
5. H_2S - CH_4 - Tetra-ethylene-glycol-dimethyl-ether
6. H_2S - CH_4 - Tetra-hydrothiophene-1-1-dioxide

Experimental measurements were made at pressures to 1000 psia and temperatures from 50 to 150°F. These cover the range of typical operating conditions for natural gas sweetening operations.

CHAPTER II

LITERATURE SURVEY

Information on equilibrium vaporization (VLE) for physical solvents in sour gas streams is practically nonexistent and those data that do exist are proprietary and not published.

The sulfolane process for acid gas removal was developed in early 1950.⁴⁰ Sulfolane has been thoroughly investigated by Shell but the data cannot be seen without signing a secrecy agreement. The use of propylene carbonate as physical solvent for acid gas removal was patented by the Fluor Corporation and was originally described by Kohl and Buckingham.⁴

However, the literature data on vapor liquid equilibrium studies on other systems other than the physical solvents is full and various approaches had been used to obtain these data. This chapter is not intended to be an exhaustive review of such studies but a survey of some of the most important methods of measurement and usable data collections to be able to see the similarities and differences with the technique developed for this study.

The work of Katz and Hachmuth²⁴ was one of the early works to be published. They investigated naturally occurring

mixtures of crude oil-natural gas in an equilibrium bomb at pressures up to 3000 psia and temperatures ranging from 40° to 200°F. Samples of both the liquid and vapor phases were obtained and analyzed in fractionating columns.

Donnelly and Katz¹¹ studied phase equilibrium for the CH₄ - CO₂ system with a glass-windowed pressure cell in an alcohol bath. Equilibrium was obtained by recirculating vapor through the liquid. Samples of vapor and liquid were withdrawn by expansion to atmospheric pressure and analyzed by absorbing the carbon dioxide in caustic solution.

Reamer⁵⁵ and co-workers studied the methane-hydrogen sulfide system employing a modified mercury displacement dew-point bubble-point apparatus. The composition of the dew-point gas was determined by direct analytical methods. They studied the phase and volumetric behavior of five mixtures of these two components at temperatures ranging from 40° to 340°F and pressures from 200 to 1000 psia. In addition to the volumetric measurements, they sampled the gas phase from the heterogeneous mixtures of methane and hydrogen sulfide and determined the composition by measurement of the specific weight.

Kohn and Kurata²⁷⁻²⁸ also made measurements on the methane-hydrogen sulfide system at high pressures from 118° to 220°F. The method employed was the introduction of known increments of homogeneous gas mixtures into a glass equilibrium cell maintained at fixed temperature. The attainment of equilibrium was facilitated by agitating the

mixture with a magnetically actuated steel ball. The gas mixtures were analyzed by vapor density measurements.

Muhlbauer et al.,⁴⁶ Jones, et al.²² and Martin, et al.³⁹ investigated chemically reacting systems. Muhlbauer et al.⁴⁴ measured CO_2 and H_2S equilibrium data in ethan-amine solutions. In their work, equilibrium was established by bubbling the gas through the solution. Both liquid and gas samples were taken at equilibrium and analyzed. The liquid samples were analyzed by potentiometric titration while the gas samples were analyzed by mass spectrometer.

Jones et al.²² determined the solubility of H_2S and CO_2 in MEA at high pressure and temperatures of 40 to 140°C. Equilibrium was established by rocking the equilibrium vessel. The vapor sample was taken and analyzed by mass spectrometer while the amount of sample in the liquid phase was determined by weight.

Martin et al.⁴¹ determined the solubility of H_2S and CO_2 in diglycolamine. The apparatus used in that study consisted of a Jerguson gauge mounted at the top of the equilibrium cell. A magnetic pump was used to circulate the gas phase from the gas reservoir to the bottom of the gauge. Ten-junction copper-constantan thermopiles were used to measure the temperature of the cell. Samples of the vapor were withdrawn and analyzed by gas chromatograph. The partial pressure of CO_2 or H_2S was calculated from the analysis. Liquid samples were also withdrawn from the cell at atmospheric pressure and their temperature was measured. From

the P-V-T data, the amount of gas which evolved was determined and the ratio of CO₂ or H₂S to DGA in the liquid phase was calculated.

Oghaki et al.⁵⁰ measured equilibrium data for the methanol-carbon dioxide system isothermally at 25 and 40°C. They employed a static method of data collection and vapor samples were withdrawn and compositions determined by gas chromatograph. By using the Lewis rule and the Redlich Kwong equation of state for CO₂ in the vapor phase, they were able to compute the activity coefficients in the liquid phase and the fugacity coefficients in the vapor phase.

Amongst the work reported in the literature for physical solvents is that of Isaac et al.²¹ on propylene carbonate. They utilized the same apparatus and technique as that of Martin et al.⁴¹ to measure the solubility of H₂S and CO₂ in propylene carbonate. Worth mentioning in the work of Martin et al.⁴¹ and Isaac et al.²¹ is that they used pure component pressure over the solution as the equivalent partial pressure in the solution. This study used mixtures of methane with the acid gases to measure the solubilities.

CHAPTER III

EQUIPMENT

Experimental Apparatus

The idea behind the experimental rig presented in this study came from the work of Woertz.⁷⁰ Vapor-liquid equilibrium constants were measured by sampling only the vapor phase and determining equilibrium ratios by material balance. Full details of proving this technique for obtaining equilibrium ratios are discussed in detail in Chapter IV.

The experimental set up as depicted in Figure 1 consisted of the equilibrium cell with an HTL gauge mounted at the top, the gas feed lines, and the liquid feed lines. Compositions were determined using a gas chromatograph. The approach to equilibrium was determined by removing samples at different time periods till there was no further change.

Equilibrium Cell

There were two equilibrium cells identical in all respects. They were obtained from Whitey (304-HDF4) made of stainless steel and each had a volume of approximately 1 liter. The volume calibration of the cells were made by displacement of liquid water at known temperature. There

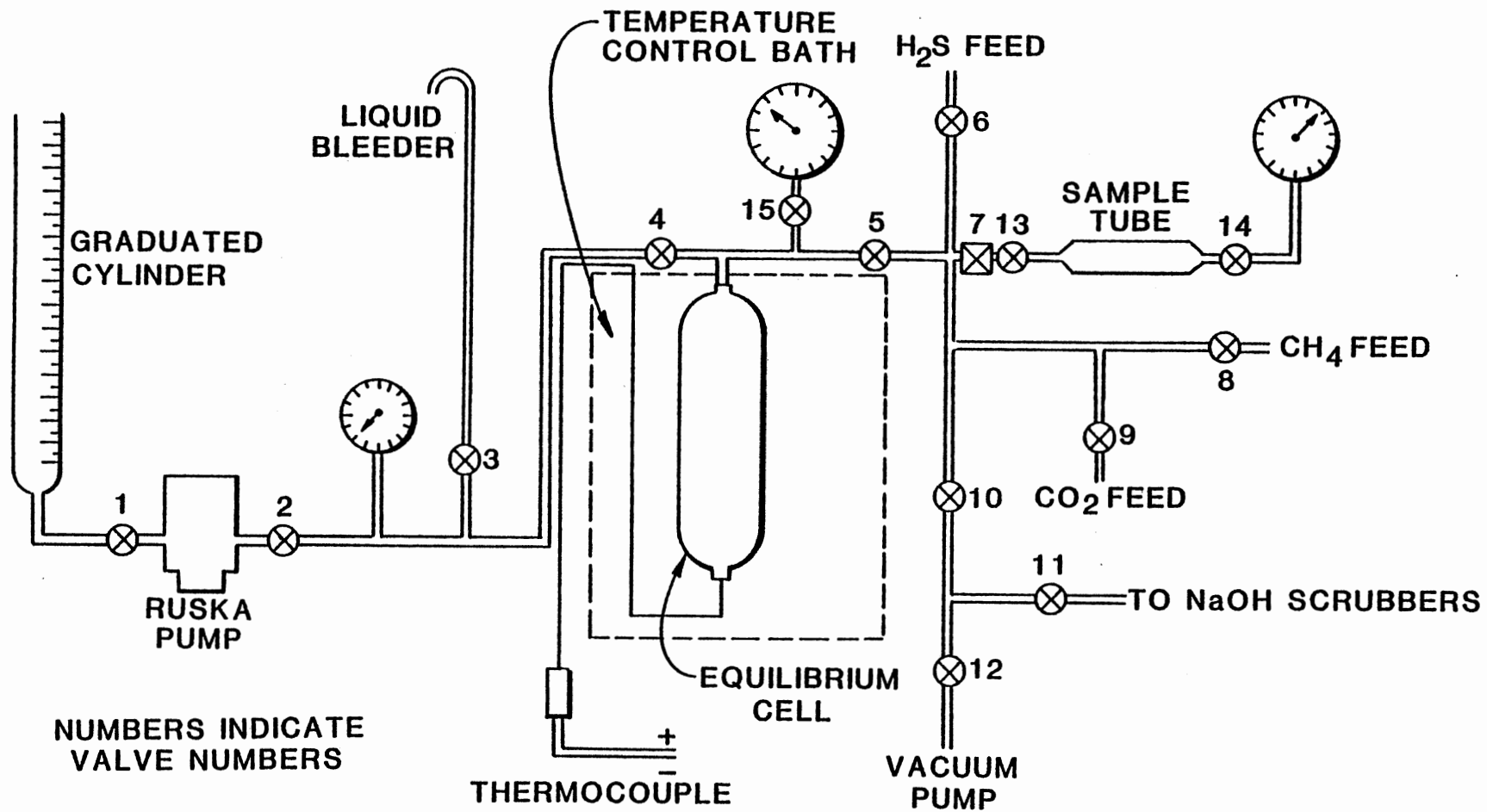


Figure 1. Schematic Diagram of the Experimental Set Up

were two major (1/4") entrances into each of the cells, one at the top and the other at the bottom. The top entrance served the purpose of material charging and gas sample withdrawal from the cell while the bottom entrance made installation of a thermocouple into the cells possible. All connection lines are 1/4" O.D. 304 stainless steel tubing.

Pressure Measuring Device

All pressure measurements were made with a HTL pressure gauge (model # 101FTM13A41, Perma CA) with 10 psi subdivisions (range 0 to 2000 psi). The accuracy of the gauge specification is stated to be 1/4% of full scale. The calibration of the pressure gauge was carried out using a Ruska Model 2400 HL dead weight tester. The calibration data are presented in Appendix C.

Gas Feed System

The gas feed system consisted of H₂S, CO₂ and CH₄ cylinders to simulate raw natural gas. Each gas cylinder was fitted with a regulator and valve (1/8") leading to the gas feed system. The whole system is connected to a vacuum pump (Welch Duo-seal, 1/3 horse power) capable of pumping the test cell and sample container down to 1×10^{-3} mm Hg. to remove air.

Liquid Feed System

The liquid feed system consisted of a Ruska displace-

ment pump at the center. To the outlet of the pump is the equilibrium cell and to the inlet is the 500 ml. burette (Kimax) in which is contained the solvent to be transferred into the equilibrium cell. The volume of the liquid held up in the liquid line between the pump and the entrance of the equilibrium cell was calibrated to be approximately 9 ml. The amount of liquid transferred from the burette through the pump into the equilibrium cell is simply determined by taking the difference between the initial and final readings of the graduated burette.

Temperature Measurement and Control Bath

The major components of the bath were the heater, the cooler, and the temperature controller. The bath fluid was water.

The temperature controller was Fisher (model 44, catalog No. 15-177) with a range of -40 to 150°C . The unit responded to a temperature change of $\pm 0.003^{\circ}\text{C}$.

For low temperature measurement (50°F), the water bath was put under a cooling load from a Sargent water cooler (E. H. Sargent & Co., Catalog No. S84890). The coolant employed was 1-propanol which was circulated through a copper coil to maintain the temperature constant at the desired value.

The temperature of the coolant was held constant to within $\pm 1^{\circ}\text{C}$ by means of the controller which regulated the on-off cycle of the circulating pump. Temperature

measurements were made by the use of a cromel-alumel thermocouple. The thermocouple was installed with pressure transducer gland 1/4" Conax obtained from Barnard Equipment Co., Tulsa. The instrument was calibrated using N.B.S Leeds and Northrup platinum resistance thermometer (serial # 1761202). The calibration data are presented in Appendix B.

Materials

The physical solvents investigated in this study (propylene carbonate, tetra-ethylene-glycol-dimethyl-ether, tetra-hydrothiophene-1-1- dioxide) were research grade (purity not stated) from Pfaltz and Bauer, Inc., Stamford, Connecticut. The compressed gases (CH_4 , CO_2 , H_2S) were obtained from Matheson Co. Inc. Hydrogen sulfide and methane were C.P. grade. Minimum purities of the gases were given as: hydrogen sulfide 99.5%; methane 99.0%; carbon dioxide 99.5%. The materials were used as received without further purification.

Gas Chromatograph

The gas chromatograph was an isothermal Perkin-Elmer 990 G.C. equipped with a thermal conductivity detector with 1 milivolt recorder. It is a 10" long and 0.125" O.D. stainless steel column packed with 80/100 mesh n-octane on porasil C. The gas chromatograph was calibrated each day for which the analysis is needed with a standard mixture

and each of the gas samples was replicated for at least three times.

Auxiliary Equipment

The auxiliary equipment consisted of (1) a vacuum pump, (2) potentiometer, (3) sodium hydroxide rinse bottles, (4) sample bombs, (5) lead and glass beads, (6) barometer, (7) thermometer, (8) snoop (leak detector), (9) valves and fittings.

The vacuum pump (Welch Duo-seal, 1/3 horse power) was used to evacuate the test cell and sample container. The potentiometer was Leeds and Northrup model 8686. The potentiometer was capable of measuring potentials to within a temperature of 0.08°F .

The sodium hydroxide scrubbing system consisted of 3 filter flasks arranged in series. A flask was put in the line ahead of the NaOH rinse flasks to prevent sucking the NaOH solution into the equilibrium cell. The NaOH solutions were prepared by dissolving 100 gm. NaOH pellets in one liter of water. The H_2S containing gases were vented from the equilibrium cell through the NaOH. The vacuum pump was used to take more before venting because of the inefficiency of the fume hood in the laboratory.

The sample bombs for collecting gas samples for analysis were twelve in number and made from stainless steel from Whitey (304 HDF2-40). Each of the bombs had a volume of approximately 40 ml. with two openings, one at the top and

the other at the bottom. The entrance at the bottom was plugged while the one at the top was equipped with a 1/8" Parker valve 10v-2071 to make control of passage of materials in and out of the bomb possible.

To prevent stratification of gas layers in the equilibrium cell, lead or glass balls were added for homogenizing gas mixture for each run. The outside diameter of each of the balls was about 0.12" and about eight were used for each run. The fluid used for checking for leaks was Snoop (leak detector) from Arlington, Illinois.

All valves (Autoclave, 10v-2071) and fittings were manufactured by Autoclave.

CHAPTER IV

TECHNIQUE DEVELOPMENT

As pointed out in Chapter II, equilibrium ratios in general are obtained by analyzing both liquid and gas samples obtained at equilibrium conditions. Since the data presented in this project were obtained by using a single equilibrium cell and sampling only the vapor phase, it is necessary to first prove that the data of this work are reproducible, consistent, and reliable.

The purpose of this study is not to obtain extremely accurate and refined equilibrium constants for testing the validity of an equation of state, but to take experimental data that are within approximately $\pm 10\%$ that are suitable for use in Chemical Engineering process calculations.

To prove the technique used in this study, the first thing that was done was to use the constant volume equilibrium cell at room temperature to carry out various preliminary tests.

The first of these series of test was conducted by using the constant volume equilibrium cell at room temperature with mixture of about 10% carbon dioxide in methane at pressures of 500 psi or greater. The physical solvent employed was propylene carbonate. Gas samples were collected

using a carbon steel bomb. The inconsistency in the K-values obtained is very pronounced as shown in Table I. The thing that was suspected to be responsible for the inconsistency of the data was insufficiency of mixing of the gas. Therefore, some mixing tests were carried out to see how long it takes for the gas to mix.

A mixture of about 10% CO_2 in methane at 500 psi was made. About eight lead balls were added for mixing the gas mixture. Gas samples were withdrawn at different times. Mixing was complete after about one half hour as shown in Table II.

The next thing that was done was to measure the equilibrium constant incorporating the new mixing technique (the use of lead balls for shaking the gas mixture). Mixtures of 5% and 10% respectively of CO_2 in methane at pressures of 500 psi or greater were used. The small beads as discussed in Chapter III were introduced for rapid mixing of the gases to prevent stratification. Lead beads were used for CO_2 runs while glass beads were used for H_2S runs to prevent H_2S from reacting with the lead. The physical solvents employed were methanol and N-methyl-pyrrolidone. Approximately 100 ml. of the solvent was used for each of the runs. The data obtained from this test as presented in Table III begin to show a high level of consistency. The data were fitted by plotting $\log K$ versus $\log P$ on a digital computer. The results as shown in Table IV, and Figure 2 further show that average absolute percent deviation for

TABLE I
 INCONSISTENT EQUILIBRIUM CONSTANT
 FOR CO₂ IN PROPYLENE CARBONATE

Total Pressure (psia)	Temp OF	% CO ₂ Initially	% CO ₂ Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{CO₂}	Liquid Mole Fraction X _{CO₂}	K-value
517.56	78.0	8.1	7.0	98.0	7x10 ⁻²	8.694x10 ⁻²	0.805
543.41	77.4	9.2	7.1	96.0	7.1x10 ⁻²	7.06x10 ⁻²	1.006

TABLE II
RESULTS OF MIXING

Procedure	% CO ₂
1. Before Mixing	2.8
2. After Mixing and Waiting for 15 Minutes	10.7
3. After Mixing and again Waiting for another 15 Minutes	11.7
4. After Mixing again and Waiting for another 1 Hour	11.7

TABLE III
RESULTS OF PRELIMINARY RUNS FOR CO₂ K-VALUES IN
M-PYROL AND METHANOL AT ROOM TEMPERATURE

1-methyl-2-pyrrolidone							
Total Pressure (psia)	Temp (°F)	% CO ₂ Initially	% CO ₂ Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{CO₂}	Liquid Mole Fraction X _{CO₂}	K-value
503.82	76.0	7.72	5.48	97.5	5.48x10 ⁻²	3.51x10 ⁻²	1.56
511.28	76.0	12.10	8.39	97.0	8.39x10 ⁻²	5.73x10 ⁻²	1.46
961.36	78.0	5.69	4.57	95.0	4.57x10 ⁻²	3.85x10 ⁻²	1.19
974.23	78.0	12.86	8.47	93.0	8.47x10 ⁻²	6.61x10 ⁻²	1.28
Methanol							
511.08	79.0	7.68	5.75	102.0	5.75x10 ⁻²	1.38x10 ⁻²	4.17
516.53	79.0	12.02	8.83	100.0	8.83x10 ⁻²	2.28x10 ⁻²	3.87
964.38	76.0	10.64	8.37	98.0	8.37x10 ⁻²	3.05x10 ⁻²	2.74
959.59	76.0	5.71	4.68	93.0	4.68x10 ⁻²	1.58x10 ⁻²	2.96

TABLE IV
RESULTS OF COMPUTER FITS FOR CO₂ K-VALUES IN
M-PYROL AND METHANOL AT ROOM TEMPERATURE

1-methyl-2-pyrrolidone					
Total Pressure (psia)	Temp (°F)	Experimental K-value	Calculated K-value	% Error	Average Absolute % Deviation for all the Points
503.82	76.0	1.56	1.510	3.18	
511.28	76.0	1.46	1.503	-2.98	3.46
961.36	78.0	1.119	1.234	-3.70	
974.23	78.0	1.28	1.229	3.99	
Methanol					
511.1	79.0	4.17	4.023	3.51	
516.5	79.0	3.87	4.000	-3.37	2.095
964.38	76.0	2.74	2.834	-3.53	
959.59	76.0	2.96	2.845	3.90	

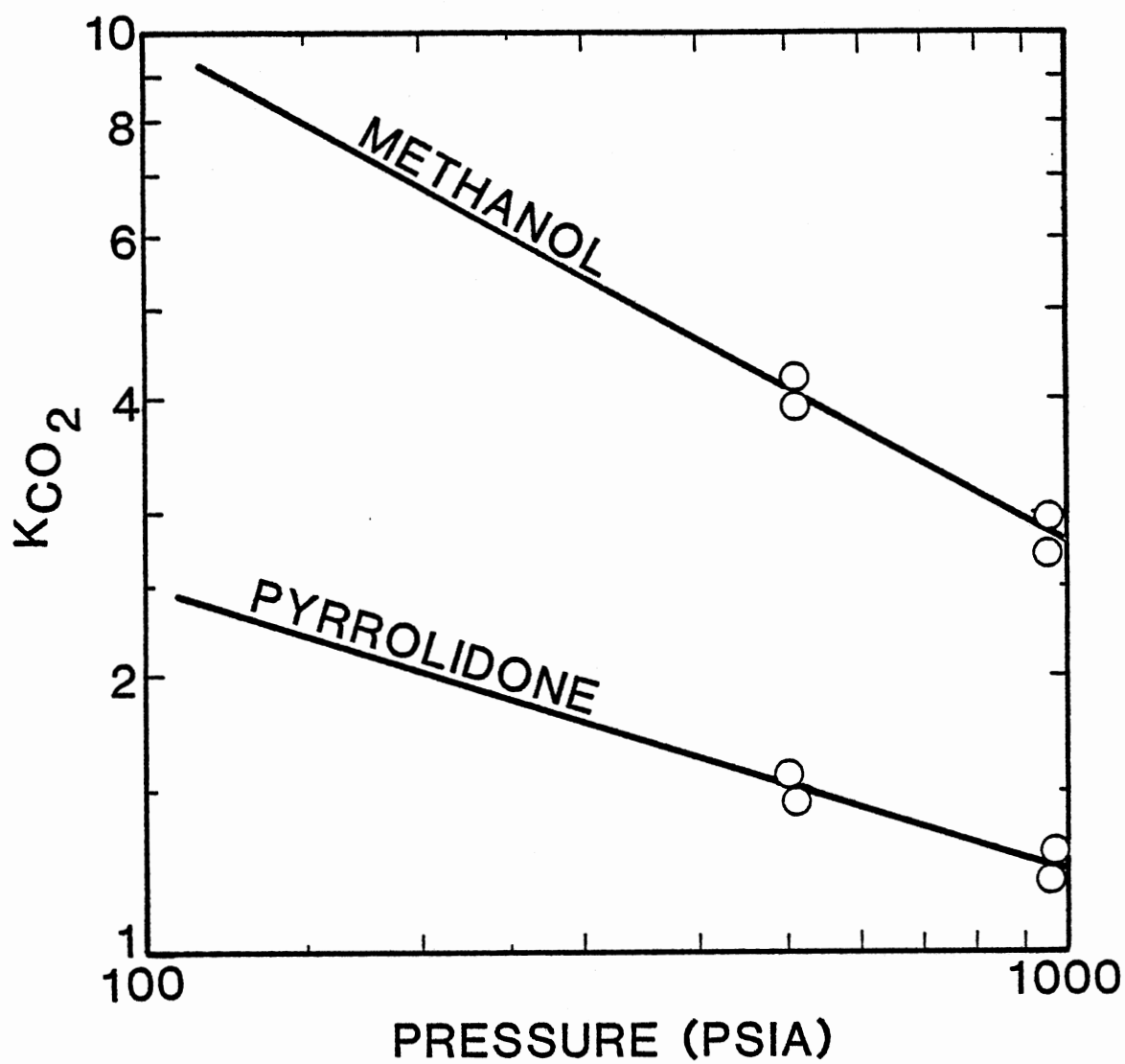


Figure 2. Preliminary Runs For CO₂ K-values in M-Pyrol and Methanol at Room Temperature

M-pyrol and Methanol are 3.46 and 2.095 respectively.

To ascertain that the same technique by mixing with glass balls and collecting samples in a carbon steel bomb will work for H_2S as well, similar runs were made on H_2S . The results were erratic. Many of the analyses after the introduction of the solvent showed no trace of H_2S . The preliminary conclusion was that the use of a carbon-steel sample bomb will not be suitable for H_2S runs. Even coating the carbon steel bomb with H_2S before taking the samples yielded poor gas chromatograph analyses. Tygon tubing in the line between the standard gas and the chromatograph was also a problem. Gas sample containing H_2S that stayed fairly in tygon tubing did not give consistent results because the H_2S is adsorbed on the tygon. Use of a stainless steel sample container and replacing the tygon tube on the gas chromatograph line with stainless steel pipe solved the problem.

To further prove that the data of this study are reliable, some of the data published by Isaac et al.²¹ were reproduced with the apparatus used in this study. This was in essence to determine the solubility of pure CO_2 in propylene carbonate at $40^\circ C$ and a pressure of about 500 psi. Three runs were made. Two of the three runs were almost identical using 197 ml. of propylene carbonate each to check the reproducibility of the apparatus used in this study. The other run was made using about 355 ml. of propylene carbonate. The solubilities were measured by observation of

the drop in pressure of the gas when the solvent was added. Results as presented in Table V. show that the data obtained in this work are within 10% of that of Isaac et al.²¹ Moreover, we obtained excellent reproducibility with our apparatus.

The next four sets of runs to determine solubility of both H₂S and CO₂ in propylene carbonate are the following: (a) mixtures of H₂S, CO₂ and CH₄; (b) mixtures of H₂S and CO₂ without CH₄; (c) mixtures of CO₂ and CH₄; (d) mixtures of H₂S and CH₄. Runs (a) and (b) were made at temperature of 40°C with 100 ml. and 120 ml. of propylene carbonate respectively, while runs (c) and (d) were made each with approximately 100 ml. of propylene carbonate each at temperature of 40°C. Gas samples were withdrawn for analysis before the solvent was added and after the solvent was added to measure the solubilities of the acid gases.

The results as presented in Tables VI, VII, and VIII show that the data of this work in comparison with Isaac et al.²¹ are in excellent agreement. They are within ±10% in every case except for two cases where the deviation went as high as 17% and 76%. Detailed sample calculations are presented in Appendix F.

TABLE V
LITERATURE COMPARISON OF PURE CO₂ SOLUBILITY
IN PROPYLENE CARBONATE

Author	Temperature (°C)	Pressure of CO ₂ (kp)	Mole Ratio in Liquid α	Deviation %
This Work	40.0	2533.13	0.2846	
Isaac <u>et al.</u> ²¹	40.0	2533.13	0.2650	+7.40
This Work	40.0	2482.11	0.2826	
Isaac <u>et al.</u> ²¹	40.0	2482.11	0.2600	+8.69
This Work	40.0	2119.44	0.2310	
Isaac <u>et al.</u> ²¹	40.0	2119.44	0.2140	+7.36

(α = Mole Ratio in Liquid, CO₂/Propylene Carbonate)

TABLE VI
LITERATURE COMPARISON OF CO₂ AND H₂S
SOLUBILITY IN PROPYLENE CARBONATE

Author	Temperature (°C)	Partial Pressure of CO ₂ (kp)	K-value	α for CO ₂	Deviation %
This Work	40.0	579.30	1.9369	0.102	+9.68
Isaac <u>et al.</u> ²¹	40.0	579.30	—	0.093	
Author	Temperature (°C)	Partial Pressure of H ₂ S (kp)	K-value	α for H ₂ S	Deviation %
This Work	40.0	452.43	0.6738	0.0455	-17.27
Isaac <u>et al.</u> ²¹	40.0	452.43	—	0.0550	

(This Work used mixtures of CO₂ + H₂S and CH₄
Isaac et al. used either pure H₂S or CO₂
 α = mole ratio in liquid)

TABLE VII

LITERATURE COMPARISON OF CO₂ AND H₂S
SOLUBILITY IN PROPYLENE CARBONATE

Author	Temperature (°C)	Partial Pressure of CO ₂ (kp)	K-value	α for CO ₂	Deviation %
This Work	40.0	2683.64	4.1766	0.2950	
Isaac <u>et al.</u> ²¹	40.0	2683.64	—	0.2930	+0.68

Author	Temperature (°C)	Partial Pressure of H ₂ S (kp)	K-value	α for H ₂ S	Deviation %
This Work	40.0	435.75	1.4212	0.141	
Isaac <u>et al.</u> ²¹	40.0	435.75	—	0.08	+76.25

(This Work used mixtures of CO₂ and H₂S without CH₄
Isaac et al. used either pure H₂S or CO₂
 α = mole ratio in liquid)

TABLE VIII
LITERATURE COMPARISON OF CO₂ AND H₂S
SOLUBILITY IN PROPYLENE CARBONATE²

Author	Temperature (°C)	Partial Pressure of CO ₂ (kp)	K-value	α for CO ₂	Deviation %
This Work	40.0	689.47	1.87	0.0566	-5.7
Isaac <u>et al.</u> ²¹	40.0	689.47	—	0.06	
Author	Temperature (°C)	Partial Pressure of H ₂ S (kp)	K-value	α for H ₂ S	Deviation %
This Work	40.0	689.47	0.643	0.185	-7.5
Isaac <u>et al.</u> ²¹	40.0	689.47	—	0.20	

(This Work used mixtures of CO₂+CH₄ and H₂S+CH₄
Isaac et al. used either pure H₂S or CO₂
α = mole ratio in liquid)

CHAPTER V

EXPERIMENTAL PROCEDURE

The procedure used in taking the experimental data and calculating the experimental K-values will be described.

Operational Procedure

The equilibrium cell was cleaned, assembled insuring that some few lead or glass beads were put in for shaking the gas mixture to prevent stratification. Set the temperature control bath to the desired temperature and go through the following steps:

1. Evacuate the equilibrium cell and the gas feed lines with valves 6, 7, 8, 9, 11, and 15 closed.
2. close valves 10 and 12, then admit a small amount of H_2S or CO_2 into the equilibrium cell to ensure that pressure in the equilibrium cell is slightly above atmospheric. Open valve 15. This step is to prevent pulling a vacuum on the pressure gauge.
3. Add a predetermined amount of H_2S or CO_2 into the cell by observation of the pressure and wait for about two minutes for the cell pressure to stabilize.
4. Check for leakage with snoop.

5. Record the pressure.

6. Isolate the equilibrium cell from the rest of the system by breaking it off from valves 4 and 5. Shake vigorously and set it into the constant temperature bath for at least one hour. Then record the temperature and the pressure.

7. Re-connect the equilibrium cell to the rest of the system and evacuate the gas feed lines up to valve 5 with valves 6, 7, 8, 9, and 11 closed.

8. Close valves 10 and 12, and add methane until approximately the total pressure desired is reached. Wait for about two minutes.

9. Check for leakage with snoop.

10. Isolate the equilibrium cell and shake the gas mixture to avoid stratification.

11. Set the equilibrium cell in the constant temperature bath. When the temperature is steady, record the pressure.

12. Re-connect the equilibrium cell to the rest of the system and evacuate the gas feed lines and the sample bomb with valves 6, 8, 9, and 11 closed.

13. Close valves 10 and 12, open valve 5 and withdraw a gas sample. Make sure that the pressure of the sample in the sample bomb is above atmospheric to prevent leakage of air into the sample.

14. Set the equilibrium cell back into the temperature bath for about one half hour and record the total pressure.

15. Insert the equilibrium cell back into the liquid feed line by connections at valve 4. Make sure that the lines are carefully bled of air to ensure adequate pumping of the solvent.

16. Introduce about 100 ml. of the solvent with the Ruska displacement pump and set the equilibrium cell back into the constant temperature bath. Shake the cell periodically for 18 to 20 hours.

17. After equilibrium has been reached, record the final total pressure and temperature.

18. Take gas sample as in steps 12 and 13.

19. Vent the remaining gas mixture through the sodium hydroxide scrubber to remove the acidic components of the mixture.

20. Clean the equilibrium cell with soap and water. Rinse the lines with acetone and repeat steps 1 to 19 for another run.

21. The used solvent is filtered and regenerated for re-use by heating gently under the hood to bubble off the absorbed gas.

Determination of Experimental Equilibrium K-values

Before absorption: From the equilibrium cell volume, the gas temperature and pressure prior to the introduction of the solvent absorber, the total number of moles of gas

present is known. Since the gas sample is taken before the introduction of the solvent, the composition of the input gas, and the number of moles of each component are known.

After absorption: From the analysis of the gas sample taken at equilibrium the composition of the equilibrium vapor phase is known. At this point, three assumptions are made:

1. The liquid phase at equilibrium is assumed to have a volume equal to that of the liquid solvent charged to the system.
2. None of the liquid solvent is present in the vapor phase.
3. No methane is absorbed in the liquid.

From the volume of the gas at equilibrium, $(V_{\text{cell}} - V_{\text{liquid}})$, the temperature, and equilibrium total pressure of the gas, the total number of moles, and the number of moles of each component of the gas are known. From a mass balance around the closed system, the number of moles of each component in the liquid phase and the liquid composition are known. The equilibrium K-values for each component are determined as $K_i = y_i/x_i$. A sample calculation is presented in Appendix E.

CHAPTER VI

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental equilibrium ratio data were obtained for carbon dioxide and hydrogen sulfide in several physical solvents over a range of temperatures and pressures. This chapter presents the results of an examination and analysis of the experimental data. The experimental data are presented in graphical and tabular form. Appendix D contains the raw experimental data from which the results reported here were obtained.

The data were taken on the following systems:

1. Carbon dioxide - Methane - Propylene Carbonate
2. Carbon dioxide - Methane - Selexol
3. Carbon dioxide - Methane - Sulfolane
4. Hydrogen sulfide - Methane - Propylene Carbonate
5. Hydrogen sulfide - Methane - Selexol
6. Hydrogen sulfide - Methane - Sulfolane

Each of the systems was run at temperatures of 50 to 150°F and pressures from 100 to 1000 psia. The experimental equilibrium constants for systems 1 to 3 for carbon dioxide are given in Tables IX to XI.

Those of hydrogen sulfide listed in 4 to 6 are presented in Tables XII to XIV. Figures 3 to 8 illustrate the K-values

of systems 1 through 6.

There were no physical solvent data in the literature which could be used to make a direct comparison with the data presented in this study. However, the overall results show a great deal of reliability for reproducibility and consistency.

Data Trends

Based on the experimental results of this work, some general comments are possible regarding the effects of the physical solvents on the K-values of carbon dioxide and hydrogen sulfide.

For carbon dioxide the equilibrium ratio in sulfolane is from 8 to 44% higher than in propylene carbonate for the measurements made at 50°F and room temperature while the reverse is observed at 150°F. Propylene carbonate is higher from 19 to 44%. The greater deviations are at higher pressures at 50°F and room temperature while it occurred at lower pressure at 150°F.

Carbon dioxide K-value in propylene carbonate is higher than in selexol over the complete temperature range (50 to 150°F). The equilibrium ratio is from 90 to 290% higher and the greater deviations are at lower pressures and higher temperatures.

Just the opposite effect of carbon dioxide is seen for the hydrogen sulfide K-values. In propylene carbonate, the

hydrogen sulfide K-values are approximately 10 to 50% higher than in sulfolane. However, hydrogen sulfide K-values in selexol remain the lowest of the three physical solvents.

TABLE IX
EXPERIMENTAL K-VALUES OF CARBON DIOXIDE
IN PROPYLENE CARBONATE

Total Pressure (psia)	Temperature (°F)	% CO ₂ Initially	% CO ₂ Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{CO₂}	Liquid Mole Fraction X _{CO₂}	K-value
145.7	48.2	13.2	10.0	100.0	1.0x10 ⁻¹	1.33x10 ⁻²	7.5188
496.3	48.2	9.98	7.37	95.0	7.37x10 ⁻²	3.91x10 ⁻²	1.8849
993.3	48.2	9.34	7.24	95.0	7.24x10 ⁻²	7.12x10 ⁻²	1.0169
145.26	74.3	13.34	10.65	98.0	1.065x10 ⁻¹	1.18x10 ⁻²	9.0254
520.32	75.2	10.0	7.94	98.0	7.94x10 ⁻²	2.88x10 ⁻²	2.7569
1050.26	74.8	9.15	7.71	98.0	7.71x10 ⁻²	4.46x10 ⁻²	1.7287
153.32	148.2	14.45	13.04	98.0	1.304x10 ⁻¹	6.25x10 ⁻³	20.8640
543.25	146.35	11.33	10.01	96.0	1.01x10 ⁻¹	1.80x10 ⁻²	5.5556
1084.25	145.1	10.51	9.48	96.0	9.48x10 ⁻²	3.26x10 ⁻²	2.9080

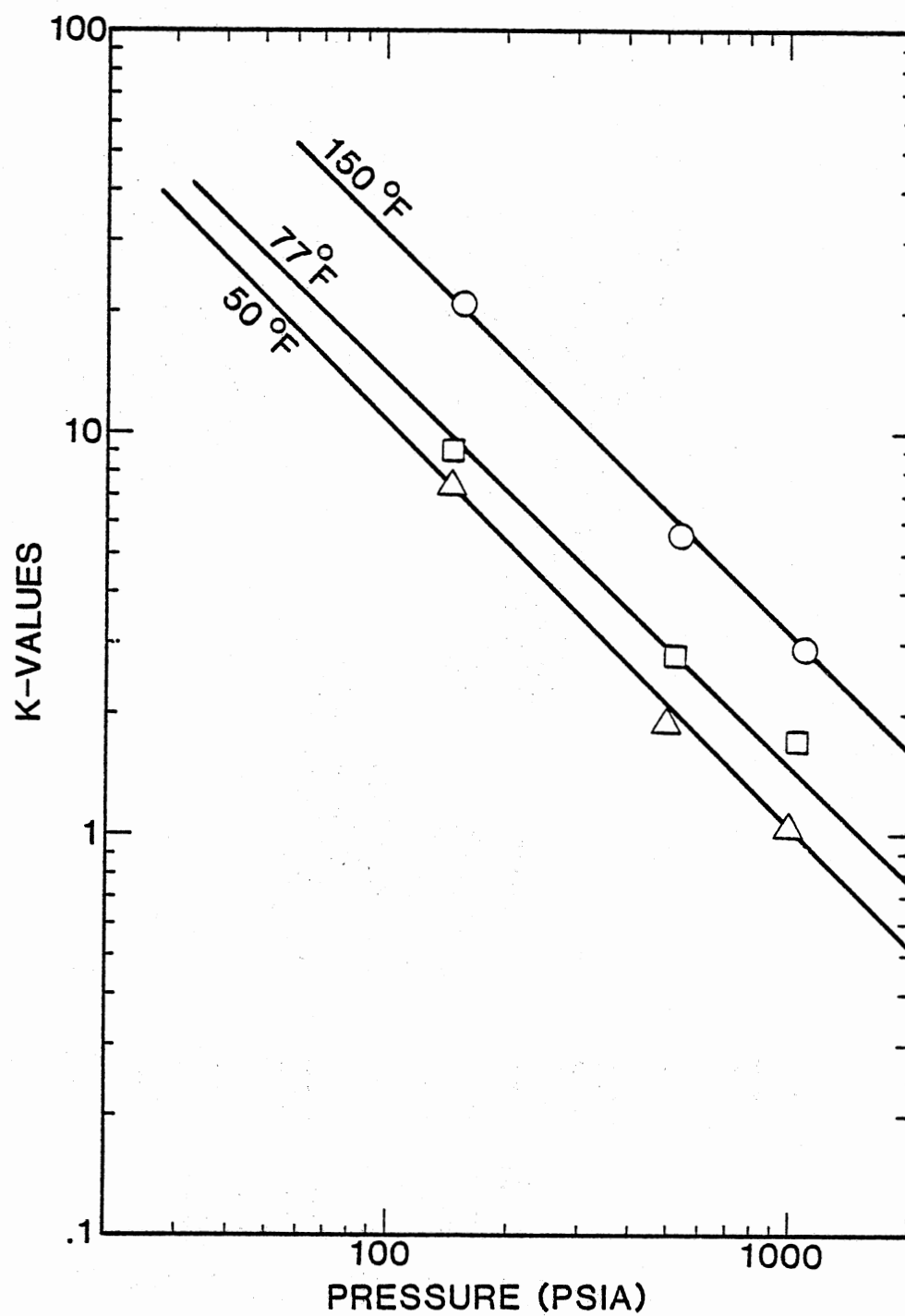


Figure 3. K-values for Carbon Dioxide in Propylene Carbonate

TABLE X
EXPERIMENTAL K-VALUES OF CARBON DIOXIDE
IN SELEXOL

Total Pressure (psia)	Temperature (°F)	% CO ₂ Initially	% CO ₂ Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{CO₂}	Liquid Mole Fraction X _{CO₂}	K-value
149.23	47.0	12.07	9.04	98.0	9.04x10 ⁻²	3.47x10 ⁻²	2.6052
504.45	46.3	9.24	6.83	97.5	6.83x10 ⁻²	8.62x10 ⁻²	0.7923
1000.23	47.0	8.89	7.07	97.0	7.07x10 ⁻²	1.34x10 ⁻¹	0.5276
150.31	85.2	12.95	10.42	102.0	1.042x10 ⁻¹	2.58x10 ⁻²	4.0388
527.31	81.2	9.64	7.84	100.0	7.84x10 ⁻²	6.31x10 ⁻²	1.2425
169.26	147.6	13.87	12.01	95.0	1.201x10 ⁻¹	2.22x10 ⁻²	5.4099

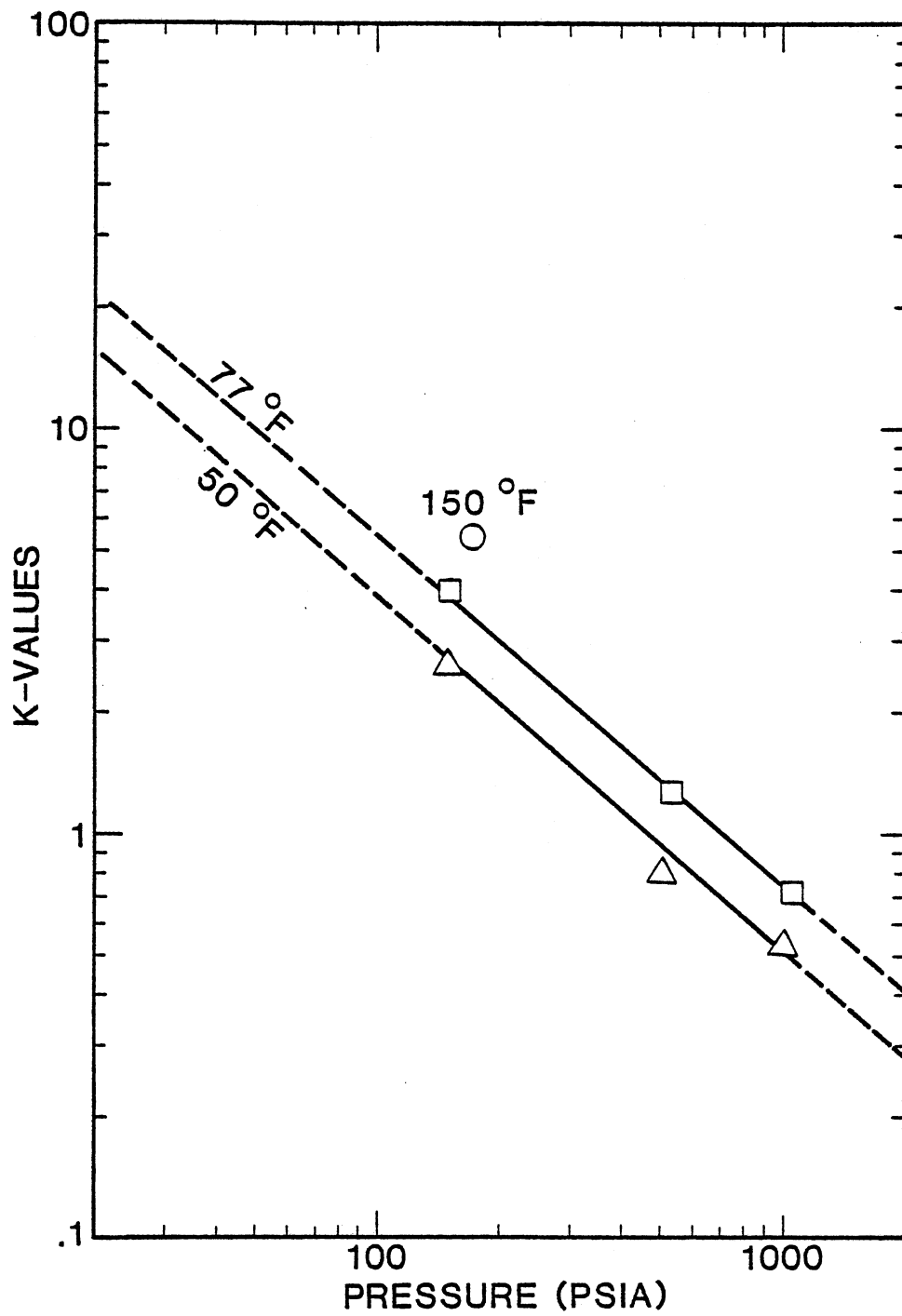


Figure 4. K-values for Carbon Dioxide in Selexol

TABLE XI
EXPERIMENTAL K-VALUES OF CARBON DIOXIDE
IN SULFOLANE

Total Pressure (psia)	Temperature (°F)	% CO ₂ Initially	% CO ₂ Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{CO₂}	Liquid Mole Fraction X _{CO₂}	K-value
153.79	49.5	12.48	10.4	96.0	1.04x10 ⁻¹	1.20x10 ⁻²	8.6667
512.29	49.2	9.82	7.79	100.0	7.79x10 ⁻²	3.23x10 ⁻²	2.4118
152.79	77.4	13.10	10.71	95.0	1.07x10 ⁻¹	1.04x10 ⁻²	10.2981
530.44	77.9	9.72	8.07	95.0	8.07x10 ⁻²	2.70x10 ⁻²	2.9889
159.33	145.4	14.04	12.29	100.0	1.23x10 ⁻¹	8.51x10 ⁻³	14.4418

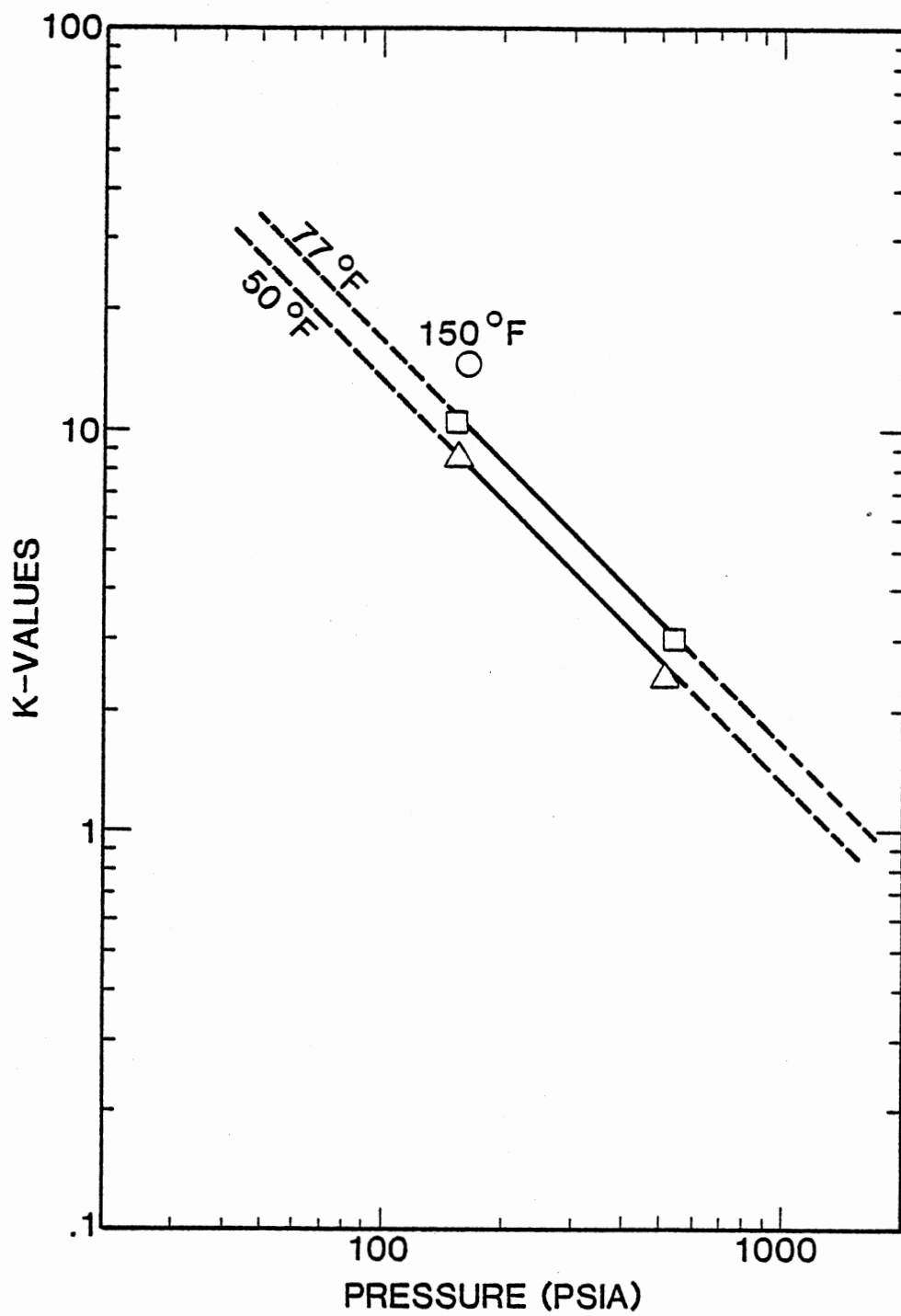


Figure 5. K-values for Carbon Dioxide in Sulfolane

TABLE XII
 EXPERIMENTAL K-VALUES OF HYDROGEN SULFIDE
 IN PROPYLENE CARBONATE

Total Pressure (psia)	Temperature (°F)	% H ₂ S Initially	% H ₂ S Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{H₂S}	Liquid Mole Fraction X _{H₂S}	K-value
155.68	48.5	13.24	5.55	95.0	5.55x10 ⁻²	3.24x10 ⁻²	1.7130
515.4	48.8	9.35	4.04	96.0	4.04x10 ⁻²	7.31x10 ⁻²	0.5527
158.21	83.7	13.22	6.21	105.0	6.21x10 ⁻²	2.72x10 ⁻²	2.2831
166.38	146.3	14.65	9.76	95.0	9.76x10 ⁻²	2.11x10 ⁻²	4.6256

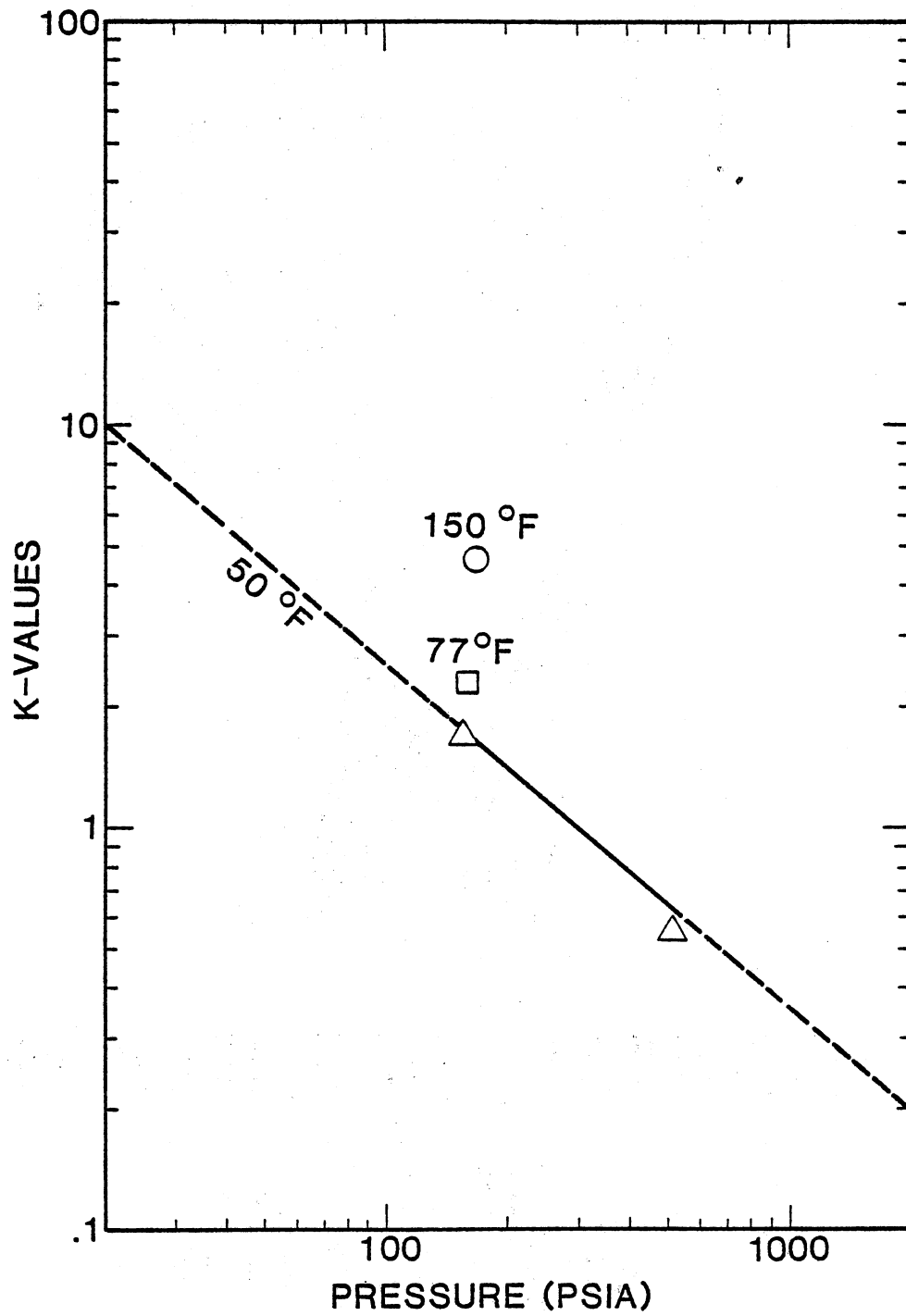


Figure 6. K-values for Hydrogen Sulfide in Propylene Carbonate

TABLE XIII
 EXPERIMENTAL K-VALUES OF HYDROGEN SULFIDE
 IN SELEXOL

Total Pressure (psia)	Temperature (°F)	% H ₂ S Initially	% H ₂ S Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{H₂S}	Liquid Mole Fraction X _{H₂S}	K-value
148.8	45.2	13.66	2.95	96.5	2.95x10 ⁻²	1.04x10 ⁻¹	0.2837
497.33	47.9	9.79	2.59	100.0	2.59x10 ⁻²	2.03x10 ⁻¹	0.1276
151.33	77.0	14.57	4.67	97.0	4.67x10 ⁻²	9.45x10 ⁻²	0.4942
495.38	74.1	10.29	3.20	95.0	3.20x10 ⁻²	1.90x10 ⁻¹	0.1684
161.43	148.4	15.73	8.13	100.0	8.13x10 ⁻²	7.08x10 ⁻²	1.1483

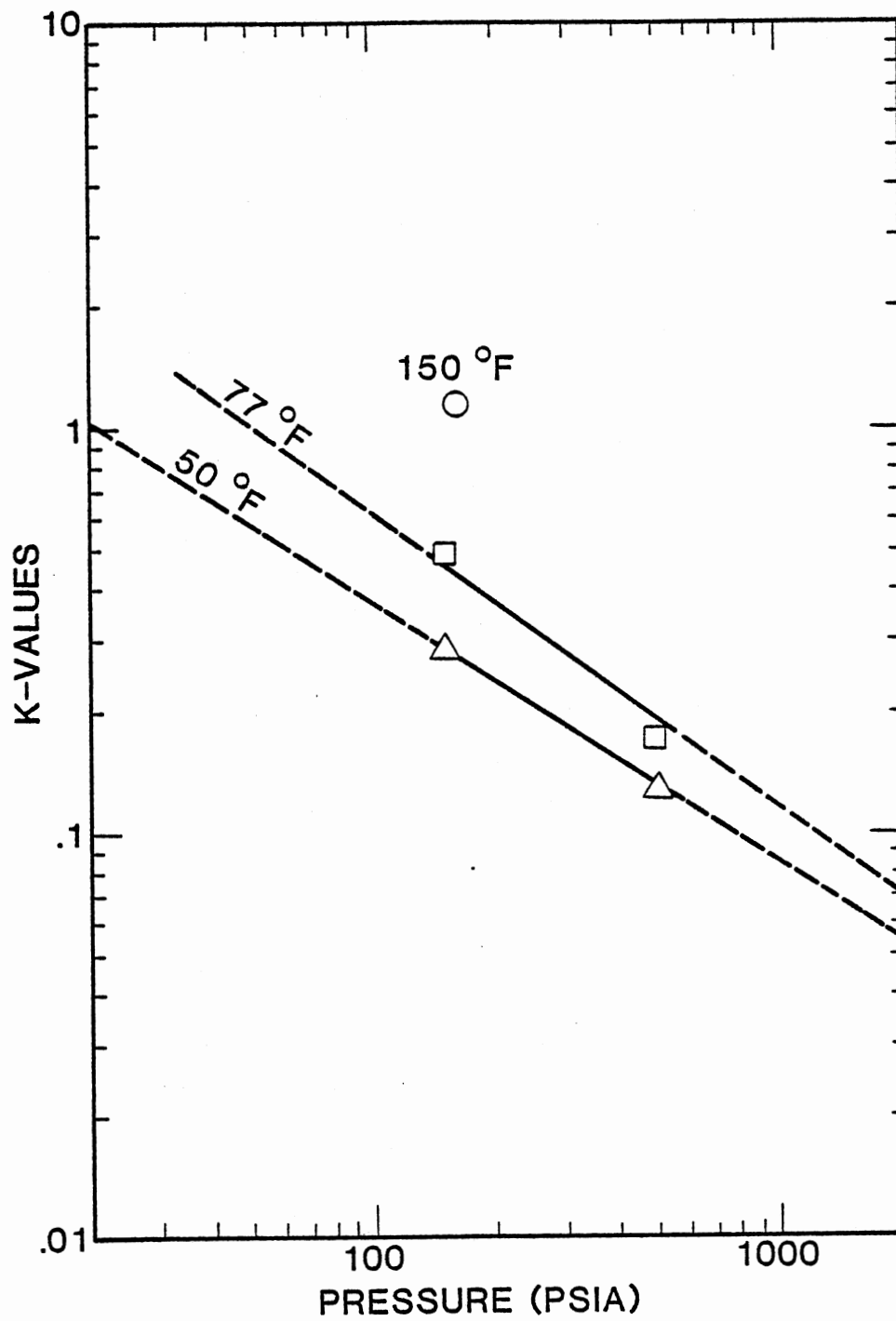


Figure 7. K-values for Hydrogen Sulfide in Selexol

TABLE XIV
EXPERIMENTAL K-VALUES OF HYDROGEN SULFIDE
IN SULFOLANE

Total Pressure (psia)	Temperature (°F)	% H ₂ S Initially	% H ₂ S Finally	Volume of Solvent (ml.)	Vapor Mole Fraction Y _{H₂S}	Liquid Mole Fraction X _{H₂S}	K-value
148.56	44.7	14.30	5.92	100.0	5.92x10 ⁻²	3.77x10 ⁻²	1.5703
518.36	41.5	9.72	3.18	101.0	3.18x10 ⁻²	8.33x10 ⁻²	0.3818
156.23	73.2	14.72	6.26	96.0	6.26x10 ⁻²	3.94x10 ⁻²	1.5888
516.23	73.4	9.98	4.59	94.0	4.59x10 ⁻²	8.14x10 ⁻²	0.5639
166.2	142.3	15.34	9.37	97.0	9.37x10 ⁻²	2.83x10 ⁻²	3.3110

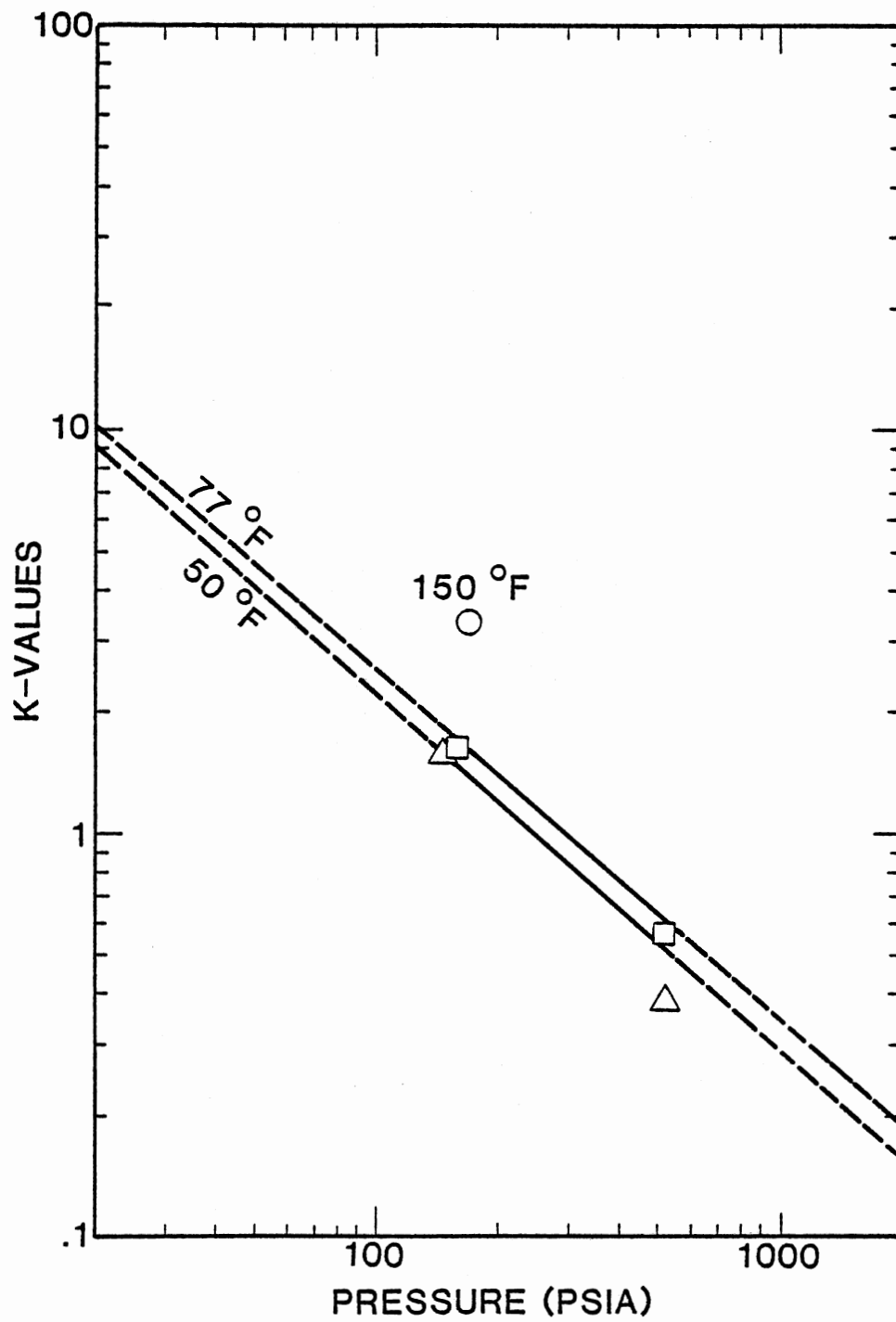


Figure 8. K-values for Hydrogen Sulfide in Sulfolane

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

This study consists of developing a simple procedure and an investigation of the vaporization equilibrium ratios of carbon dioxide and hydrogen sulfide in physical solvents. A simple procedure using a single equilibrium cell was developed for the determination of the K-values for the components and conditions of interest in this study. The method employed using a single equilibrium cell and sampling only the vapor phase.

The following conclusions were made from this study:

1. The technique developed and the apparatus designed were sound as illustrated by the consistency and the reliability of the data taken.
2. For carbon dioxide K-values in sulfolane, propylene carbonate and selexol comparisons, the order is sulfolane > propylene carbonate > selexol except for the measurements at 150°F where propylene carbonate values are higher than sulfolane.
3. For hydrogen sulfide K-values in sulfolane, propylene carbonate and selexol, the order is propylene carbonate > sulfolane > selexol.
4. Out of the three physical solvents investigated,

selexol is the most effective for both hydrogen sulfide and carbon dioxide removal from sour gas streams as reflected from the results of K-values determinations.

The following recommendations are made from the results of this study for future work in this area of research:

1. An attempt to house the whole experimental set up in a temperature control environment as opposed to taking the cell out each time for sampling should be considered to increase the accuracy of the measurements.

2. A mechanical device for mixing or shaking the equilibrium cell content should be introduced to make the rocking mechanism simple and more uniform.

3. The Ruska pump should be replaced if at all possible because the packing is worn-out and caused frequent leakages through the packing nut. Moreover, this change is recommended to make the introduction of the solvent easier.

4. To substantiate the assumption that no appreciable amount of methane dissolves in the solvents, attempts should be made to sample the liquid and check methane K-values.

BIBLIOGRAPHY

1. Bhattacharyya, Dibakar; and G. Thodos, J. Chem. Eng. Data, 9, 530 (1964).
2. Bradford, M. L., and G. Thodos, J. Chem. Eng. Data, 12, 373 (1967).
3. Brewer, J., N. Rodewald, and F. Kurata, AIChE J., 7, 13 (1961).
4. Buckingham, P. A., Hydrocarbon Processing & Petroleum Refiner, 43 (14), 113 (1964).
5. Casteel, J. F., and P. G. Sears, J. Chem. Eng. Data, 19, 196 (1974).
6. Catherall, N. F., and A. G. Williamson, J. Chem. Eng. Data, 16, 335 (1971).
7. Chen, N. H., J. Chem. Eng. Data, 10, 207 (1975).
8. Chool, J. K., and M. J. Joncich, J. Chem. Eng. Data, 16, 87 (1971).
9. Dalager, P., J. Chem. Eng. Data, 14, 298 (1969).
10. Davalos, J., W. R. Anderson, R. E. Phelps, and A. J. Kidnay, J. Chem. Eng. Data, 21, 81 (1976).
11. Donnelly, H. G., and D. L. Katz, Ind. Eng. Chem., 46, 511 (1954).
12. Douslin, D. H., P. H. Harrison, R. T. Moore, and J. P. McCullough, J. Chem. Eng. Data, 9, 358 (1964).
13. Gibbard, H. F., and J. L. Creek, J. Chem. Eng. Data, 19, 308 (1974).
14. Gonzalez, M. H. and A. L. Lee, J. Chem. Eng. Data, 13, 172, (1968).
15. Gordon, J. S., J. Chem. Eng. Data, 6, 190 (1961).
16. GPSA Engineering Data Book, 9th Ed. (revised) Gas Processors Suppliers Association (1976).

17. Harrison, R. H., R. T. Moore, and D. R. Douslin, J. Chem. Eng. Data, 18, 131 (1973).
18. Hensel, W. E. Jr., and F. E. Massoth, J. Chem. Eng. Data, 9, 352 (1964).
19. Isaacs, E. E., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 22, 71 (1971).
20. Isaacs, E. E., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 22, 317 (1977).
21. Isaacs, E. E., F. D. Otto, and A. E. Mather, The Canadian J. Chem. Eng., 55, 751 (1977).
22. Jones, J. H., H. R. Froning, and E. E. Claytor, Jr., J. Chem. Eng. Data, 4, 85 (1959).
23. Katz, D. L., D. Cornell, R. Kobayashi, F.H. Roettmann, J. A. Vary, J. R. Elenbass, R. Jack, and C. F. Weinaug, Handbook of Natural Gas Engineering, McGraw Hill Book (1959).
24. Katz, D. L., and K. H. Hachmuth, Ind. Eng. Chem., 29, 1072 (1937).
25. Kay, W. B., and G. M. Rambosek, Ind. Eng. Chem., 45, 221 (1953).
26. Kay, W. B., and D. B. Brice, Ind. Eng. Chem. 45, 615 (1953).
27. Kohn, J. P., and F. Kurata, AIChE J., 2, 211 (1958).
28. Kohn, J. P., and F. Kurata, J. Chem. Eng. Data, 4, 33 (1959).
29. Lannung, A. and J. C. Gjaldbaek, Acta Chemica Scandinavica, 14, 1124 (1960).
30. Lawson, D. J., and A. W. Garst, J. Chem. Eng. Data, 21, 20 (1976).
31. Lawson, D. J., and A. W. Garst, J. Chem. Eng. Data, 21, 30 (1976).
32. Lee, L. H., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 17, 465 (1972).
33. Lee, L. H., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 18, 71 (1973).

34. Lee, L. H., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 18, 420 (1973).
35. Lee, L. H., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 20, 161 (1975).
36. Lee, L. H., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 21, 207 (1976).
37. Lewis, L. C., and W. J. Fredericks, J. Chem. Eng. Data, 13, 482 (1968).
38. Liley, P. E., J. Chem. Eng. Data, 4, 238 (1959).
39. Lu, B. C.-Y., J. A. Ruether, C. Hsi, and C.-H Chiu, J. Chem. Eng. Data, 18, 241 (1973).
40. Maddox, R. N., Gas and Liquid Sweetening, 2nd Ed., J. M. Campbell (1974).
41. Martin, J. L., F. D. Otto, and A. E. Mather, J. Chem. Eng. Data, 23, 163 (1978).
42. Martin, J. L., J. Chem. Eng. Data, 8, 311 (1963).
43. Mikhail, S. Z., and W. R. Kimel, J. Chem. Eng. Data, 6, 533 (1961).
44. Miller, G. A., J. Chem. Eng. Data, 9, 418 (1964).
45. Mraw, S. C., S-C Hwang and R. Kobayashi, J. Chem. Eng. Data, 23, 135 (1978).
46. Muhlbauer, H. G., and P. R. Monaghan, The Oil and Gas J., 139 (1957).
47. Murphy, J. A., and G. L. Gains, Jr., J. Chem. Eng. Data, 19, 359 (1974).
48. McDowell, R. S. and F. H. Kruse, J. Chem. Eng. Data, 8, 547 (1963).
49. Nakanishi, K., J. Chem. Eng. Data, 8, 355 (1963).
50. Ohgaki, K., and T. Katayama, J. Chem. Eng. Data, 21, 53 (1976).
51. Perry, H. R., and C. H. Chilton, Chemical Engineering Handbook, 5th Ed., McGraw Hill (1976).
52. Petrov, V. M., and L. E. Sandler, Russian J. Physical Chem., 49 (11), 1649 (1957).

53. Rackett, H. G., J. Chem. Eng. Data, 15, 514 (1970).
54. Raymond, J. L., J. Chem. Eng. Data, 7, 190 (1962).
55. Reamer, H. H., B. H. Sage, and W. N. Lacey, Ind. Eng. Chem., 43, 976 (1951).
56. Riddick, J. A., and W. B. Bunger, Physical Properties and Method of Purification of Organic Solvents, 3rd Ed., John Wiley & Sons (1970).
57. Roberts, L. R., and J. J. M^cKetta, J. Chem. Eng. Data, 8, 478 (1963).
58. Robinson, D. B., and J. A. Bailey, The Canadian J. Chem. Eng., 35, 151 (1957).
59. Robinson, D. B., R. E. Hughes, and J. A. W. Sandercock, The Canadian J. Chem. Eng., 143 (1964).
60. Robinson, D. B., and T. R. Krishman, J. Chem. Eng. Data, 22, 85 (1977).
61. Robinson, D. B., A. P. Lorenzo, and C. A. Macrygeorgos, The Canadian J. Chem. Eng., 37, 212 (1959).
62. Silverberg, P. M. and I. A. Wenzel, J. Chem. Eng. Data, 10, 363 (1965).
63. Souders, M. Jr., C. W. Selheimer, and G. G. Brown, Ind. Eng. Chem., 24, 517 (1932).
64. Spencer, C. F., and R. P. Danner, J. Chem. Eng. Data, 18, 230 (1973).
65. Van Huff, N. E., G. Houghton, and J. Coul, J. Chem. Eng. Data, 8, 336 (1963).
66. Vei, D., S. F. Shakhova, L. I. Titelman, and R. I. Maslenkova, International Chem. Eng., 10, 639 (1970).
67. Vennix, A. J., T. W. Leland, Jr., and R. Kobayashi, J. Chem. Eng. Data, 15, 238 (1970).
68. Wang, R. H., and J. J. M^cKetta, J. Chem. Eng. Data, 9, 30 (1964).
69. Wiesepape, C. F., H. T. Kennedy, and P. B. Crawford, J. Chem. Eng. Data, 22, 260 (1977).
70. Woertz, B. B., The Canadian J. Chem. Eng., 50, 425 (1972).

71. Yarborough, L., J. Chem. Eng. Data, 17, 129 (1972).

APPENDIX A

PHYSICAL PROPERTIES OF MATERIALS

TABLE XV
CRITICAL PROPERTIES OF GASES

Gas	Critical Pressure P_c (psia)	Critical Temperature T_c (°R)
H ₂ S	1306	672.7
CO ₂	1073	548
CH ₄	667.8	343.37

TABLE XVI
DENSITIES OF SOLVENTS

Solvents	Molecular Weight	Density at 50°F (gm./ml.)	Density at 77°F (gm./ml.)	Density at 150°F (gm./ml.)
Propylene Carbonate	102.09	1.212	1.198	1.157
Sulfolane	120.17	1.2447	1.2229	1.1569
Selexol	222.0	1.0296	1.0164	0.9808

APPENDIX B

CALIBRATION OF THERMOCOUPLE

CALIBRATION OF THERMOCOUPLE

A cromel-alumel thermocouple was used to measure the system temperature for this study. The thermocouple was calibrated in a constant temperature bath. An NBS platinum resistance thermometer was used to measure the temperature of the bath.

The thermocouple was calibrated by reading the temperature from the platinum resistance thermometer and reading the emf of the thermocouple. Figure 9 shows a plot of the difference between the thermocouple reading and the reading of the platinum resistance thermometer.

The data were fitted to a quadratic equation represented at the bottom of Table XVII by a regression analysis method.

Define T_c = corrected temperature

T_p = temperature read from table

Then $T_c = T_p + \Delta T$

TABLE XVII
CALIBRATION OF CHROMEL-ALUMEL THERMOCOUPLE DATA

Thermocouple Number	Thermocouple Table Reading T_p (°C)	Platinum Resistance Thermocouple Reading T_c (°C)	Difference ΔT °C
1	26.894	27.035	0.141
2	26.875	27.035	0.160
3	26.875	27.035	0.160
1	53.333	53.563	0.230
2	53.333	53.564	0.231
3	53.333	53.561	0.228
1	112.714	112.792	0.078
2	112.714	112.790	0.076
3	112.708	112.789	0.081
1	145.250	145.318	0.068
2	145.250	145.317	0.067
3	145.250	145.320	0.070
1	162.575	162.866	0.291
2	162.575	162.867	0.292
3	162.575	162.867	0.292

$$\text{Quadratic Regression} = a_0 + a_1 T_p + a_2 T_p^2$$

$$\text{Where } a_0 = 0.345355$$

$$a_1 = 0.005912$$

$$a_2 = 0.000032$$

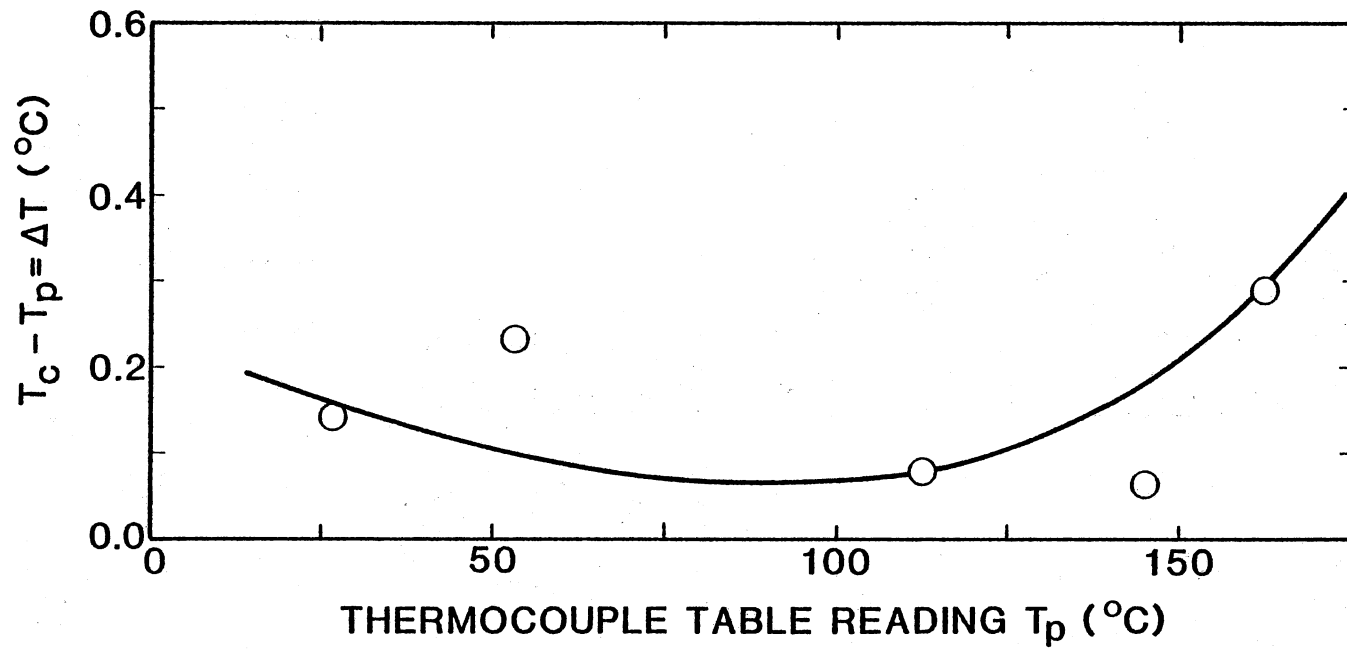


Figure 9. Deviation of Thermocouple Readings From Thermocouple Table Readings as a Function of Temperature

APPENDIX C

PRESSURE GAUGE CALIBRATION DATA

PRESSURE GAUGE CALIBRATION DATA

The calibration of the pressure gauge were carried out using Ruska Model 2400 HL Dead weight tester.

TABLE XVIII
HTL PRESSURE GAUGE CALIBRATION DATA

Model No: 101FTM13A41			Serial No: 579108
Applied Pressure (psi)	Indicated Pressure (Increasing) (psi)	Indicated Pressure (Decreasing) (psi)	
0	0	0	
400	398	403	
800	798	803	
1000	998	1003	
1200	1199	1203	
1600	1599	1602	
2000	1996	1996	
Model No: 101FTM13A41			Serial No: 107896
0	0	0	
400	400	401	
800	799	802	
1000	999	1002	
1200	1200	1203	
1600	1600	1602	
2000	1998	1998	

APPENDIX D

EXPERIMENTAL RAW DATA

TABLE XIX
 RAW DATA FOR OBTAINING K-VALUES OF CO₂
 IN CO₂-CH₄-PROPYLENE CARBONATE

CO ₂ Feed Pressure (psia)	Total Feed Pressure With CH ₄ (psia) ⁴	Temperature of Run (°F)	Volume of Solvent Used (ml.)	Equilibrium Total Pressure (psia)
18.7	140.2	48.2	100.0	145.7
46.3	474.3	48.2	95.0	496.3
93.3	942.3	48.2	95.0	993.3
20.93	140.26	74.3	98.0	145.26
50.32	486.32	75.2	98.0	520.32
100.26	990.26	74.8	98.0	1050.26
24.33	144.82	148.2	98.0	153.32
60.25	505.25	146.35	96.0	543.25
113.25	1016.25	145.1	96.0	1084.25

TABLE XX
 RAW DATA FOR OBTAINING K-VALUES OF
 CO₂ IN CO₂-CH₄-SELEXOL

CO ₂ Feed Pressure (psia)	Total Feed Pressure With CH ₄ (psia)	Temperature of Run (°F)	Volume of Solvent Used (ml.)	Equilibrium Total Pressure (psia)
18.7	146.23	47.0	98.0	149.23
46.45	483.45	46.3	97.5	504.45
93.23	948.23	47.0	97.0	1000.23
20.98	143.31	85.2	102.0	150.31
50.31	496.31	81.2	100.0	527.31
100.33	993.33	78.7	97.0	1057.33
23.12	160.26	147.6	95.0	169.26
55.21	504.21	145.0	95.0	535.21
114.26	1015.26	145.6	95.5	1086.26

TABLE XXI
 RAW DATA FOR OBTAINING K-VALUES OF
 CO₂ IN CO₂-CH₄-SULFOLANE

CO ₂ Feed Pressure (psia)	Total Feed Pressure With CH ₄ (psia)	Temperature of Run (°F)	Volume of Solvent Used (ml.)	Equilibrium Total Pressure (psia)
18.79	145.29	49.5	96.0	153.79
46.29	478.3	49.2	100.0	512.29
94.25	944.29	47.5	98.0	1018.29
20.96	140.29	77.4	95.0	152.79
50.44	494.44	77.9	95.0	530.44
100.44	988.44	77.9	95.0	1066.44
23.2	149.33	145.4	100.0	159.33
56.31	527.31	144.7	95.0	564.31
113.31	1066.31	141.7	95.0	1138.31

TABLE XXII

RAW DATA FOR OBTAINING K-VALUES OF H₂S
IN H₂S-CH₄-PROPYLENE CARBONATE

H ₂ S Feed Pressure (psia)	Total Feed Pressure With CH ₄ (psia)	Temperature of Run (°F)	Volume of Solvent Used (ml.)	Equilibrium Total Pressure (psia)
18.68	154.68	48.5	95.0	155.68
45.4	496.4	48.8	96.0	515.4
93.4	970.4	48.8	100.0	1023.4
20.88	158.71	83.7	105.0	158.21
50.21	498.21	85.0	100.0	510.21
101.18	987.18	87.4	97.0	1052.18
23.25	162.38	146.3	95.0	166.38
56.41	530.41	147.1	100.0	557.41
113.38	1043.38	146.7	95.0	1098.38

TABLE XXIII
 RAW DATA FOR OBTAINING K-VALUES OF
 H₂S IN H₂S-CH₄-SELEXOL

H ₂ S Feed Pressure (psia)	Total Feed Pressure With CH ₄ (psia)	Temperature of Run (°F)	Volume of Solvent Used (ml.)	Equilibrium Total Pressure (psia)
18.8	153.8	45.2	96.5	148.8
45.33	488.33	47.9	100.0	497.33
93.3	975.3	50.0	102.0	1012.3
21.0	155.33	77.0	97.0	151.33
50.38	490.38	74.1	95.0	495.38
100.43	1013.43	71.2	94.5	1033.43
23.3	160.43	148.4	100.0	161.43
56.33	507.33	145.8	95.0	517.33
113.33	1062.33	147.1	95.0	1098.33

TABLE XXIV
 RAW DATA FOR OBTAINING K-VALUES OF
 H₂S IN H₂S-CH₄-SULFOLANE

H ₂ S Feed Pressure (psia)	Total Feed Pressure With CH ₄ (psia) ⁴	Temperature of Run (°F)	Volume of Solvent Used (ml.)	Equilibrium Total Pressure (psia)
19.06	148.06	44.7	100.0	148.56
46.36	500.36	41.5	101.0	518.36
93.36	990.36	41.5	100.0	1043.36
20.9	155.73	73.2	96.0	156.23
50.23	497.23	73.4	94.0	516.23
99.56	1016.56	74.3	97.0	1096.56
23.07	161.7	142.3	97.0	166.2
56.43	492.45	147.6	96.0	515.43
113.2	1090.2	145.4	95.0	1158.2

APPENDIX E

SAMPLE CALCULATIONS OF K-VALUES
DETERMINATION

SAMPLE CALCULATIONS

System = CO₂-CH₄-propylene carbonate

Temperature of run = 508.2°R

Volume of equilibrium cell = 0.998 liter

Density of propylene carbonate at the operating
condition = 1.212 gm./ml.

$$P_{\text{CO}_2} = 93.3 \text{ psia}$$

$$P_{\text{Total}} = 954.3 \text{ psia}$$

$$P_{\text{Total}} \text{ after taking sample} = 942.3 \text{ psia}$$

Compute moles of CO₂ introduced initially:

$$T_r = \frac{T}{T_c} = \frac{508.2}{548} = 0.93$$

$$P_r = \frac{P}{P_c} = \frac{93.3}{1073} = 0.087$$

From reference (40), Fig. 2.13

$$Z = 0.95$$

$$\begin{aligned} n_{\text{CO}_2} &= \frac{PV}{ZRT} \\ &= \frac{(93.3 \text{ psia})(0.998 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.95)(10.73 \frac{\text{psia-ft}^3}{\text{lbmole } ^\circ\text{R}})(508.2^\circ\text{R})} \\ &= 6.36 \times 10^{-4} \text{ lbmole} \end{aligned}$$

Compute total moles of gas initially:

From gas chromatograph analysis of the gas mixture before the introduction of the solvent

$Y_{\text{CO}_2} = 0.0934$ $Y_{\text{CH}_4} = 0.906$
--

$$P_{pc} = Y_i P_{ci} + Y_j P_{cj}$$

$$T_{pc} = Y_i T_{ci} + Y_j T_{cj}$$

$$P_{pc} = (0.0934)(1073) + (0.906)(667.8) = 705.25$$

$$T_{pc} = (0.0934)(548) + (0.906)(343.37) = 362.28 \text{ } ^\circ\text{R}$$

Adjusting the pseudo critical temperature for the presence of CO_2 in natural gas

$$T_{pc}' = T_{pc} - \epsilon$$

$$T_{pc}' = \text{adjusted pseudo critical temperature, } ^\circ\text{R}$$

ϵ = pseudo critical adjustment factor.

From figure 2.14, reference (40),

$$\epsilon = 11.5 \text{ } ^\circ\text{R for } 9.34\% \text{ CO}_2, 0\% \text{ H}_2\text{S}$$

$$T_{pc}' = 362.26 - 11.5 = 351.28 \text{ } ^\circ\text{R}$$

Adjusting the pseudo critical pressure for the presence of CO_2 in natural gas

$$P_{pc}' = \frac{P_{pc} \times T_{pc}'}{T_{pc} + B(1-B)\epsilon}$$

where P_{pc}' = adjusted pseudo critical pressure; psia

B = mole fraction of H₂S in the sour gas

$$P_{pc}' = P_{pc} \times \frac{T_{pc}'}{T_{pc}}$$

$$= \frac{(705.25)(351.28)}{362.28} = 683.84 \text{ psia}$$

$$P_r = \frac{P}{P_{pc}'} = \frac{942.3}{683.84} = 1.38$$

$$T_r = \frac{T}{T_{pc}'} = \frac{508.2}{351.28} = 1.45$$

From reference (40), figure 2.13,

$$Z = 0.85$$

$$N_{\text{Total}} = \frac{PV}{ZRT}$$

$$= \frac{(942.3 \text{ psia})(0.998 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.85)(10.73 \frac{\text{psia-ft}^3}{\text{lbmole}^\circ\text{R}})(508.2^\circ\text{R})}$$

$$= 7.18 \times 10^{-3} \text{ lbmole}$$

G.C. calculation of the amount of CO₂ introduced initially:

$$= (0.0934)(7.18 \times 10^{-3}) = 6.71 \times 10^{-4} \text{ lbmole}$$

Volume of propylene carbonate used = 95.0 ml.

Number of moles:

$$95 \text{ ml.} \left| \frac{1.212 \text{ gm.}}{\text{ml.}} \right| \frac{\text{gmmole}}{102.09 \text{ gm.}} \left| \frac{1 \text{ lbmole}}{454 \text{ gmmole}} \right|$$

$$= 2.48 \times 10^{-3} \text{ lbmole}$$

Mole fraction of CO₂ in the vapor phase from gas chromatograph analysis at equilibrium:

$Y_{\text{CO}_2} = 0.0724$ $Y_{\text{CH}_4} = 0.928$
--

Compute N_{Total} in the vapor phase after the solvent is added and equilibrium is established:

$$P_{\text{Total}} \text{ (Equilibrium)} = 993.3 \text{ psia}$$

$$P_{\text{pc}} = (0.0724)(1073) + (0.928)(667.8) = 697.40 \text{ psia}$$

$$T_{\text{pc}} = (0.0724)(548) + (0.928)(343.37) = 358.32$$

$$\epsilon = 10^\circ\text{R for } 7.24\% \text{ CO}_2, 0\% \text{ H}_2\text{S}$$

$$T_{\text{pc}}' = 358.32 - 10 = 348.32^\circ\text{R}$$

$$P_{\text{pc}}' = \frac{(697.4)(348.32)}{358.32} = 677.94 \text{ psia}$$

$$P_r = \frac{993.3}{677.94} = 1.47$$

$$T_r = \frac{508.2}{348.32} = 1.46$$

$$Z = 0.845$$

Volume of vapor phase:

$$V = 0.998 \text{ liters} - \frac{95}{1000} \text{ liters} = 0.903 \text{ liters}$$

$$N_{\text{Total}} = \frac{(993.3 \text{ psia})(0.903 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.845)(10.73 \frac{\text{psia-ft}^3}{\text{lbmole}^\circ\text{R}})(508.2^\circ\text{R})}$$

$$= 6.89 \times 10^{-3} \text{ lbmole}$$

Moles of CO_2 in the gas phase at equilibrium:

$$(0.0724)(6.89 \times 10^{-3}) = 4.99 \times 10^{-4} \text{ lbmole}$$

Moles of CO_2 absorbed by propylene carbonate:

$$= \begin{bmatrix} \text{Moles of CO}_2 \\ \text{introduced} \\ \text{initially} \end{bmatrix} - \begin{bmatrix} \text{Moles of CO}_2 \\ \text{in the gas phase} \\ \text{at equilibrium} \end{bmatrix} = n_{\text{CO}_2}$$

$$= 6.71 \times 10^{-4} - 4.99 \times 10^{-4} = 1.72 \times 10^{-4} \text{ lbmole}$$

Mole fraction of CO_2 (x_{CO_2}) in propylene carbonate assuming

no CH_4 dissolves in propylene carbonate.

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{CO}_2} + n_{\text{propylene carbonate}}}$$

$$= \frac{1.72 \times 10^{-4}}{1.72 \times 10^{-4} + 2.48 \times 10^{-3}} = 6.49 \times 10^{-2}$$

$$K_{\text{CO}_2} = \frac{y_{\text{CO}_2}}{x_{\text{CO}_2}} = \frac{7.24 \times 10^{-2}}{6.49 \times 10^{-2}} = \boxed{1.1156}$$

APPENDIX F

SAMPLE CALCULATION OF CO₂ SOLUBILITY
IN PROPYLENE CARBONATE

(A) Solubility Calculated from Pressure Drop After
the introduction of the Solvent

System = CO₂-propylene carbonate

Temperature of run = 559.5°R

Density of propylene carbonate at the operating
condition = 1.19022 gm./ml.

Volume of the equilibrium cell = 1 liter

Initial pressure of CO₂ = 485.4 psia

Final pressure of CO₂ = 307.4 psia

Volume of propylene carbonate used = 355 ml.

Final volume of equilibrium cell V_f:

$$V_f = 0.998 - \frac{355}{1000} = 0.645 \text{ liters}$$

CO₂ compressibility factor at the initial condition

$$= 0.8362$$

CO₂ compressibility factor at the final condition

$$= 0.8960$$

Compute moles of CO₂ initially:

$$n = \frac{PV}{ZRT}$$

$$n_{i\text{CO}_2} = \frac{(485.4 \text{ psia})(0.998 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.8362)(10.73 \frac{\text{psia-ft}^3}{\text{lbmole}^\circ\text{R}})(559.5^\circ\text{R})}$$

$$= 3.41 \times 10^{-3} \text{ lbmole}$$

Compute moles of CO₂ finally:

$$n_{f, \text{CO}_2} = \frac{(307.4 \text{ psia})(0.645 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.8960)(10.73 \frac{\text{psia-ft}^3}{\text{lbmole}^\circ\text{R}})(559.5^\circ\text{R})}$$

$$= 1.30 \times 10^{-3} \text{ lbmole}$$

Moles of CO₂ dissolved in propylene carbonate

$$3.41 \times 10^{-3} - 1.30 \times 10^{-3} = 2.11 \times 10^{-3} \text{ lbmole}$$

Moles of propylene carbonate used:

355 ml.	1.19022 gm.	gmmole	lbmole
	ml.	102.09 gm.	454 gmmole

$$= 9.12 \times 10^{-3} \text{ lbmole}$$

$$= \text{mole ratio} = \frac{\text{mole of CO}_2 \text{ in liquid}}{\text{mole of propylene carbonate}}$$

$$= \frac{2.11 \times 10^{-3}}{9.12 \times 10^{-3}} = 0.231$$

With the final pressure of 307.4 psia = 2119.44 kp

$$\alpha = 0.214 \text{ (see figure 10, the work of Isaac et al.²¹)}$$

$$\text{Deviation} = \frac{0.231 - 0.214}{0.231} \times 100$$

$$= 7.36\%$$

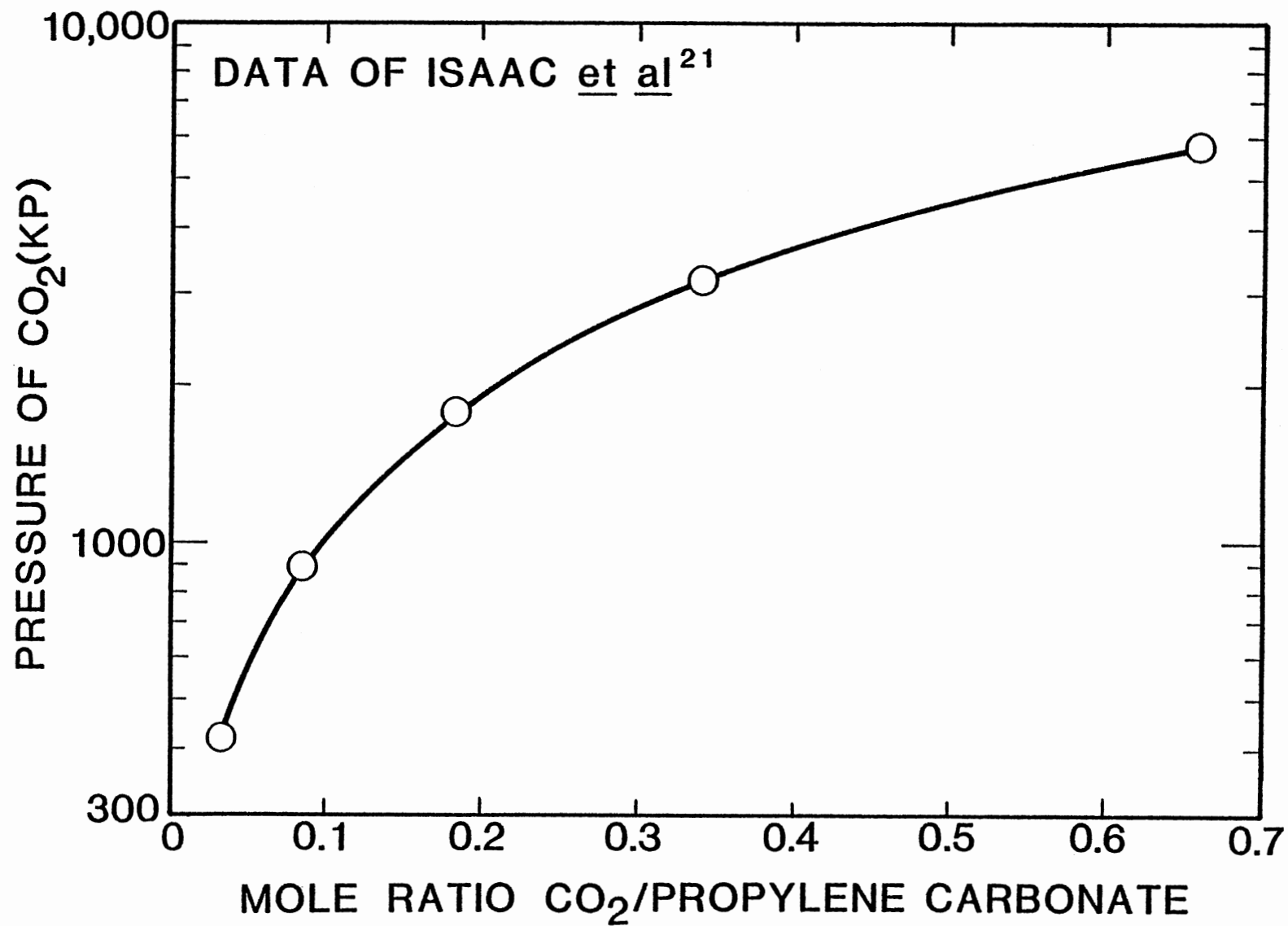


Figure 10. Solubility of CO₂ In Propylene Carbonate At 40°C

(B) Solubility Calculated from G.C. Analysis
 Taking Samples Before and After the
 Introduction of the Solvent

System = $\text{H}_2\text{S}-\text{CH}_4-\text{CO}_2$ -propylene carbonate

Temperature of run = 559.3°R

Density of propylene carbonate at the operating
 condition = 1.19022 gm./ml.

Volume of the equilibrium cell = 1 liter

P_{Total} of the mixture = 1070.43 psia

P_{Total} after taking sample = 1048.43 psia

From gas chromatograph analysis of the gas mixture before
 the introduction of the solvent

$Y_{\text{H}_2\text{S}} = 0.0905$ $Y_{\text{CO}_2} = 0.0866$ $Y_{\text{CH}_4} = 0.8228$

Compute total moles initially

$$P_{\text{pc}} = Y_i P_{ci} + Y_j P_{cj} + Y_k P_{ck}$$

$$T_{\text{pc}} = Y_i T_{ci} + Y_j T_{cj} + Y_k T_{ck}$$

$$P_{\text{pc}} = (0.0905)(1306) + (0.0866)(1073) + (0.8228)(667.8)$$

$$= 760.58 \text{ psia}$$

$$T_{pc} = (0.0905)(672.7) + (0.0866)(548) + (0.8228)(343.37)$$

$$= 390.86^{\circ}\text{R}$$

Adjusting the pseudo critical temperature for the presence of CO_2 and H_2S in natural gas

$$T_{pc}' = T_{pc} - \epsilon$$

From figure 2.14, reference (40),

$$\epsilon = 22.5 \text{ for } 9.05\% \text{ H}_2\text{S}, 8.66\% \text{ CO}_2$$

$$T_{pc}' = 390.86 - 22.5 = 368.36^{\circ}\text{R}$$

$$P_{pc}' = \frac{P_{pc} \times T_{pc}'}{T_{pc} + B(1-B)\epsilon}$$

$$= \frac{(760.58)(368.36)}{390.86 + (0.0905)(1-0.0905)(22.5)}$$

$$= 715.30 \text{ psia}$$

$$P_r = \frac{1048.43}{715.30} = 1.47; \quad T_r = \frac{559.3}{368.36} = 1.52$$

From figure 2.13, reference (40),

$$Z = 0.87$$

$$N_{\text{Total}} = \frac{PV}{ZRT}$$

$$= \frac{(1048.43 \text{ psia})(0.998 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.87)(10.73 \text{ psia-ft}^3)(559.3^{\circ}\text{R})}$$

$$\text{lbmole}^{\circ}\text{R}$$

$$= 7.09 \times 10^{-3} \text{ lbmole}$$

$$\text{Moles of H}_2\text{S initially} = (0.0905)(7.09 \times 10^{-3})$$

$$= 6.42 \times 10^{-4} \text{ lbmole}$$

$$\begin{aligned} \text{Moles of CO}_2 \text{ initially} &= (0.0866)(7.09 \times 10^{-3}) \\ &= 6.14 \times 10^{-4} \text{ lbmole} \end{aligned}$$

Volume of propylene carbonate used = 95 ml.

Number of moles:

$$\begin{array}{r|l|l|l} 95 \text{ ml.} & 1.19022 \text{ gm.} & \text{gm. mole} & 1 \text{ lbmole} \\ & \text{ml.} & 102.09 \text{ gm.} & 454 \text{ gmmole} \\ \hline & & & \end{array}$$

$$= 2.44 \times 10^{-3} \text{ lbmole}$$

Mole fraction of CO₂ and H₂S in the vapor phase from gas chromatograph analysis at equilibrium:

$Y_{\text{H}_2\text{S}}$	=	0.0599
Y_{CO_2}	=	0.0767
Y_{CH_4}	=	0.8635

Compute N_{Total} in the vapor phase after the solvent is added and equilibrium is established:

$$P_{\text{Total}} \text{ (Equilibrium)} = 1095.43 \text{ psia}$$

$$\begin{aligned} P_{\text{pc}} &= (0.0599)(1306) + (0.0767)(1073) + (0.8635)(667.8) \\ &= 737.17 \text{ psia} \end{aligned}$$

$$\begin{aligned} T_{\text{pc}} &= (0.0599)(672.7) + (0.0767)(548) + (0.8635)(343.37) \\ &= 378.83^\circ\text{R} \end{aligned}$$

$$\epsilon = 19^\circ\text{R} \text{ for } 5.99\% \text{ H}_2\text{S}, 7.67\% \text{ CO}_2$$

$$T_{\text{pc}}' = 378.83 - 19 = 359.83^\circ\text{R}$$

$$P_{pc}' = \frac{(737.17)(359.83)}{378.83 + (0.0599)(1-0.0599)(19)}$$

$$= 698.48 \text{ psia}$$

$$P_r = \frac{P}{P_{pc}'} = \frac{1095.43}{698.48} = 1.57$$

$$T_r = \frac{T}{T_{pc}'} = \frac{559.3}{359.83} = 1.55$$

$$Z = 0.89$$

Volume of vapor phase:

$$V = 0.998 \text{ liters} - \frac{95}{1000} \text{ liter} = 0.905 \text{ liters}$$

$$N_{\text{Total}} = \frac{(1095.43 \text{ psia})(0.905 \text{ liters})(0.03532 \text{ ft}^3/\text{liter})}{(0.89)(10.73 \frac{\text{psia-ft}^3}{\text{lbmole}^\circ\text{R}})(559.3^\circ\text{R})}$$

$$= 6.56 \times 10^{-3} \text{ lbmole}$$

Moles of H_2S in the gas phase at equilibrium

$$= (0.0599)(6.56 \times 10^{-3}) = 3.93 \times 10^{-4} \text{ lbmole}$$

Moles of CO_2 in the gas phase at equilibrium

$$= (0.0767)(6.56 \times 10^{-3}) = 5.03 \times 10^{-4} \text{ lbmole}$$

Moles of H_2S in propylene carbonate:

$$6.42 \times 10^{-4} - 3.93 \times 10^{-4} = 2.49 \times 10^{-4} \text{ lbmole}$$

Moles of CO_2 in propylene carbonate:

$$6.14 \times 10^{-4} - 5.03 \times 10^{-4} = 1.11 \times 10^{-4} \text{ lbmole}$$

$$\alpha = \text{mole ratio} = \frac{\text{mole of acid gas in liquid}}{\text{mole of liquid}}$$

$$\alpha_{\text{H}_2\text{S}} = \frac{2.49 \times 10^{-4}}{2.44 \times 10^{-3}} = 0.102$$

$$\alpha_{\text{CO}_2} = \frac{1.11 \times 10^{-4}}{2.44 \times 10^{-3}} = \boxed{0.0455}$$

Partial pressures:

$$P_{\text{H}_2\text{S}} = (0.0599)(1095.43) = 65.62 \text{ psia} = \boxed{452.43 \text{ kp}}$$

$$P_{\text{CO}_2} = (0.0767)(1095.43) = 84.02 \text{ psia} = \boxed{597.30 \text{ kp}}$$

$$\begin{aligned} X_{\text{H}_2\text{S}} &= \frac{2.49 \times 10^{-4}}{2.49 \times 10^{-4} + 1.11 \times 10^{-4} + 2.44 \times 10^{-3}} \\ &= 8.89 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} X_{\text{CO}_2} &= \frac{1.11 \times 10^{-4}}{1.11 \times 10^{-4} + 2.49 \times 10^{-4} + 2.44 \times 10^{-3}} \\ &= 3.96 \times 10^{-2} \end{aligned}$$

$$K_{\text{H}_2\text{S}} = \frac{Y_{\text{H}_2\text{S}}}{X_{\text{H}_2\text{S}}} = \frac{5.99 \times 10^{-2}}{8.89 \times 10^{-2}} = \boxed{0.6738}$$

$$K_{\text{CO}_2} = \frac{Y_{\text{CO}_2}}{X_{\text{CO}_2}} = \frac{7.67 \times 10^{-2}}{3.96 \times 10^{-2}} = \boxed{1.9369}$$

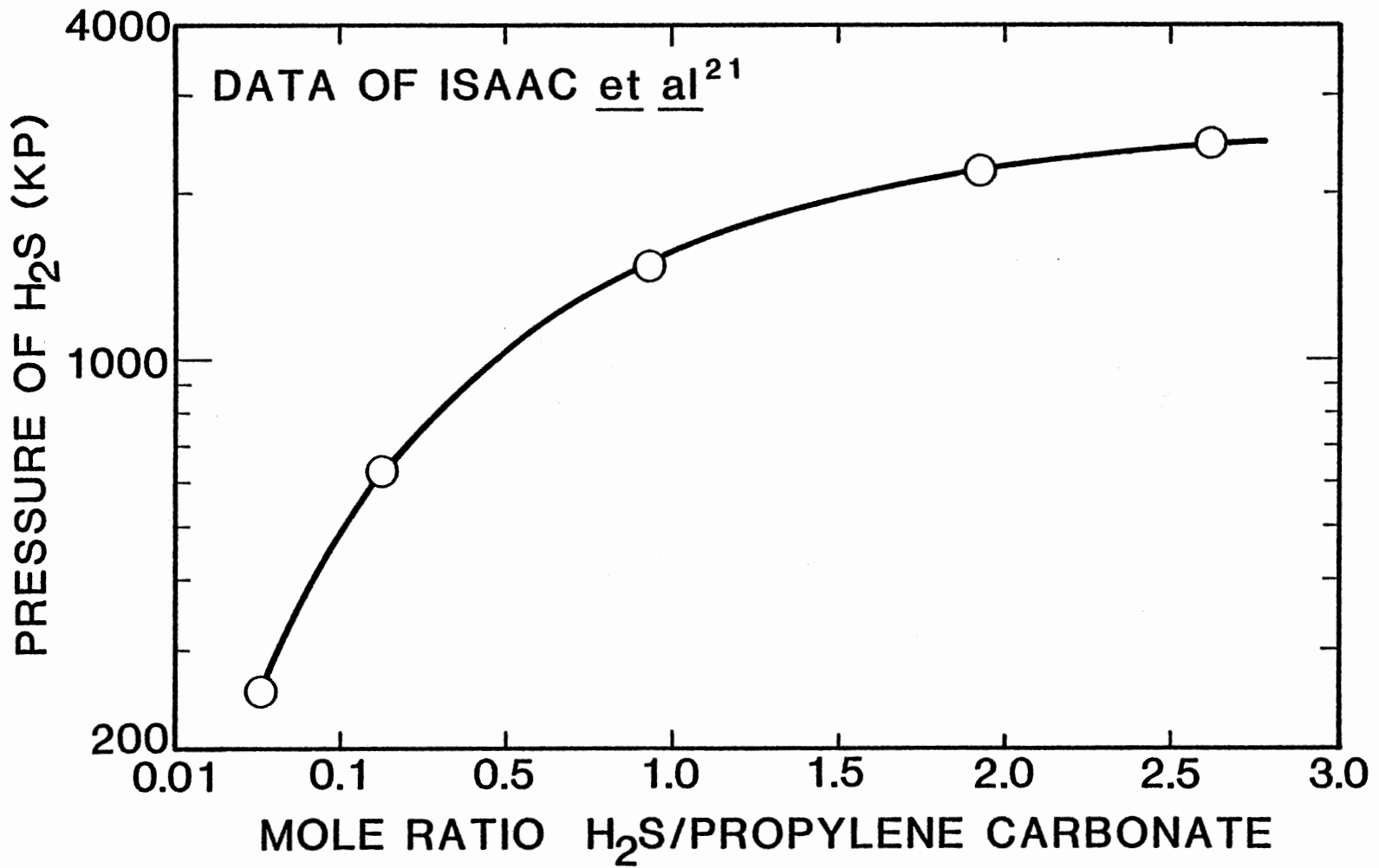


Figure 11. Solubility of H₂S In Propylene Carbonate At 40°C

VITA

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