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LIQUID-VAPOR EQUILIBRIA IN THE TERNARY SYSTEM
METHANE, ETHANE, AND CARBON DIOXIDE AT 250.00°K

By

Robert E. Phelps

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in Partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

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ABSTRACT

A previously constructed experimental apparatus for measuring temperature, pressure and composition was employed to analyze equilibrium data in the ternary system consisting of methane, ethane, and carbon dioxide. This system was investigated over its entire two phase region at 250.00°K and 30.00, 25.00, and 21.00 atmospheres.

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DEDICATION

To my Mom and Dad, and
Larry and Richard

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INTRODUCTION

The composition of phases in equilibrium is of great importance in just about every industrial process one can imagine. The temperature, pressure, and composition relationships in multiphase systems at equilibrium form the basis for the quantitative treatment of all distillation, absorption, and extraction processes.

This thesis is the final stage of a phase equilibrium project to study the $\text{CO}_2 + \text{C}_2\text{H}_6$, the $\text{CO}_2 + \text{CH}_4$, and the $\text{CH}_4 + \text{C}_2\text{H}_6$ binary systems and the $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ ternary system. The same equipment and conditions were used for each system.

It was the purpose of this thesis to study the ternary system at 250.00°K and 30.00, 25.00, and 21.00 atmospheres. For each pressure several vapor plus liquid points were taken to define the shape of the isobar. These particular pressures were chosen in order to understand the effect of the $\text{C}_2\text{H}_6 + \text{CO}_2$ azeotrope on the ternary system.

EXPERIMENTAL PROCEDURE

The final design and construction of the apparatus used in this study was done by Juan C. Davalos. The system is divided into four sections, which are discussed by the following people:

Refrigeration System	G. Baughman (1972, p. 26, 27)
Equilibrium System	J. Davalos (1974, p. 3, 5, 6)
Pressure and Temperature System	G. Baughman (1972, p. 31, 32, 33)
Analysis System	J. Davalos (1974, p. 9, 10)

Each run was started by flowing Liquid Nitrogen to the cryostat bath until a temperature of 250.00°K was reached. This temperature was monitored by taking readings of the Mueller bridge setting as described by G. Baughman (1972, p. 55, 56, and 66). A detailed description of the cooldown procedure is described by G. Baughman (1972, p. 45, 46, 48).

While the system is cooling down, the chromatograph is turned on using the procedure described by G. Baughman (1972, p. 40, 41). The settings of the chromatograph are listed in APPENDIX A.

Also, while the system was cooling, the vacuum pump was started and the entire apparatus was purged with pure methane. The system was then left to vacuum for a minimum of thirty minutes. This included all high pressure lines in order to prevent leakage into the system which would alter the zero

setting of the gauges and thus cause an error in all pressure readings. When the system had been completely purged, the gauges were zeroed. The gauges are those described by J. Davalos (1974, p. 15, 16), except that the Heise psia gauge is now a 0 to 500 psia two revolution gauge.'

When the system reached 250.00°K , carbon dioxide was injected into the cell if a point to the right of the azeotrope was desired and ethane was injected if a point to the left of the azeotrope was desired. Depending upon the particular location of the point in question the initial amount of either carbon dioxide or ethane ranged from 5 to 11 grams. Since both of these components are condensable the amount injected into the cell had to be carefully controlled to avoid overfilling. The cell is illustrated in figure 1. When the location of the point was selected, and the proper component was injected, it was allowed to come to equilibrium with it's own vapor pressure. This vapor pressure was measured in the following manner:

1. Close the valve on the fill line.
2. Open valves G_1 and G_2 .
3. Turn on the recirculation pump.
4. Pump until the pressure stabilizes.
5. Turn off the recirculation pump.
6. Read the vapor pressure on the Heise atmosphere gauge and also on the Heise psia gauge if possible.

Refer to figures 2, 3, and 4 for the valve and equipment configuration.

Ethane or carbon dioxide was the second component to be injected. This depended upon which was chosen for the initial injection. Again the recirculation pump was turned on and the system was left to come to equilibrium. Using figure 23 of Anderson (1974, p. 47) the approximate location with respect to the azeotrope could be determined. The gas was injected slowly to avoid splashing the liquid and entraining liquid in the gas sampling line.

Methane was used to raise the pressure of the system to the desired isobar. Recirculation of the ternary system lasted until both temperature and pressure were constant. In general this took 2 to 2½ hours.

The samples are now taken using the following procedure:

1. Turn on the heater in the liquid sampling loop.
2. Turn off the recirculation pump and read the temperature.
3. Turn on the recirculation pump for about ten minutes.
4. Turn off the recirculation pump.
5. Quickly read the pressure while closing valves G_1 and G_2 . This isolates the gas phase sample.
6. With V_1 (vacuum) and L_2 open, open L_1 .
7. Wait several seconds to purge gas that was trapped

in the liquid sample line.

8. Close L_2

9. Close L_1

The samples are now analyzed and the sensitivity checks are taken as described by J. Davalos (1974, p. 14).

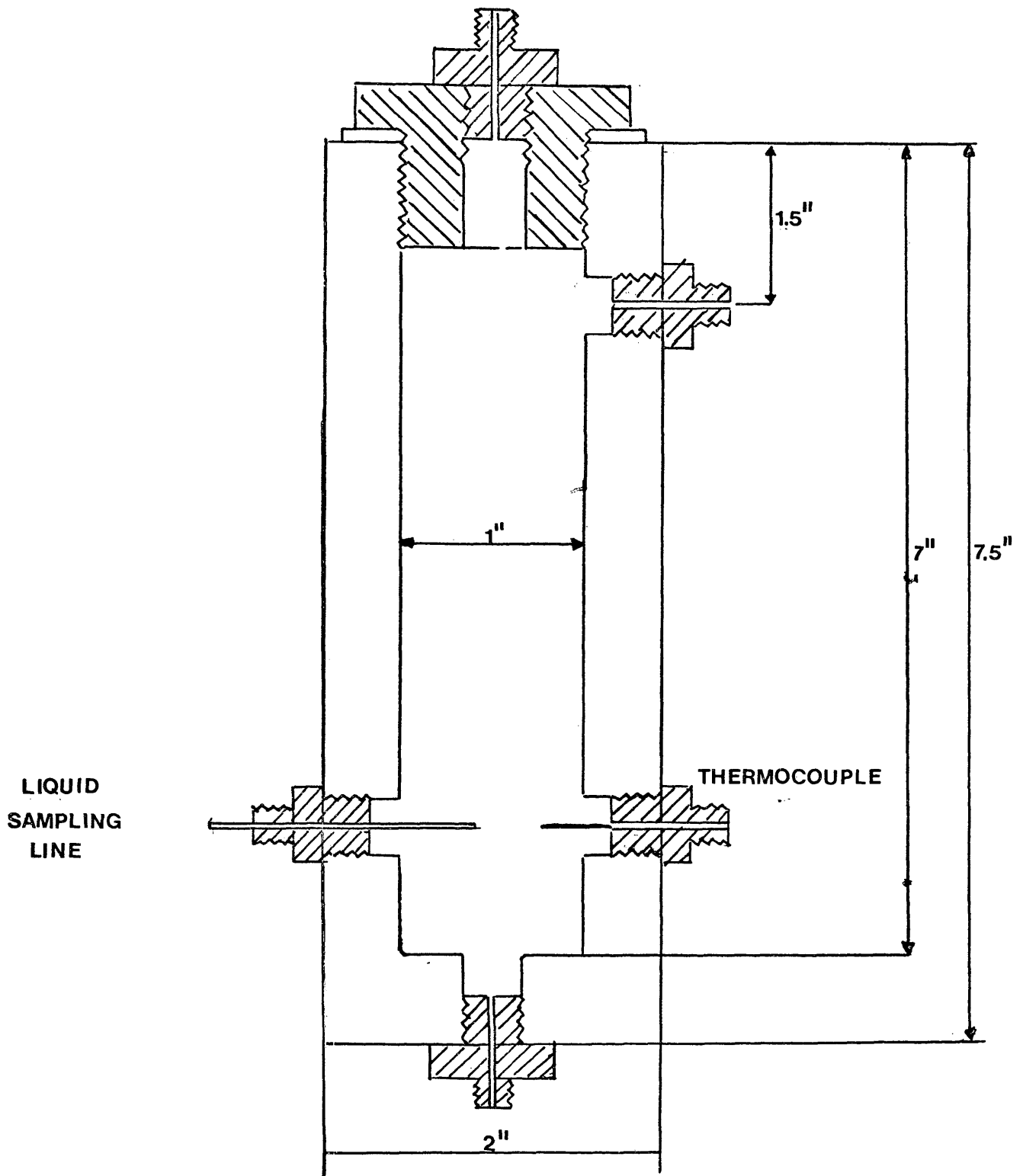


FIGURE 1 EQUILIBRIUM CELL ASSEMBLY

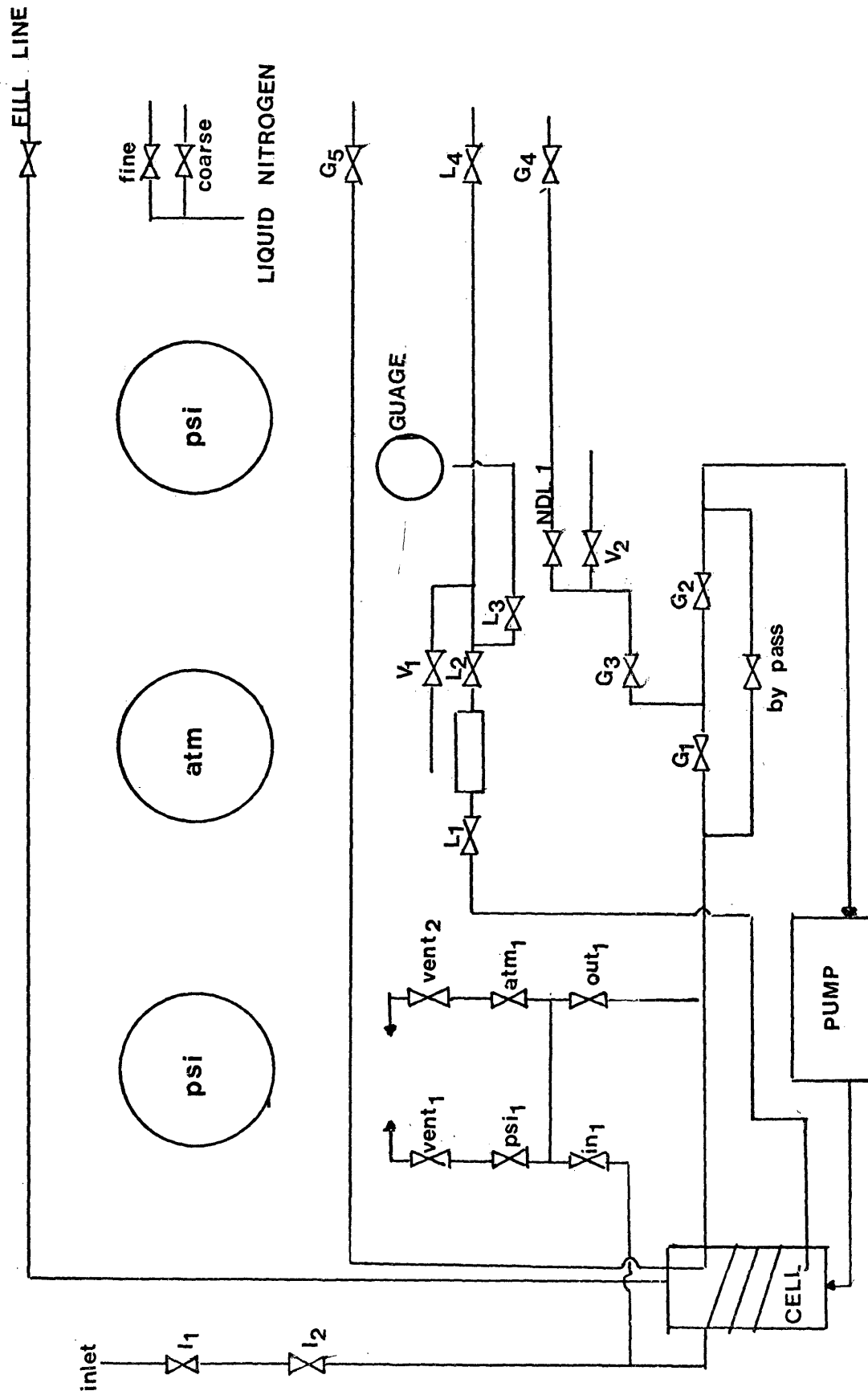
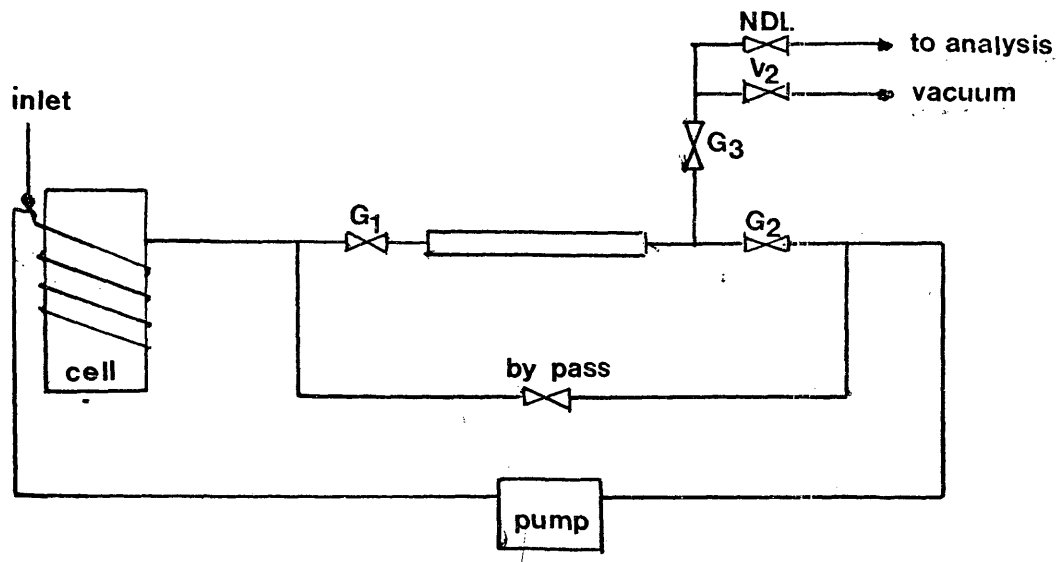
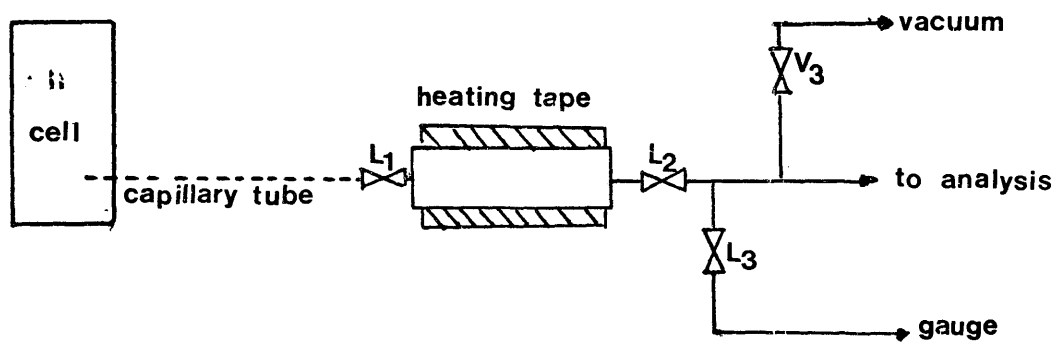


FIGURE 2 DIAGRAM OF THE INSTRUMENT PANEL



GAS PHASE SAMPLING



LIQUID PHASE SAMPLING

FIGURE 3 SCHEMATIC OF SAMPLING SYSTEMS

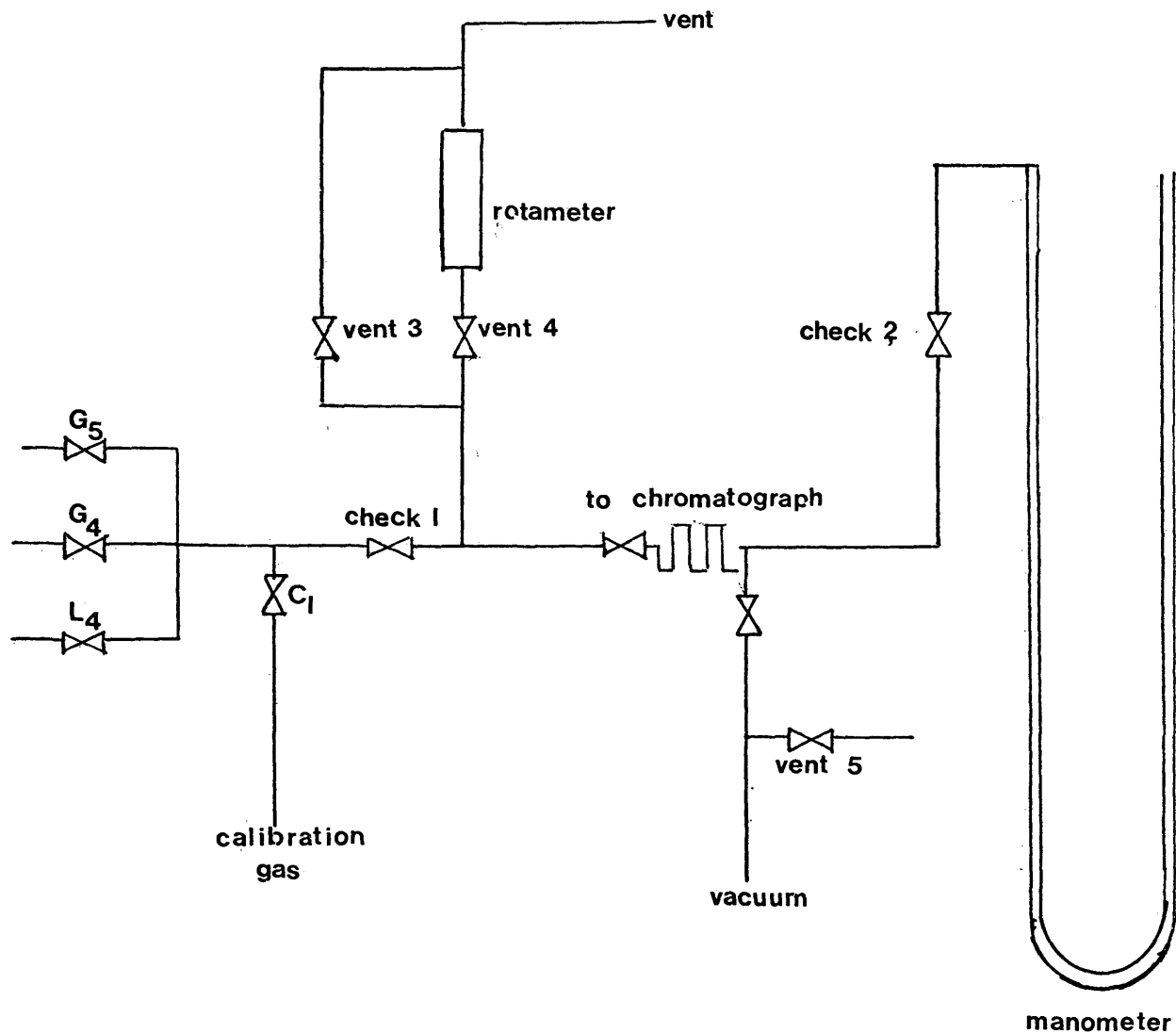


FIGURE 4 SCHEMATIC OF THE ANALYSIS SYSTEM

CALCULATIONAL PROCEDURES

In order to calibrate the gas chromatograph, different amounts of pure methane, ethane, and carbon dioxide were injected and the resulting peak heights noted. The peak height on the chromatograph recorder is proportional to the pressure at which the sample was injected, and when corrected for attenuation, it is directly proportional to injection pressure at lower pressures. At higher pressures the slope of the curves deviates from a straight line, which is attributed to the nonideality of the gas.

A plot of peak height versus pressure was then made for methane, ethane, and carbon dioxide. The sample under analysis was injected into the chromatograph and three different peak heights were obtained of length x units. Using the calibration curves one can obtain a peak height for each gas, at this same injection pressure, of length y units. The concentration is then equal to y/x .

The sensitivity of the machine due to changes in room temperature and barometric pressure was compensated for by running a sensitivity check with a standardized gas at the time the equilibrium sample was taken. The standardized gas is a mixture of methane, ethane, and carbon dioxide. Comparison of the peak heights taken on the day the calibration curve was taken and those taken on the day in question form a

ratio. This ratio is used to correct the readings from the unknown sample to the conditions that existed on the day the calibration curve was run.

The type of data needed to make concentration calculations and a sample calculation are illustrated by J. Davalos (1974, p. 66, 67). The calibration curves that were used are found in APPENDIX A.

RESULTS

Two tables were prepared for each isobar. The first contains the raw data and the second the normalization of the data (i.e. sum of mole fractions forced to 1.0) and calculated K-values for each component. The experimental results are presented in Tables 1-6.

A graph showing liquid and vapor compositions was prepared for each pressure. See figures 5, 6, and 7. An interesting point to bring out is the fact that the minimum point on the 30.00, and 25.00 atmosphere isobars are in line with the minimum point on the 21.00 atmosphere isobar. A plot of percent ethane at the minimum point in the vapor curve for each pressure versus pressure gives a straight line. See Figure 8. It is believed by the author that any isobar can be predicted using these results at 250.00°K of the system methane, ethane, and carbon dioxide.

The vapor pressure of the condensable component was measured at the beginning of each run. This gave an indication as to the accuracy of both the temperature and pressure measurements. The vapor pressures were in close agreement with the accepted values as follows:

Vapor Pressures (Atm)

<u>Temp</u>	<u>Comp</u>	<u>Accepted Values</u>	<u>Measured Values</u>
250	CO ₂	8.818 (Davalos, 1974, p. 48) 8.80 (Anderson, 1974, p. 14)	8.81
250	C ₂ H ₆	12.85 (Goodwin, 1974) 12.85 (Anderson, 1974, p. 14)	12.85

The temperatures quoted are believed to be accurate to 0.01 K. Readings of pressure are precise to 0.03 atm. The chromatograph analysis is believed to be accurate to ± 1.0 percent.

All binary data for CH₄ + CO₂, CO₂ + C₂H₆, and CH₄ + C₂H₆ were obtained from Anderson (1974, p. 26, 38, 47).

Table 1

$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ at 250.00°K and 30.00 Atmospheres

No.	Date	Y_{CH_4}	$Y_{\text{C}_2\text{H}_6}$	Y_{CO_2}	ΣY	X_{CH_4}	$X_{\text{C}_2\text{H}_6}$	X_{CO_2}	ΣX
1	9/11	0.3963	0.4466	0.1427	0.9856	0.1324	0.7203	0.1274	0.9801
2	9/9	0.2638	0.2881	0.4607	1.0126	0.0719	0.3816	0.5665	1.020
3	9/6	0.2618	0.2455	0.5073	1.0146	0.0698	0.3310	0.6176	1.0184
4	9/6	0.2996	0.0926	0.5982	0.9904	-	-	-	-
5	9/4	0.2601	0.2245	0.5044	0.9890	0.0509	0.2443	0.6938	0.9890
6	9/1	0.3375	0.4094	0.2320	0.9789	0.1182	0.6538	0.2108	0.9828

Table 2

$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ at 250.00°K and 30.00 Atmospheres

No.	Date	<u>Normalized</u>			<u>Normalized</u>			ΣX	K_{CH_4}	$K_{\text{C}_2\text{H}_6}$	K_{CO_2}	
		Y_{CH_4}	$Y_{\text{C}_2\text{H}_6}$	Y_{CO_2}	ΣY	X_{CH_4}	$X_{\text{C}_2\text{H}_6}$					X_{CO_2}
1	9/11	0.4021	0.4531	0.1448	1.000	0.1351	0.7350	0.1300	4.000	2.976	0.6165	1.1138
2	9/9	0.2605	0.2845	0.4550	1.000	0.0705	0.3741	0.5554	1.000	3.695	0.7605	0.8192
3	9/6	0.2580	0.2420	0.5000	1.000	0.0685	0.3250	0.6064	1.000	3.766	0.7446	0.8245
4	9/6	0.3025	0.0935	0.6040	1.000	-	-	-	-	-	-	-
5	9/4	0.2630	0.2270	0.5100	1.000	0.0520	0.2495	0.7085	1.000	5.058	0.9098	0.7198
6	9/1	0.3448	0.4182	0.2370	1.000	0.1203	0.6652	0.2145	1.000	2.966	0.6287	1.1050

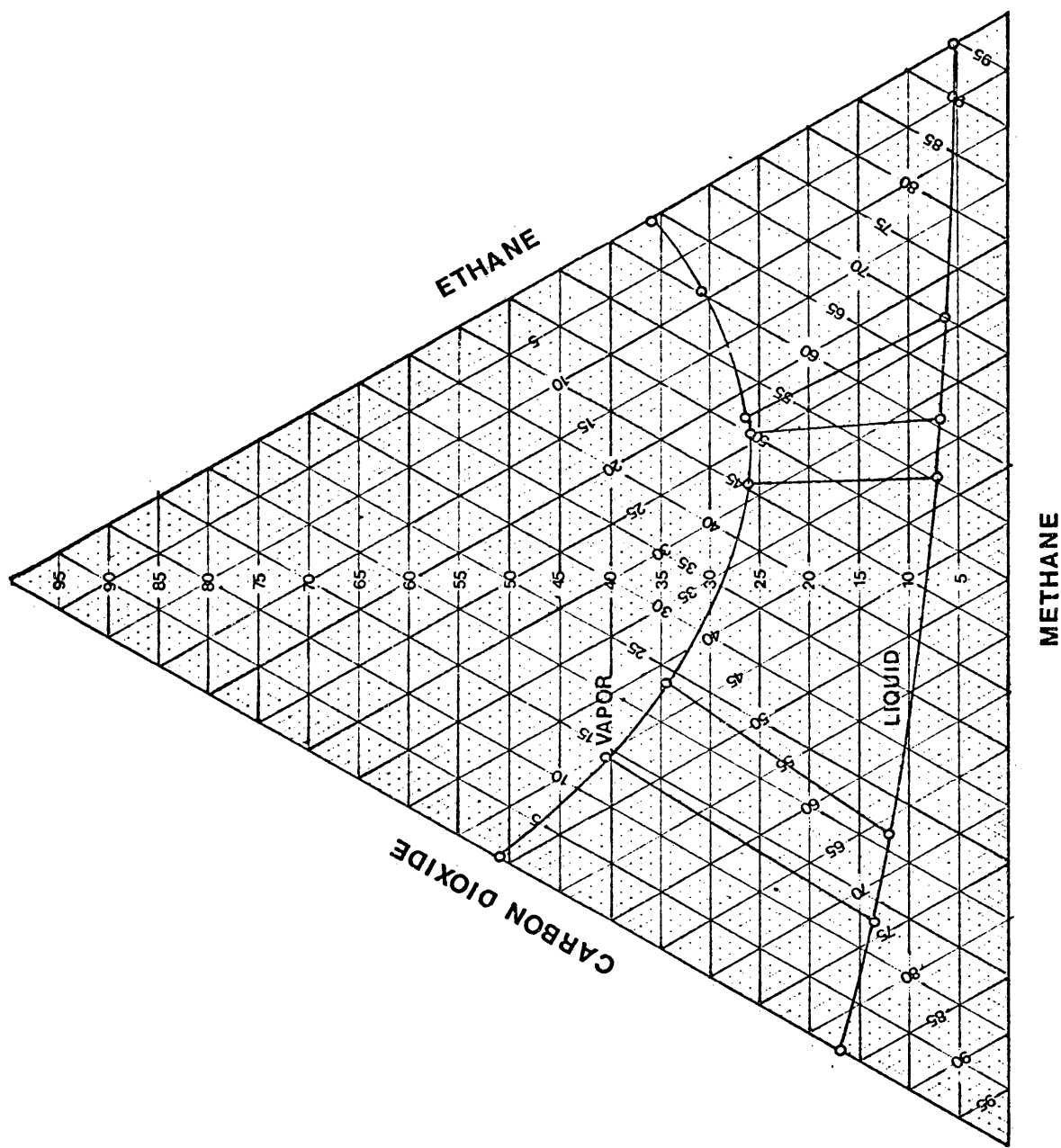


FIGURE 5 METHANE - ETHANE - CARBON DIOXIDE AT 25000°K AND 30.00 ATMOSPHERES

Table 3

$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ at 250.00°K and 25.00 Atmospheres

No.	Date	Y_{CH_4}	$Y_{\text{C}_2\text{H}_6}$	Y_{CO_2}	ΣY	X_{CH_4}	$X_{\text{C}_2\text{H}_6}$	X_{CO_2}	ΣX
1	8/1	0.3588	0.5479	0.1123	1.019	0.1009	0.8271	0.0820	1.010
2	7/29	0.3297	0.5317	0.1487	1.010	0.0953	0.8123	0.0956	1.003
3	7/26	0.1867	0.4074	0.3881	0.9822	0.0497	0.5670	0.3622	0.9789
4	7/23	0.1351	0.2999	0.5861	1.021	0.0303	0.3210	0.6655	1.0168
5	7/19	0.1373	0.2575	0.5952	0.9901	0.0276	0.2605	0.6905	0.9786
6	7/19	0.1671	0.1594	0.6558	0.9823	0.0244	0.1375	0.8261	0.9880
7	7/17	0.2439	0.4682	0.2778	0.9899				

Table 4
 $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ at 250.00°K and 25.00 Atmospheres

No.	Date	Normalized			Normalized							
		Y_{CH_4}	$Y_{\text{C}_2\text{H}_6}$	Y_{CO_2}	ΣY	X_{CH_4}	$X_{\text{C}_2\text{H}_6}$	X_{CO_2}	ΣX	K_{CH_4}	$K_{\text{C}_2\text{H}_6}$	K_{CO_2}
1	8/1	0.3521	0.5377	0.1102	1.000	0.0999	0.8189	0.0812	1.000	3.525	0.6566	1.357
2	7/29	0.3264	0.5264	0.1472	1.000	0.0950	0.8097	0.0953	1.000	3.436	0.6501	1.545
3	7/26	0.1901	0.4148	0.3951	1.000	0.0508	0.5792	0.3700	1.000	3.742	0.7462	1.068
4	7/23	0.1323	0.2937	0.5740	1.000	0.0298	0.3157	0.6545	1.000	4.439	0.9303	0.8770
5	7/19	0.1387	0.2601	0.6012	1.000	0.0282	0.2662	0.7056	1.000	4.918	0.9771	0.8520
6	7/19	0.1701	0.1623	0.6676	1.000	0.0247	0.1392	0.8361	1.000	6.887	1.1660	0.7985
7	7/17	0.2464	0.4730	0.2806	1.000							

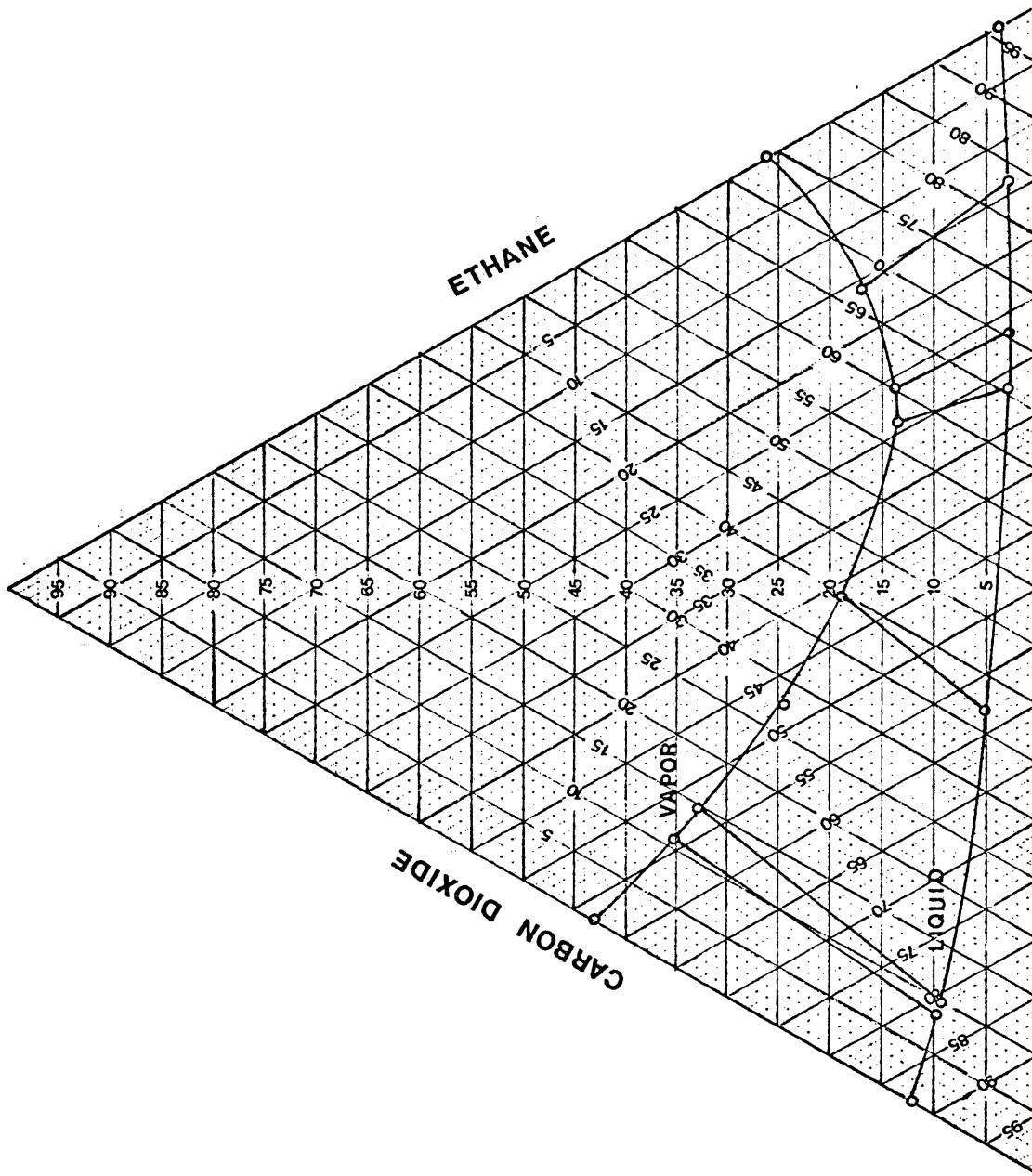


FIGURE 6 METHANE - ETHANE - CARBON DIOXIDE AT 250.00° K AND 25.00 ATMOSPHERES

Table 5

$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ at 250.00°K and 21.00 Atmospheres

No.	Date	$\frac{Y_{\text{CH}_4}}{\text{---}}$	$\frac{Y_{\text{C}_2\text{H}_6}}{\text{---}}$	$\frac{Y_{\text{CO}_2}}{\text{---}}$	$\frac{\Sigma Y}{\text{---}}$	$\frac{X_{\text{CH}_4}}{\text{---}}$	$\frac{X_{\text{C}_2\text{H}_6}}{\text{---}}$	$\frac{X_{\text{CO}_2}}{\text{---}}$	$\frac{\Sigma X}{\text{---}}$
1	10/11	0.0260	0.4343	0.5197	0.9800	0.0032	0.4413	0.5335	0.9780
2	10/10	0.1703	0.5618	0.2535	0.9856	-	-	-	-
3	10/9	0.1644	0.5762	0.2856	1.0262	-	-	-	-
4	10/8	0.2522	0.6254	0.1311	1.0087	0.0359	0.8074	0.1789	1.0222
5	10/5	0.0282	0.1964	0.7550	0.9796	-	-	-	-
6	9/22	0.0365	0.1659	0.7733	0.9757	0.00196	0.1177	0.8625	0.9822
7	9/20	0.0396	0.1584	0.7920	0.9900	0.0022	0.0986	0.8991	0.9999
8	9/17	0.0230	0.2105	0.7435	0.9770	-	-	-	-

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Table 6
 $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$ at 250.00°K and 21.00 Atmospheres

No.	Date	Normalized			Normalized							
		Y_{CH_4}	$Y_{\text{C}_2\text{H}_6}$	Y_{CO_2}	ΣY	X_{CH_4}	$X_{\text{C}_2\text{H}_6}$	X_{CO_2}	ΣX	K_{CH_4}	$K_{\text{C}_2\text{H}_6}$	K_{CO_2}
1	10/11	0.0265	0.4432	0.5303	1.000	0.0033	0.4512	0.5455	1.000	8.030	0.9823	0.9721
2	10/10	0.1728	0.5700	0.2572	1.000	-	-	-	-	-	-	-
3	10/9	0.1602	0.5615	0.2783	1.000	-	-	-	-	-	-	-
4	10/8	0.2500	0.6200	0.1300	1.000	0.0352	0.7898	0.1750	1.000	7.102	0.7850	0.7429
5	10/5	0.0288	0.2007	0.7715	1.000	-	-	-	-	-	-	-
6	9/22	0.0374	0.1700	0.7926	1.000	0.0020	0.1198	0.8782	1.000	18.70	1.419	0.9025
7	9/20	0.0400	0.1600	0.8000	1.000	0.0022	0.0986	0.8992	1.000	18.18	1.623	0.8897
8	9/17	0.0235	0.2154	0.7611	1.000	-	-	-	-	-	-	-

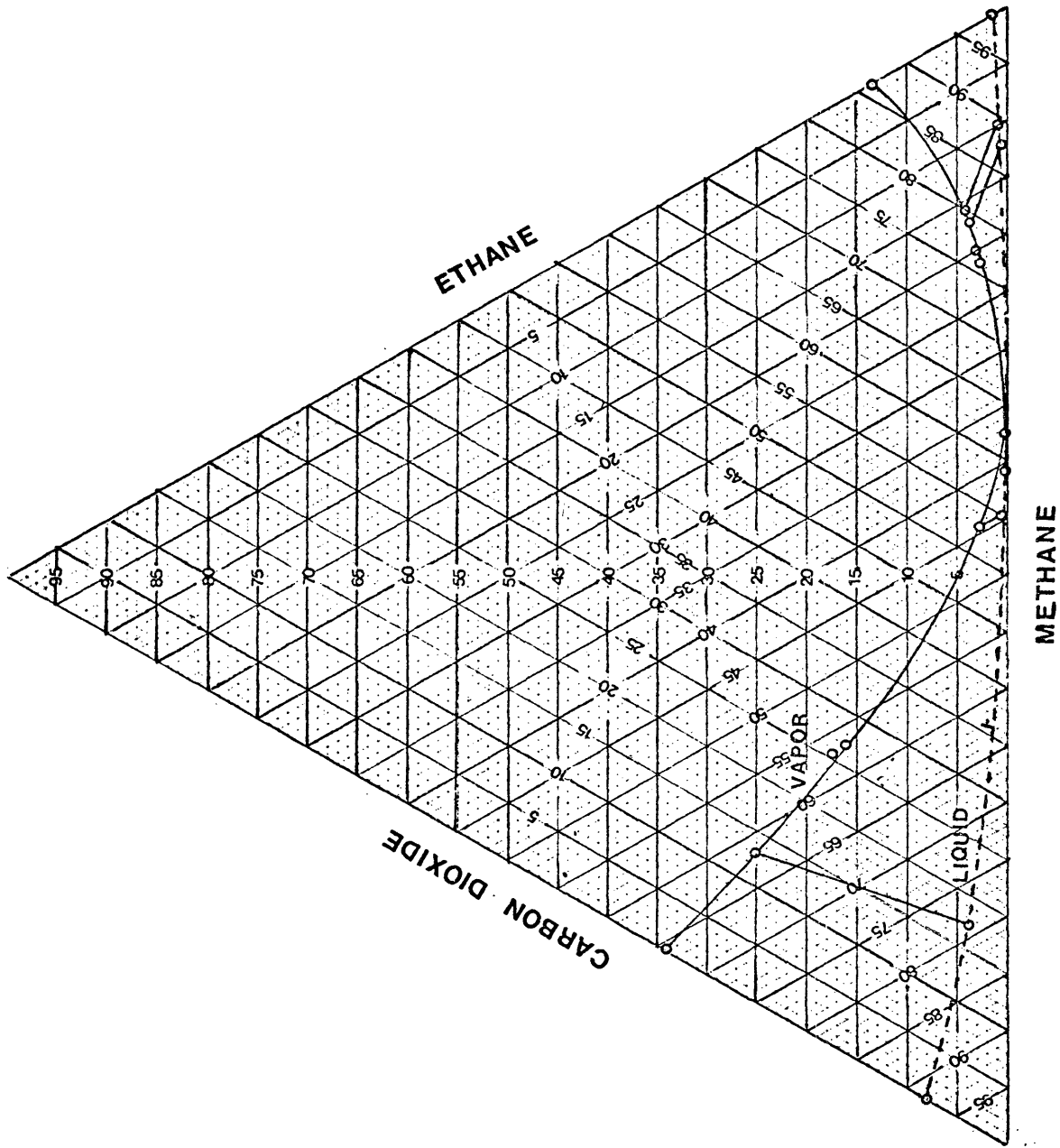
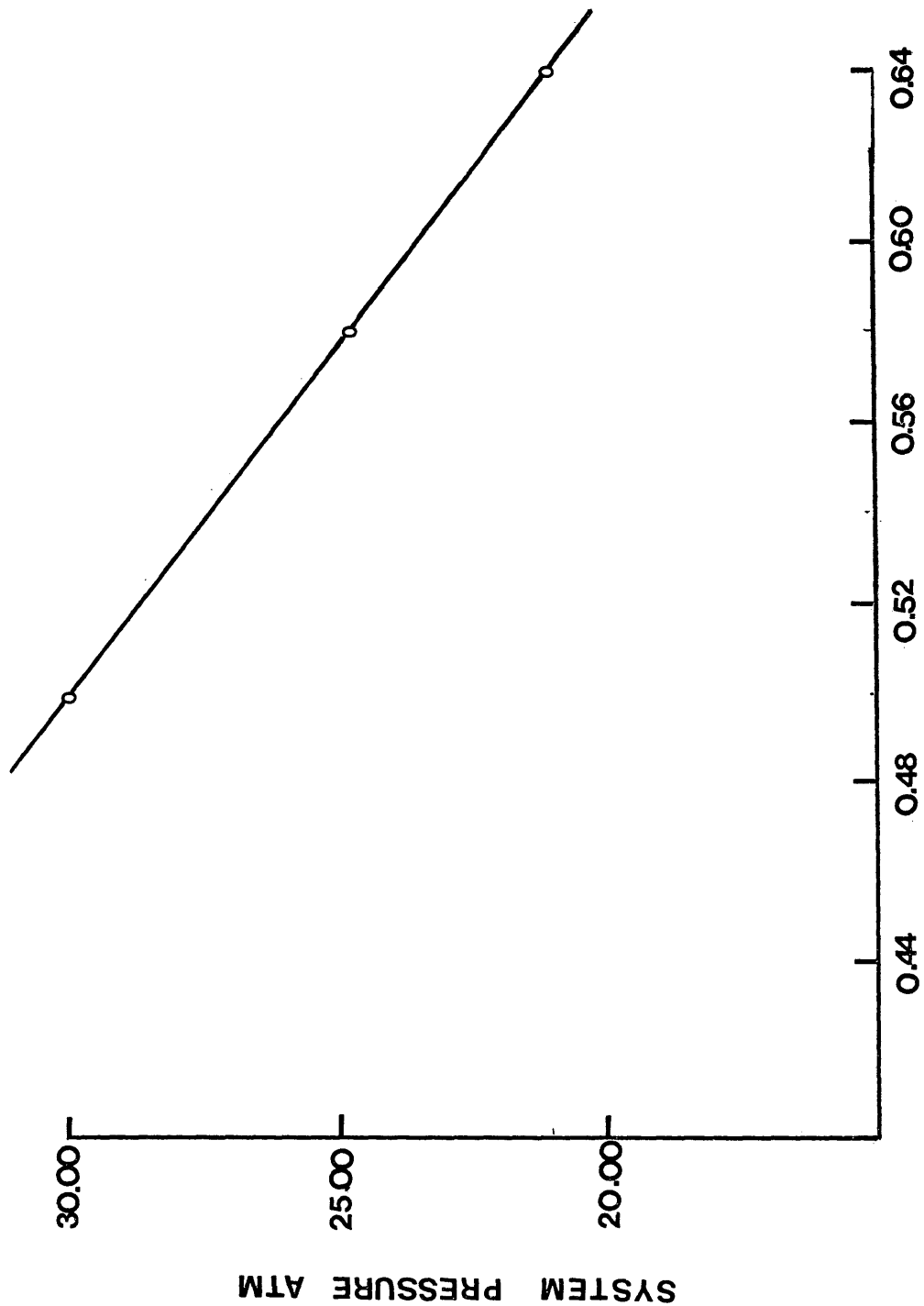


FIGURE 7 METHANE - ETHANE - CARBON DIOXIDE AT 250.00°K AND 21.00 ATMOSPHERES

FIGURE 8 PERCENT ETHANE AT MINIMUM Vs SYSTEM PRESSURE ATM



PERCENT ETHANE AT MINIMUM IN VAPOR CURVE

CONCLUSIONS

1. At 250.00°K, a decrease in pressure shifts the vapor and liquid composition curves downward. At a pressure of 21.00 atmospheres an azeotrope occurs between the binary system of C_2H_6 and CO_2 . Figure 7 illustrates this point.

2. The apparatus is quite capable of measuring liquid and vapor compositions that are consistent with both previous data and real performance of the systems studied.

RECOMMENDATIONS

1. Calculate the points and plot them on the graph as they are taken. This will detect error due to overfilling or exhausted liquid samples.
2. Inject the samples slowly to prevent liquid droplets from entering the gas sample loop.
3. Always check the vapor pressure of the first condensable component to assure that the temperature and pressure measurements are valid.
4. Longer silica gel columns would give better separation of ethane and carbon dioxide.

TABLE OF NOTATION

- RL - Right leg manometer reading. This right leg is subtracted from the left leg manometer reading to give the difference from atmospheric pressure (P).
- ATT - The attenuation reading on the chromatograph. If the peak height is off the paper of the recorder, the ATT is changed to allow the peak to be all on the paper. Higher attenuation allows the peak to be shortened and lowering the attenuation allows the peak to be higher.
- PH - The peak height that a certain component gives on the recorder.
- IP - The pressure at which the sample is injected into the chromatograph. IP is equal to the barometric pressure plus the manometer pressure.
- PP - Injection pressure times the concentration of the gas. This term is used for the chromatograph calibration curves.
- CPH - The peak height which has been corrected to some base attenuation.
- K - The distribution coefficient for a particular component. It is equal to the concentration of a particular component in the gas phase divided by the concentration of that component in the liquid phase (Y/X).

- P - The pressure in the system or in the equilibrium cell,
as seen in figure 1.
- X - The concentration of a particular component in the liquid
phase.
- Y - The concentration of a particular component in the vapor
phase.

APPENDIX A

CALIBRATION CURVE FOR SILICA GEL COLUMNS

The silica gel columns gave distinct and separate peaks for methane, ethane, and carbon dioxide. However, the columns required a considerable change in the chromatograph settings. Pure gases of these components were used for these calibration curves. The data for these calibration curves are found in Table 7, and the curves are in Figure 8.

Calibration settings -

columns - six foot silica gel columns
column temperature - 65°C
column flow rate - 75% flow
chromatograph current - 250 ma
carrier gas - helium
barometric pressure - 626.1 mm of Hg

Using a right leg of 60, which is the injection pressure used for the sensitivity checks, the calibration of the sensitivity gas was made with the following results:

Component	RL	ATT	PH
CH ₄	60	64	1.41
C ₂ H ₆	60	16	2.49
CO ₂	60	16	1.79

The inverse of the slope was calculated for each component and then multiplied by the corrected peak height for a parti-

cular point to give the corresponding partial pressure for that point. The concentration for the point is derived from the ratio of the partial pressure to the injection pressure.

. Table 7

Calibration Data for Silica Gel Columns

.Methane (base attenuation = 64)

<u>RL</u>	<u>ATT</u>	<u>PH</u>	<u>IP</u>	<u>GPH</u>
45	128	4.87	550.6	9.73
50	128	4.05	449.9	8.10
60	64	4.57	250.4	4.57
62	64	3.82	210.4	3.82
64	32	6.24	170.4	3.12
66	32	4.81	130.5	2.41
68	16	6.68	90.6	1.67
70	16	3.77	51.1	0.943

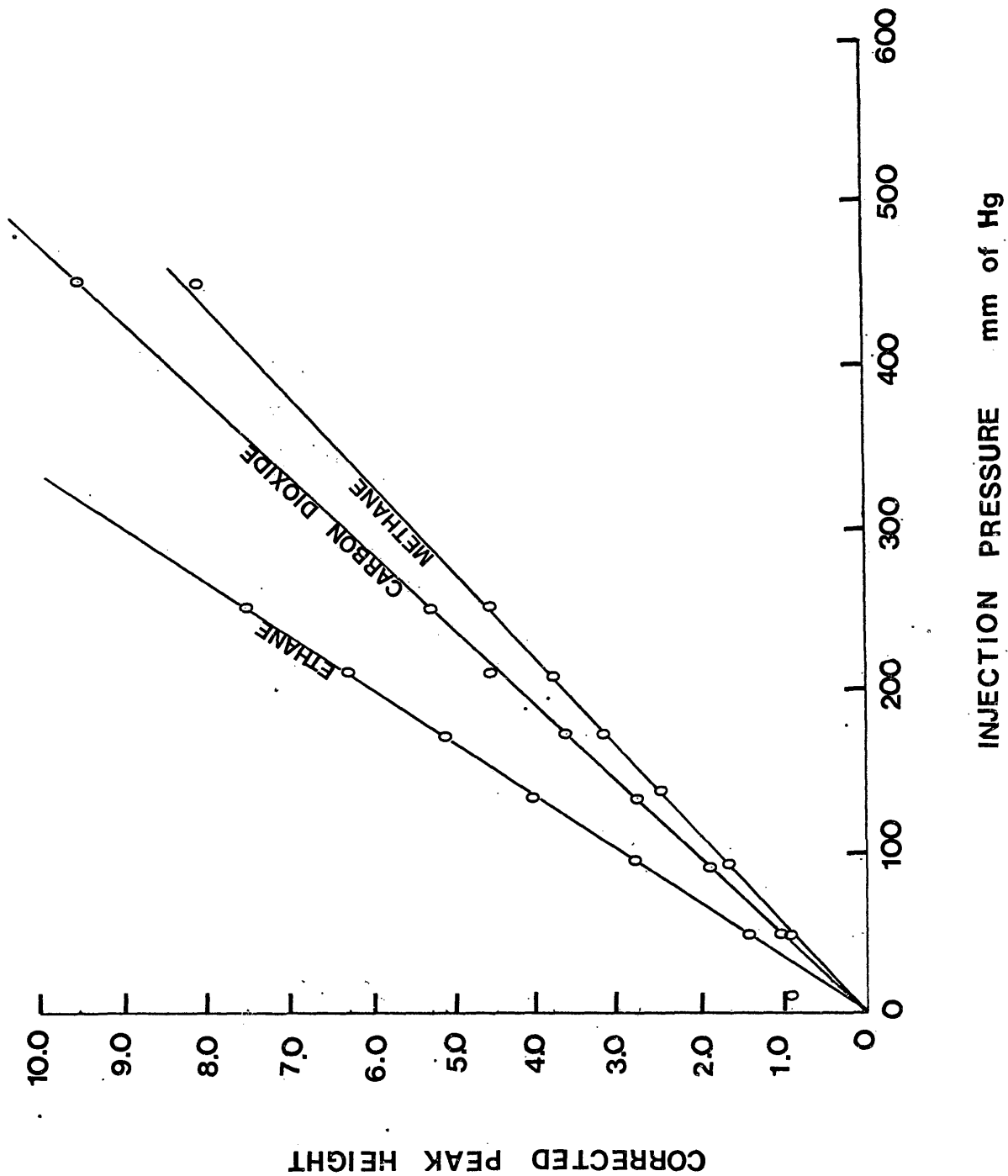
Ethane (base attenuation = 16)

45	64	4.11	550.6	16.44
50	64	3.37	449.9	13.46
60	32	3.77	250.4	7.54
62	16	6.29	210.4	6.29
64	16	5.14	170.4	5.14
66	16	3.93	130.5	3.93
68	8	5.49	90.6	2.75
70	8	3.11	51.1	1.55

Carbon Dioxide (base attenuation = 16)

45	64	3.93	550.6	15.70
50	64	2.39	449.9	9.56
60	32	2.66	250.4	5.31
62	16	4.47	210.4	4.47
64	16	3.65	170.4	3.65
66	8	5.59	130.5	2.80
68	8	3.96	90.6	1.98
70	8	2.08	51.1	1.04

FIGURE 9 CALIBRATION CURVES FOR SILICA GEL COLUMNS



REFERENCES

- Anderson, W. R., 1974, Measurement of the solid + vapor phase equilibrium of the binary systems composed of methane, ethane, and carbon dioxide: M.Sc. Thesis T-1690, Colorado School of Mines.
- Baughman, G. L., 1972, Measurement of the solid + vapor phase equilibrium of the argon + neopentane system: M.Sc. Thesis T-1519, Colorado School of Mines.
- Baughman, G. L., 1973. The solid + vapor phase equilibrium of the helium + neopentane system : Ph.D. Thesis T-1608, Colorado School of Mines.
- Davalos. J. C., 1974, The liquid + vapor equilibrium of the helium + carbon dioxide system: M.Sc. Thesis T-1637, Colorado School of Mines.