

T 1690

THE LIQUID-VAPOR EQUILIBRIA OF THE BINARY SYSTEMS  
COMPOSED OF METHANE, ETHANE, AND CARBON DIOXIDE

by

Wayne R. Anderson

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T 1690

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 Master of Science in Chemical and Petroleum-Refining Engineering.

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ABSTRACT

A previously used and tested experimental apparatus for measuring temperature, pressure and composition was employed to analyze the equilibrium compositions of 3 binary systems at a set temperature and pressure.

The  $\text{CH}_4+\text{CO}_2$  system was investigated at temperatures of 230.00 K, 250.00 K and 270.00 K. The  $\text{CH}_4+\text{C}_2\text{H}_6$  system and the  $\text{C}_2\text{H}_6+\text{CO}_2$  system were also investigated at a temperature of 250.00 K. All systems were investigated over their entire 2-phase region of pressures.

I wish to dedicate this thesis to  
my parents and Jodi and Buffi.

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## INTRODUCTION

This thesis is part of a phase equilibria project to study the  $\text{CO}_2+\text{CH}_4$ , the  $\text{CO}_2+\text{C}_2\text{H}_6$  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. All of these systems were studied using the same equipment and at nearly the same conditions in order to establish internal consistency in the data.

For this thesis isotherms were run for the  $\text{CH}_4+\text{CO}_2$  system at 230.00 K, 250.00 K and 270.00 K. Isotherms were also run for the  $\text{CO}_2+\text{C}_2\text{H}_6$  system and the  $\text{CH}_4+\text{C}_2\text{H}_6$  systems, each at 250.00 K. The ternary system  $\text{CH}_4+\text{CO}_2+\text{C}_2\text{H}_6$  is under investigation, and the results of that investigation will be reported in another thesis.

The temperature is set at the desired value and the composition for a particular pressure is determined using a gas chromatograph. The process is repeated at several different pressures to fully define the shape of the isotherm. The temperature or gases are then changed and the process is repeated.

PREVIOUS WORK ON THE  $\text{CH}_4+\text{CO}_2$ ,  $\text{CH}_4+\text{C}_2\text{H}_6$ ,  
AND THE  $\text{CO}_2+\text{C}_2\text{H}_6$  SYSTEMS

$\text{CO}_2+\text{CH}_4$

There are 7 prior investigations of vapor+liquid equilibrium for this system. However, only the following are in the same temperature region as this work (250.00 K):

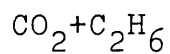
1. Arai, et al. (1971)
2. Donnely and Katz (1954)
3. Kaminishi, et al. (1968)
4. Kaminishi and Toriumi (1968)

$\text{CH}_4+\text{C}_2\text{H}_6$

The following investigators have done work on this system:

1. Bloomer, et al.
2. Chang and Lu (1963)
3. Ellington, et al. (1959)
4. Guter and Ruhemann (1940)
5. Hsi and Lu (1971)
6. Levitskaya (1941)
7. Moran (1959)
8. Price and Kobayashi (1959)
9. Ruhemann (1939)
10. Skripka, et al. (1970)

11. Uehara (1932)
12. Wichterle (1972)



1. Fredenslund and Mollerup
2. Khazanova (1966)
3. Robinson and Kalra
4. Gugnoni, et al. (1974)

The comparisons that were made of this work with the above existing data indicate close agreement.

## EXPERIMENTAL PROCEDURE

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Each run is started by flowing liquid nitrogen ( $\text{LN}_2$ ) to the cryostat bath. The temperature in the bath is monitored by taking readings of the Mueller bridge setting as described by G. Baughman (1972, p. 55, 56). Baughman (1972, p. 45, 46, 48) also describes the cooldown procedure.

While the system is cooling down, the chromatograph is checked out using the procedure of Baughman (1972, p. 40, 41). The proper settings are listed in appendices A and B.

Also, while the system is cooling, the vacuum pump is started and the system is purged of gas. It is advisable to vacuum out adjoining high pressure lines to avoid the possibility of gas leakage into the system which would alter the zero setting of the gauges and thus cause an error in all of the pressure readings. When the system is completely purged, the gauges should be zeroed. The gauges are those described by Davalos (1974, p. 15, 16) except that the Heise psi gauge is now a 0- to 500-psi 2-revolution gauge.

When the system is cooled down to the desired temperature, a condensable component is charged into the cell. About 40 grams of  $\text{CO}_2$  could be injected or 25 grams of  $\text{C}_2\text{H}_6$  without fear of overfilling the cell. The cell is illustrated in figure 1. When the condensable component is injected to

the proper amount, the following method is used to read its vapor pressure:

1. Close the valve on the fill line.
2. Open valves G1 and G2.
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 psi gauge if possible.

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

The temperature will be increased in the bath by the condensation of the gas and control of the temperature will be lost. The coarse  $\text{LN}_2$  valve is simply opened until control is restored.

The other component for a particular binary system is now injected to the cell by bubbling it through the liquid to a preselected pressure. The gas should be injected slowly to avoid splashing the liquid and entraining liquid in the gas sampling line.

The recirculation pump should be operated for about 15 min after the pressure has stabilized, to insure that the 2 phases (liquid and gas) are in equilibrium. The samples are now taken using the following procedure:

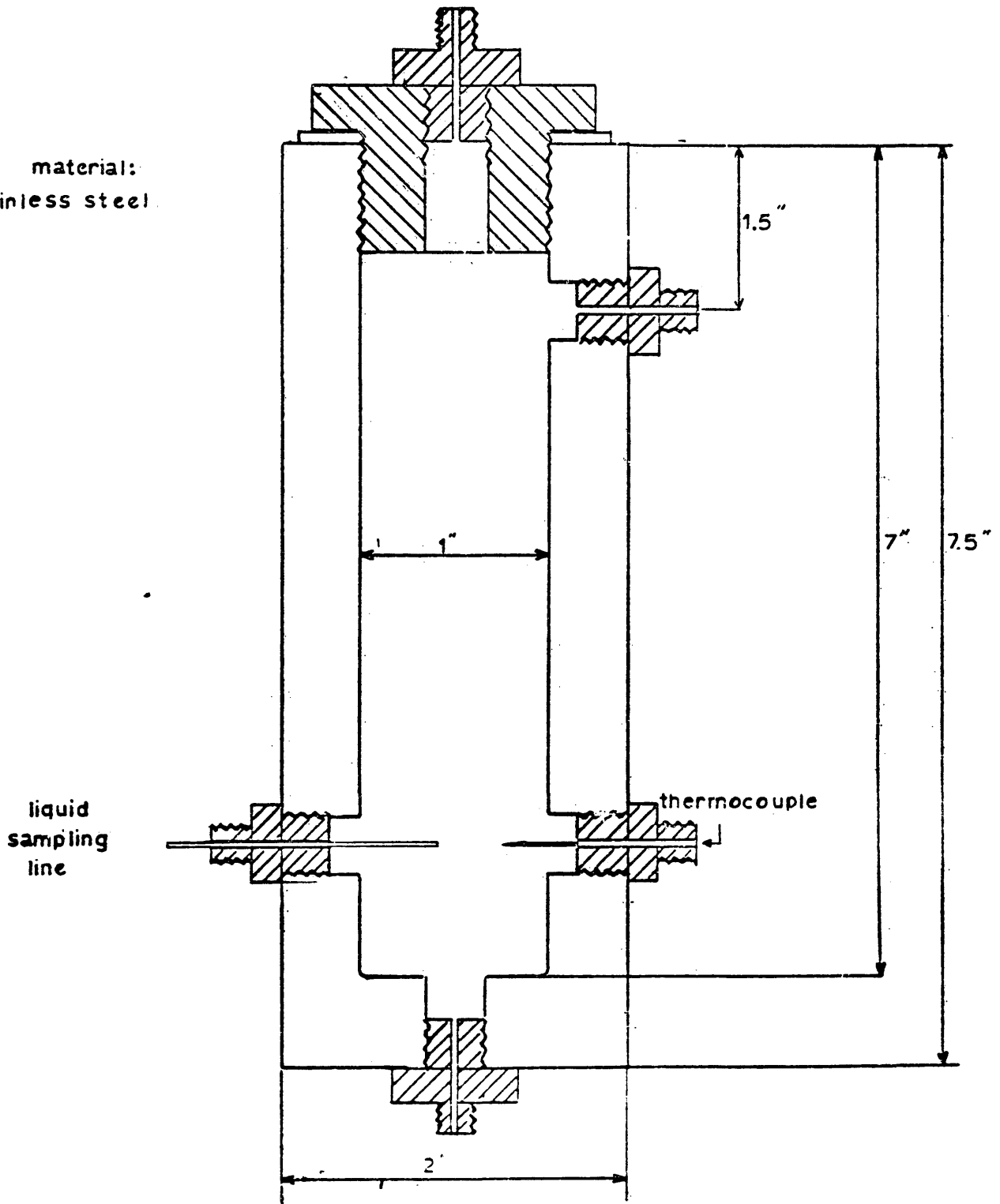
1. Turn on the heater in the liquid sampling loop.
2. Turn off the recirculation pump and read the temperature.
3. Turn on the recirculation pump for about 5 minutes.
4. Turn off the recirculation pump.
5. Quickly read the pressure while closing valves G1 and G2.
6. With V1 and L2 open, open L1.
7. Wait 2 seconds to purge gas that was trapped in the liquid sample line.
8. Close L2.
9. Close L1.

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



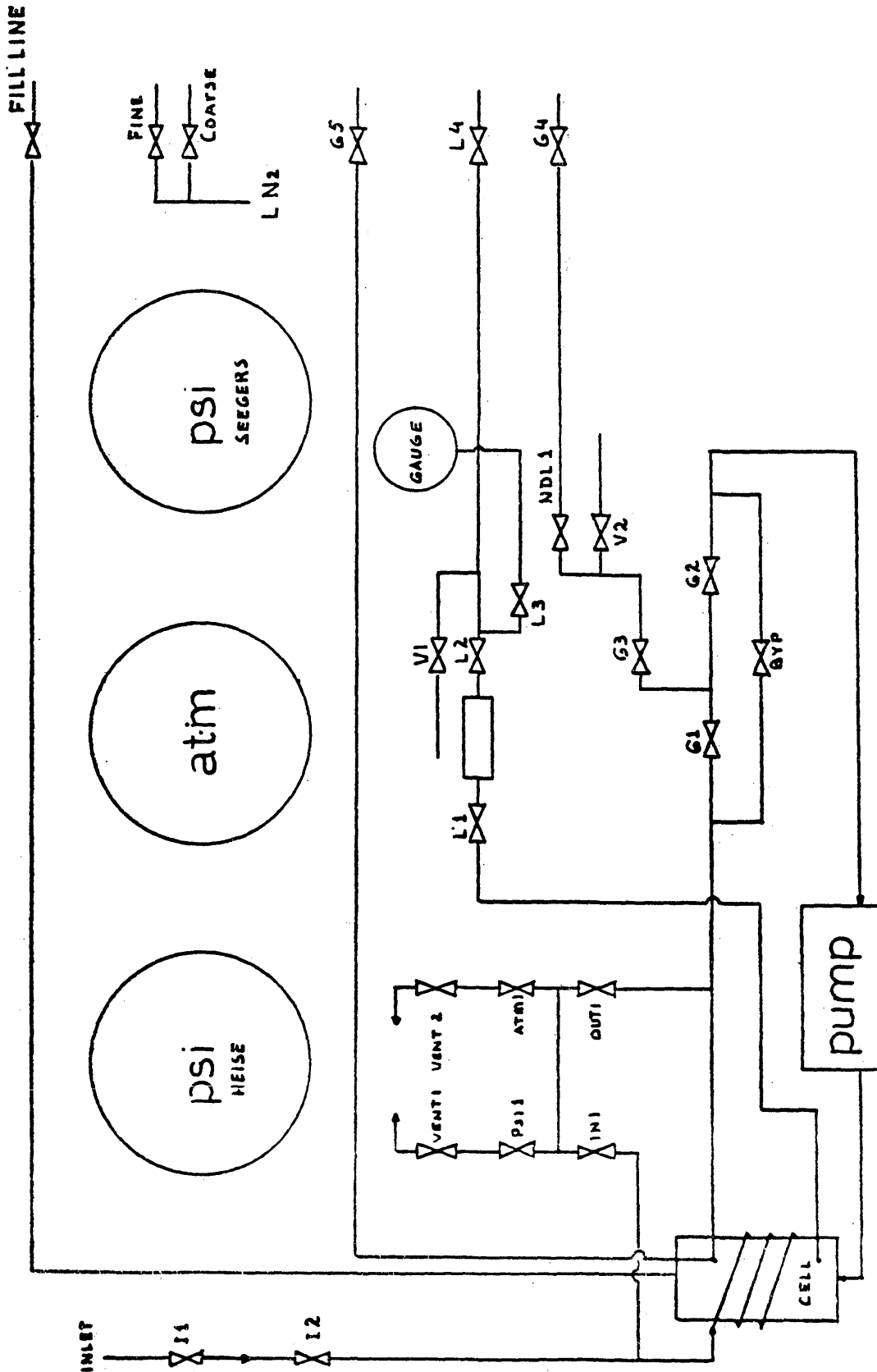
Equilibrium Cell Assembly

material:  
stainless steel



(reprinted from Davalos, 1974)

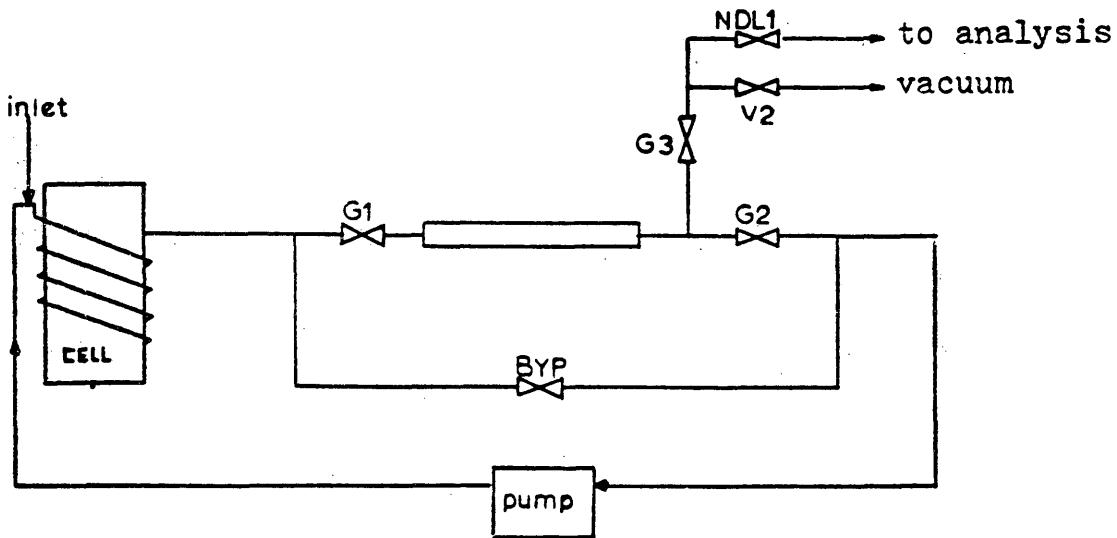
Sketch Of The Instrument Board



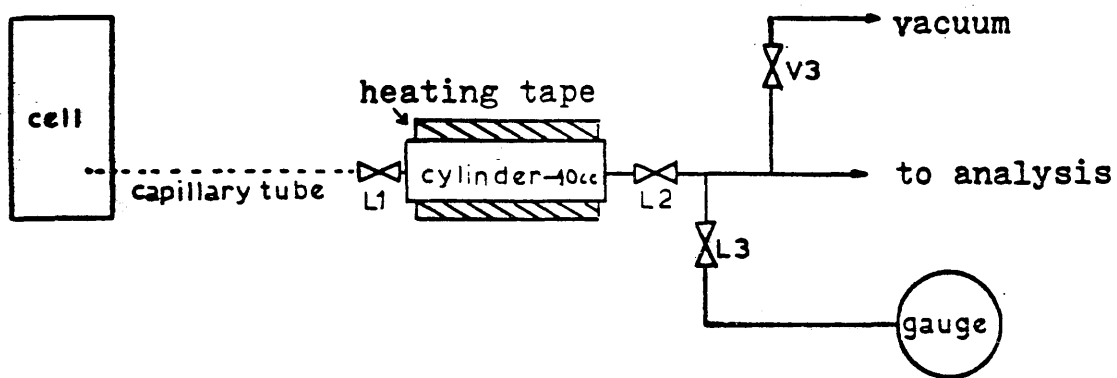
(reprinted from Davalos, 1974)

Figure 3

Schematic Of The Sampling Systems



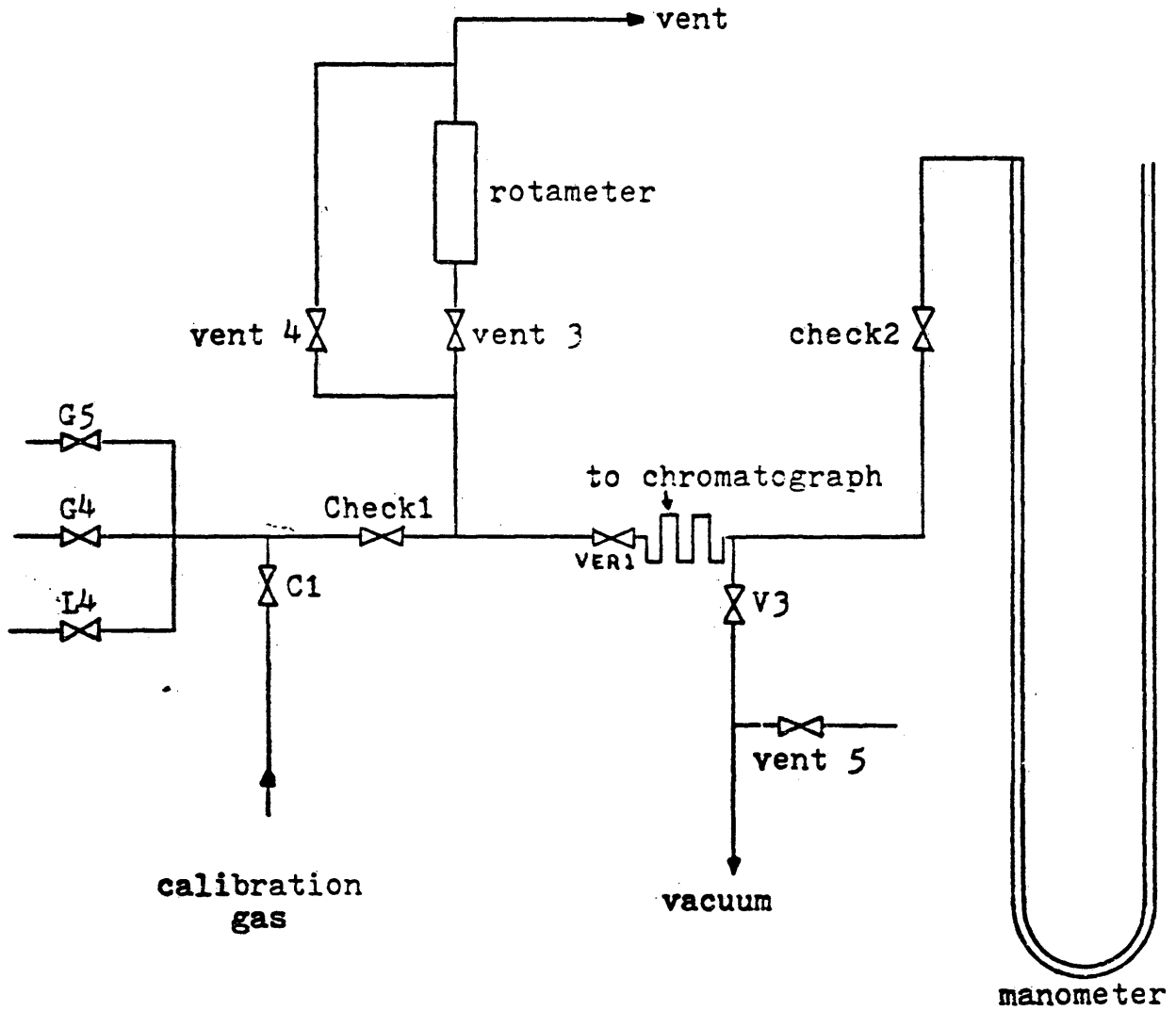
Gas Phase Sampling Loop



Liquid Phase Sampling System

(reprinted from Davalos, 1974)

Schematic Of The Analysis System



(reprinted from Davalos, 1974)

## CALCULATIONAL PROCEDURES

Prior to taking equilibrium data, the gas chromatograph must be calibrated for the gases to be analyzed. This is done by injecting samples of the pure gases under study into the manometer at several different pressures and injecting these samples individually into the chromatograph. Each sample gives a peak height on the chromatograph recorder which is proportional to the pressure at which the sample was injected. The peak heights, when corrected for attenuation, are directly proportional to injection pressure at lower pressures, but the slope of the curve deviates somewhat from a straight line at higher pressures. This deviation from a straight line is due to the nonideality of the gas. The closer to ideal a gas is, the less this deviation from a straight line.

With this calibration curve plotted with peak height versus pressure, the concentration of a given gas mixture can be determined. For instance, say that a gas mixture gives a peak height of length  $x$  units at a certain chosen injection pressure. This same injection pressure on the calibration curve gave a peak height of  $y$  units when the pure gas was used. The concentration is then equal to  $y/x$ .

The chromatograph peak height readings vary somewhat

with time due to changes in the sensitivity of the machine. These slight changes are caused mainly by changes in the chromatograph electronics due to changes in room temperature and changes in the barometric pressure. These changes in the sensitivity of the machine are compensated for by running a sensitivity check with a standardized gas at the time the equilibrium sample is taken. This sensitivity check is compared to the peak height reading that this injection pressure gave on the day the calibration curve was taken. This comparison in the form of a ratio is used to correct the readings from the unknown sample to the conditions that existed on the day the calibration curve was run.

It was originally thought that the sensitivity correction factor would be the same for all of the gases or that the same proportionality would exist between the sensitivity correction for the different gases. After testing this theory, however, it was found that for the chromatograph used, the sensitivity correction factor was not the same for all of the gases and that the proportionality between these factors changed with time.

A mixture of the three gases ( $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ) was made up to check all three machine sensitivities in the same sample. This same three-component mixture will be used for the sensitivity check when the ternary system is studied. This should add internal consistency to the data obtained.

The type of data needed to make concentration calculations and a sample calculation are illustrated by Davalos (1974, p. 66-67)

The calibration curves that were used are duplicated in appendices A and B along with the corresponding chromatograph settings. This project was started using the molecular sieve columns. The molecular sieve columns, however, adsorbed  $\text{CO}_2$  so completely that it could not be analyzed. The silica gel columns were then obtained so that  $\text{CO}_2$  could be analyzed.

## RESULTS

The results of the data taken for this thesis are presented here with a section for each isotherm. Each section has a table of the experimental data and the derived values. The data are then presented in graphical form with a graph of system pressure versus composition. The derived values are also presented graphically.

The vapor pressure of the condensible component was measured at the beginning of each run. This gave an indication of the accuracy of both the temperature and pressure measurements. The vapor pressures in all cases 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 For This Work</u>
230	CO <sub>2</sub>	8.818 (Davalos, 1974, p. 48)	8.80
250	CO <sub>2</sub>	17.620 (Davalos, 1974, p. 48)	17.62
270	CO <sub>2</sub>	31.611 (Davalos, 1974, p. 48)	31.53
250	C <sub>2</sub> H <sub>6</sub>	12.85 (Goodwin, 1974)	12.85

Each set of data is presented with a set of graphs which indicate the degree of the internal and thermodynamic consistency of the data. When, for instance, the values of the liquid-phase composition (x) versus system pressure (P) minus



vapor pressure ( $p^{\circ}$ ) form a smooth curve that intersects zero on the ordinate, it indicates that the data are likely to be in agreement with the actual situation that they represent. The system, in other words, should exhibit the vapor pressure of the condensible component when there is no other component present.

The plot of the distribution coefficient ( $K$ ) times the system pressure ( $P$ ) versus the system pressure ( $P$ ) minus vapor pressure ( $p^{\circ}$ ) will indicate the consistency of both the liquid- and vapor-phase composition data at once. If the liquid- and vapor-phase composition data are consistent, the  $KP$  versus  $P-p^{\circ}$  points will be on a smooth curve which intersects the ordinate at the vapor pressure of the condensible component. This is true because Henry's law applies at low concentrations of the dissolved component. This test of the data is fairly sensitive to deviations of the data from the real situation.

The graph of the natural logarithm of the enhancement factor ( $\ln E_1 = \ln \frac{y_1 P}{p_1^{\circ}}$ ) versus system pressure ( $P$ ) minus vapor pressure ( $p_1^{\circ}$ ) checks the consistency of the vapor-phase composition data. If the low pressure values of  $\ln E$  versus  $P-p^{\circ}$  are on a straight line or a smooth curve which intersects the ordinate at zero, then good consistency is indicated. Zero on the ordinate of  $\ln E$  versus  $P-p^{\circ}$  corresponds to a value of 1 for  $E$ . When  $E = 1$  the system pressure

(P) must equal the vapor pressure ( $p^{\circ}$ ) of the condensible component. Since the system pressure (P) equals the vapor pressure ( $p^{\circ}$ ) then only the condensible component is present. The vapor phase must then be pure condensible component and  $y$  must equal 1. The enhancement factor ( $E = \frac{yP}{p^{\circ}}$ ) must, therefore, be equal to 1.

Based on the National Bureau of Standards calibration of the platinum-resistance thermometer, the temperatures quoted are believed to be accurate to 0.01 K. Readings of pressure are precise to 0.03 atm. We believe the chromatograph analysis to be accurate to  $\pm 1.5$  percent for the  $\text{CO}_2 + \text{C}_2\text{H}_6$  system and accurate to  $\pm 1.0$  percent for all other systems that we measured. The lower confidence in the  $\text{CO}_2 + \text{C}_2\text{H}_6$  system is because there is some overlap of these two peaks and no overlap of the other combination of peaks. When data points deviate from the above confidence values, we believe the cause is non-equilibrium in the system, sampling problems, or operator reading errors. Most of the data carry figures beyond the limits of significance to avoid compounding the error as further calculations were made. The fact that the data were taken on several different days for each isotherm indicates the reproducibility of the data.

This project was started with the assistance of Mr. Juan Davalos, who designed and built a considerable portion of the apparatus. The data for the  $\text{CH}_4 + \text{C}_2\text{H}_6$  system was taken almost entirely by Mr. Davalos.

### The CH<sub>4</sub>+CO<sub>2</sub> System at 230.00 K

The data for this system are presented in table 1 and graphically in figure 5. This graph is a smooth curve and only two of the data points are slightly displaced from the curve. This discrepancy is most likely caused by the system not being at equilibrium when the point was measured. Also, the data near the top of the curve were taken at different chromatograph settings using different columns.

The points along the lower part of the graph (figure 5) were taken with the chromatograph equipped with molecular sieve columns. These columns adsorbed the CO<sub>2</sub> so strongly that CO<sub>2</sub> could not be measured. Therefore, the methane was measured, and the CO<sub>2</sub> concentration was obtained by difference.

The points along the top of the isotherm in figure 5 were analyzed with the chromatograph equipped with silica gel columns. This is the normalized data in the data tables. Since both components were measured and the total was never exactly 100 percent, each concentration was divided by the total of the two concentrations. This normalization tends to smooth the data.

Figure 6 is a graph of  $x$  versus  $P-p^0$  and since all points lie on a smooth curve intersecting the ordinate at zero, it seems that the data are consistent. The more sensitive tests of  $KP$  versus  $P-p^0$  and  $\ln E$  versus  $P-p^0$  show the points at 20 atmospheres to be slightly displaced from the smooth curve.

Since these tests are very sensitive, however, the data is still very consistent with reality.

Table 1

$\text{CH}_4 + \text{CO}_2$  System at 230.00°K,  $P_{\text{CO}_2}^0 = 8.80$  atm

Date	System P- $\text{CO}_2$ Pressure (atm)	$\frac{Y_{\text{CH}_4}}{X_{\text{CH}_4}}$	$\frac{Y_{\text{CO}_2}}{X_{\text{CO}_2}}$	$\frac{K_{\text{CH}_4}}{K_{\text{CH}_4}}$	$\frac{K_{\text{CH}_4} P}{K_{\text{CH}_4}}$	$\frac{K_{\text{CO}_2}}{K_{\text{CO}_2}}$	$\frac{K_{\text{CO}_2} P}{K_{\text{CO}_2}}$	$\frac{E_{\text{CO}_2}}{E_{\text{CO}_2}}$	$\ln \frac{E_{\text{CO}_2}}{E_{\text{CO}_2}}$	
5/26	8.80	0.00	1.00	indet.	indet.	1.00	8.80	1.00	0.00	
5/26	15.00	0.399	0.601	0.973	14.67	220.0	0.618	9.27	1.024	0.0237
5/26	20.00	0.525	0.475	0.950	10.50	210.0	0.500	10.00	1.080	0.0770
5/27&5/29	32.00	0.683	0.317	0.885	5.94	190.1	0.398	11.96	1.153	0.1424
5/27&5/29	40.00	0.728	0.170	0.830	4.28	171.2	0.328	13.12	1.236	0.2119
5/27	48.00	0.751	0.235	0.765	3.20	153.6	0.325	15.60	1.358	0.3060
5/27	55.00	0.764	0.318	0.686	2.43	133.6	0.344	18.92	1.475	0.3887
5/29	61.10	0.752	0.397	0.603	1.89	115.5	0.411	25.11	1.722	0.5435
5/30	62.00	0.762	0.394	0.606	1.93	119.7	0.393	24.37	1.677	0.5170
5/30	65.00	0.757	0.472	0.528	1.60	104.0	0.461	29.97	1.796	0.5856
5/30	68.00	0.751	0.534	0.466	1.41	95.63	0.534	36.31	1.924	0.6544
7/8	68.44	0.736	0.532	0.478						
	68.44 (Normalized)	0.732	0.526	0.474	1.39	95.24	0.565	38.70	2.084	0.7343
7/8	69.08	0.735	0.547	0.461						
	69.08 (Normalized)	0.730	0.543	0.457	1.34	92.87	0.591	40.81	2.120	0.7514
7/8	69.81	0.733	0.567	0.445						
	69.81 (Normalized)	0.725	0.561	0.439	1.29	90.22	0.626	43.73	2.182	0.7802
7/16	70.47	0.719	0.585	0.417						
	70.47 (Normalized)	0.716	0.584	0.416	1.23	86.40	0.683	48.11	2.274	0.8215
7/16	70.81	62.01	Single Phase Region							

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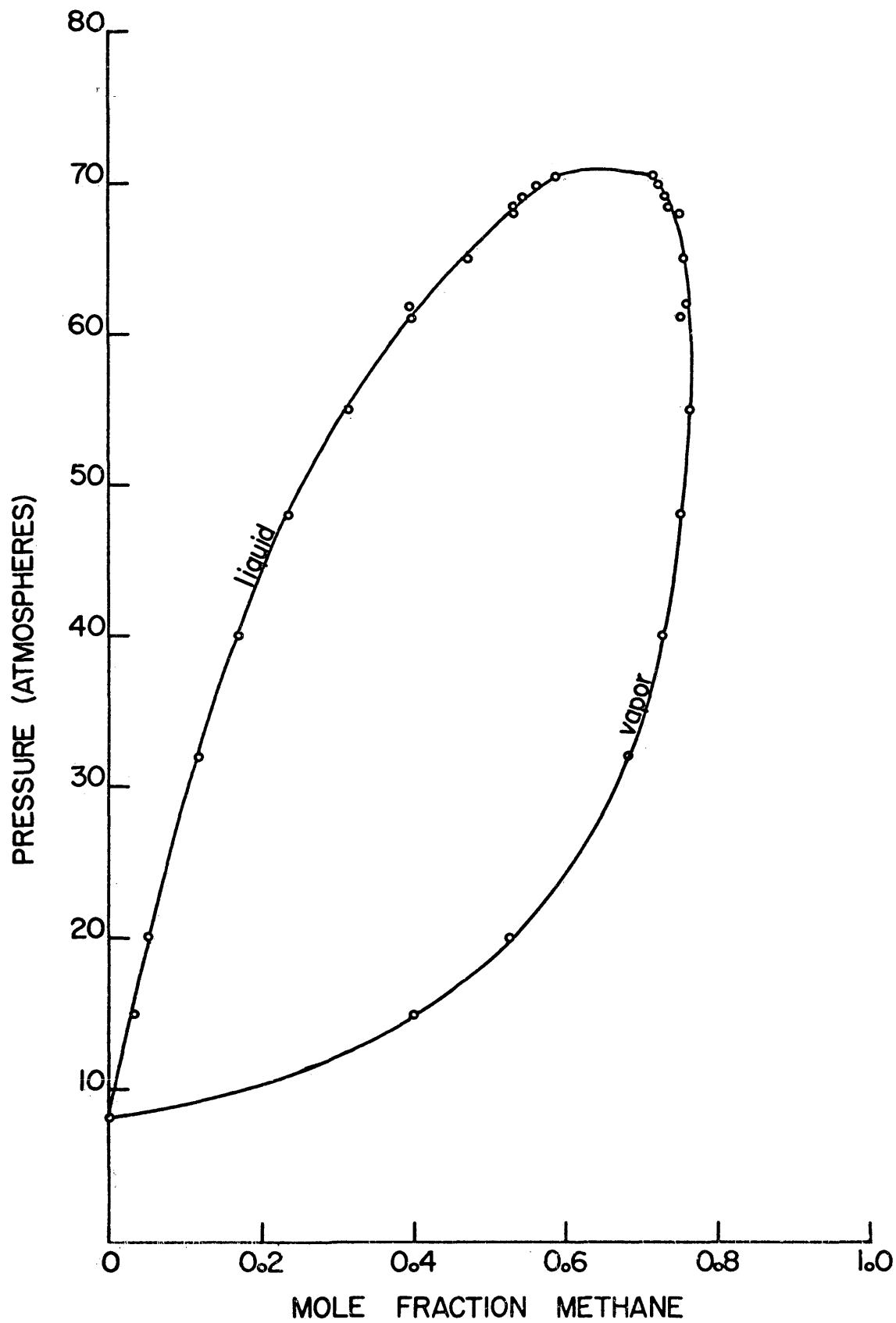
METHANE-CARBON DIOXIDE SYSTEM  
AT 230.00 K

FIGURE 6

METHANE-CARBON DIOXIDE SYSTEM  
AT 230.00 K

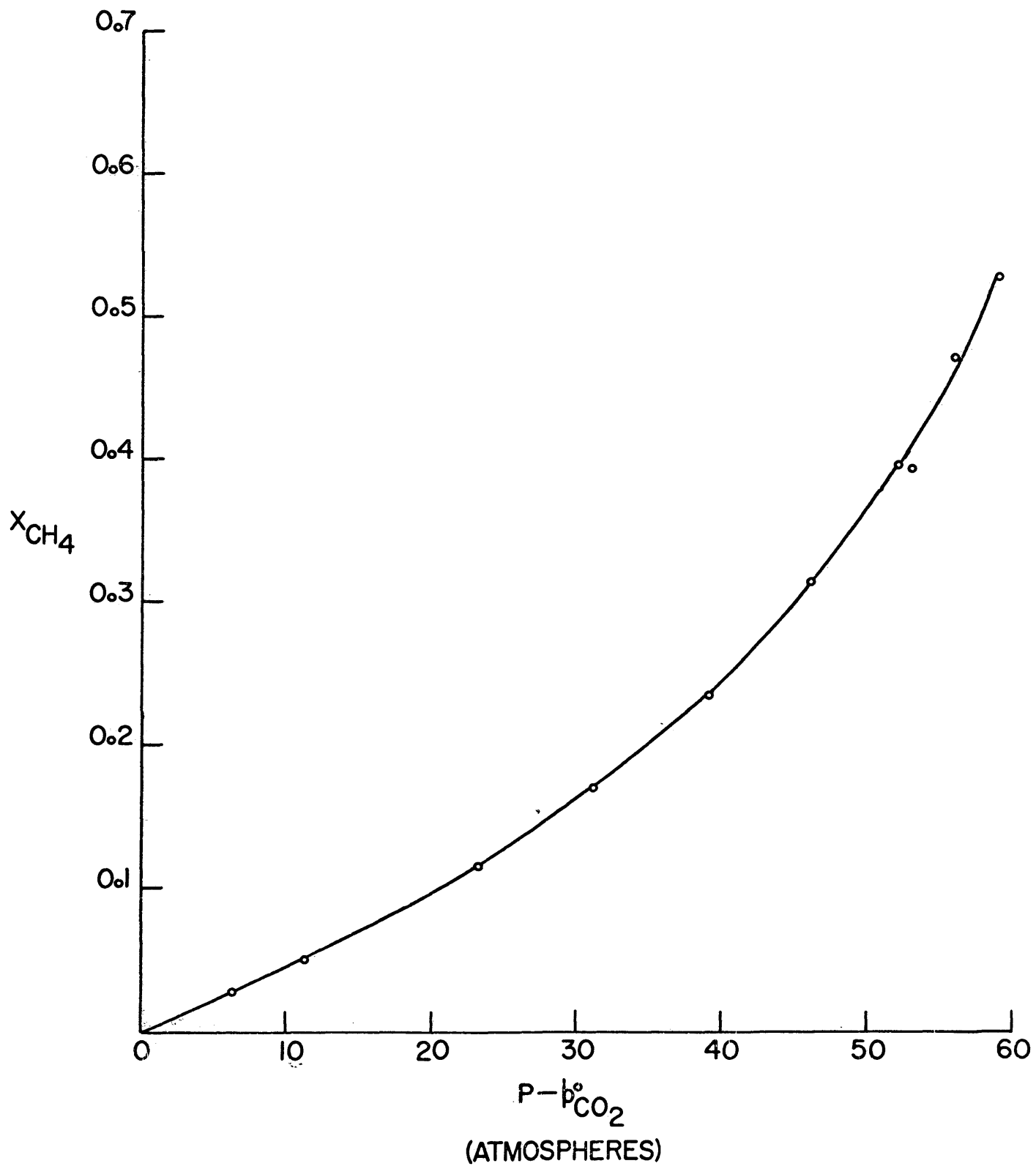


FIGURE 7

METHANE-CARBON DIOXIDE SYSTEM AT 230.00 K

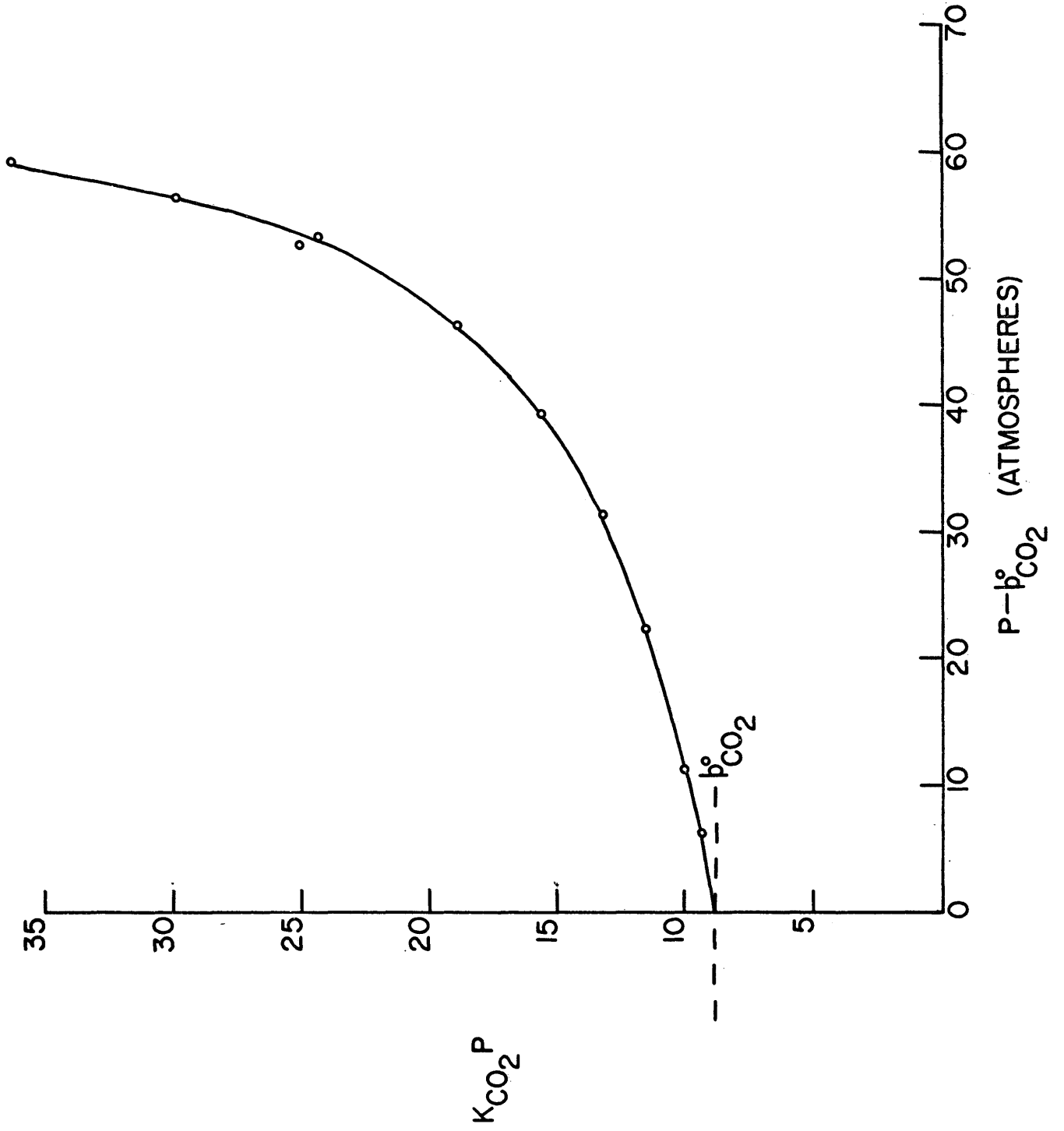
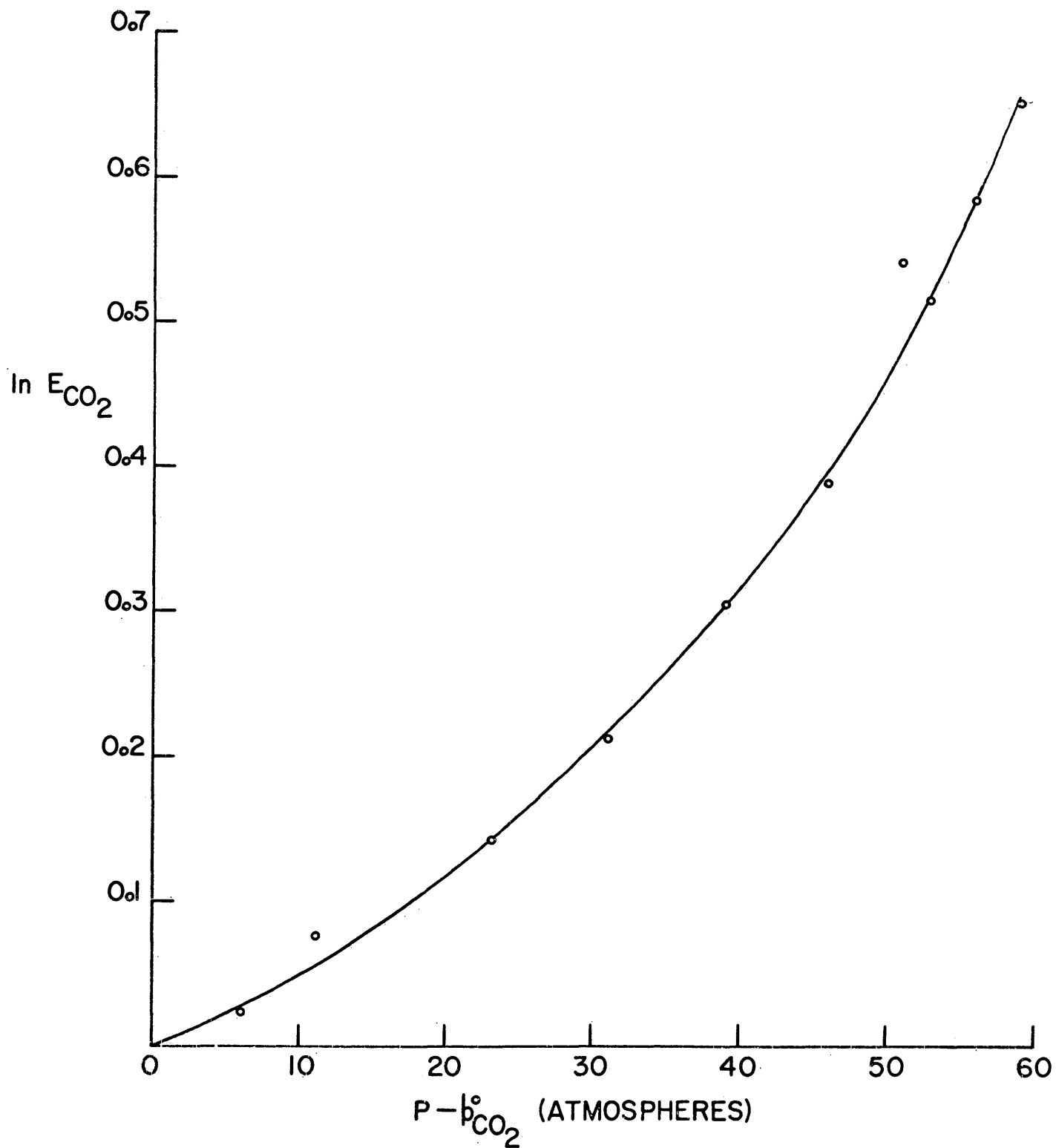




FIGURE 8

METHANE-CARBON DIOXIDE SYSTEM  
AT 230.00 K



CH<sub>4</sub>+CO<sub>2</sub> System at 250.00 K

Figure 9 and table 2 show the data of this system in graphical form and in tabular form. Figure 9 shows all of the data to be on a smooth curve except the points at 78.5 atm. Since both points are displaced to the left, it is felt that the temperature may have been set at the wrong value for this point.

The consistency graphs, figures 10, 11, and 12, indicate good consistency in all points except the one at 50 atm which is slightly off.

The data for this system was all taken while the chromatograph was equipped with the molecular sieve columns. Therefore, the methane alone was measured, and the carbon dioxide was obtained by difference. This was because the molecular sieve columns adsorbed the carbon dioxide so strongly that it couldn't be measured.

Table 2

 $\text{CH}_4 + \text{CO}_2$  System at 250.00°K,  $P_{\text{CO}_2}^0 = 17.62$  atm

Date	System Pressure (atm)	$\frac{P-P_{\text{CO}_2}^0}{(\text{atm})}$	$\frac{Y_{\text{CH}_4}}{Y_{\text{CO}_2}}$	$\frac{X_{\text{CH}_4}}{X_{\text{CO}_2}}$	$\frac{Y_{\text{CO}_2}}{Y_{\text{CO}_2}}$	$\frac{X_{\text{CO}_2}}{X_{\text{CO}_2}}$	$\frac{K_{\text{CH}_4}}{K_{\text{CH}_4}}$	$\frac{K_{\text{CH}_4} P}{K_{\text{CH}_4}}$	$\frac{K_{\text{CO}_2}}{K_{\text{CO}_2}}$	$\frac{K_{\text{CO}_2} P}{K_{\text{CO}_2}}$	$\frac{E_{\text{CO}_2}}{E_{\text{CO}_2}}$	$\frac{\ln E_{\text{CO}_2}}{\ln E_{\text{CO}_2}}$
6/10	17.62	0.00	0.00	0.00	1.00	1.00	indet.	indet.	1.00	17.62	1.00	0.00
5/24	20.00	2.38	0.104	0.010	0.896	0.990	10.40	208.0	0.905	18.10	1.017	0.0169
6/6	23.32	5.70	0.223	0.023	0.777	0.977	9.70	226.1	0.795	18.55	1.028	0.0276
6/10	24.68	7.06	0.254		0.746						1.045	0.0440
5/24	30.00	12.38	0.361	0.053	0.639	0.947	6.81	204.3	0.675	20.24	1.088	0.0843
5/24	40.00	22.38	0.491	0.105	0.509	0.895	4.68	187.0	0.569	22.75	1.155	0.1441
5/25	50.00	32.38	0.575	0.166	0.425	0.834	3.46	173.2	0.510	25.48	1.206	0.1873
5/25	60.00	42.38	0.605	0.237	0.395	0.763	2.55	153.2	0.518	31.06	1.345	0.2964
5/25	70.00	52.38	0.615	0.326	0.385	0.674	1.89	132.1	0.571	39.98	1.530	0.4253
5/25	77.00	59.38	0.605	0.400	0.395	0.600	1.51	116.5	0.658	50.69	1.726	0.5458
6/10	78.50	60.88	0.564	0.405	0.436	0.595	1.39	109.3	0.733	57.52	1.942	0.6637
6/10	79.88	62.26	0.558	0.446	0.442	0.554	1.25	99.94	0.798	63.73	2.004	0.6951
6/6	80.70											

Single Phase Region

METHANE—CARBON DIOXIDE SYSTEM AT 250.00 K

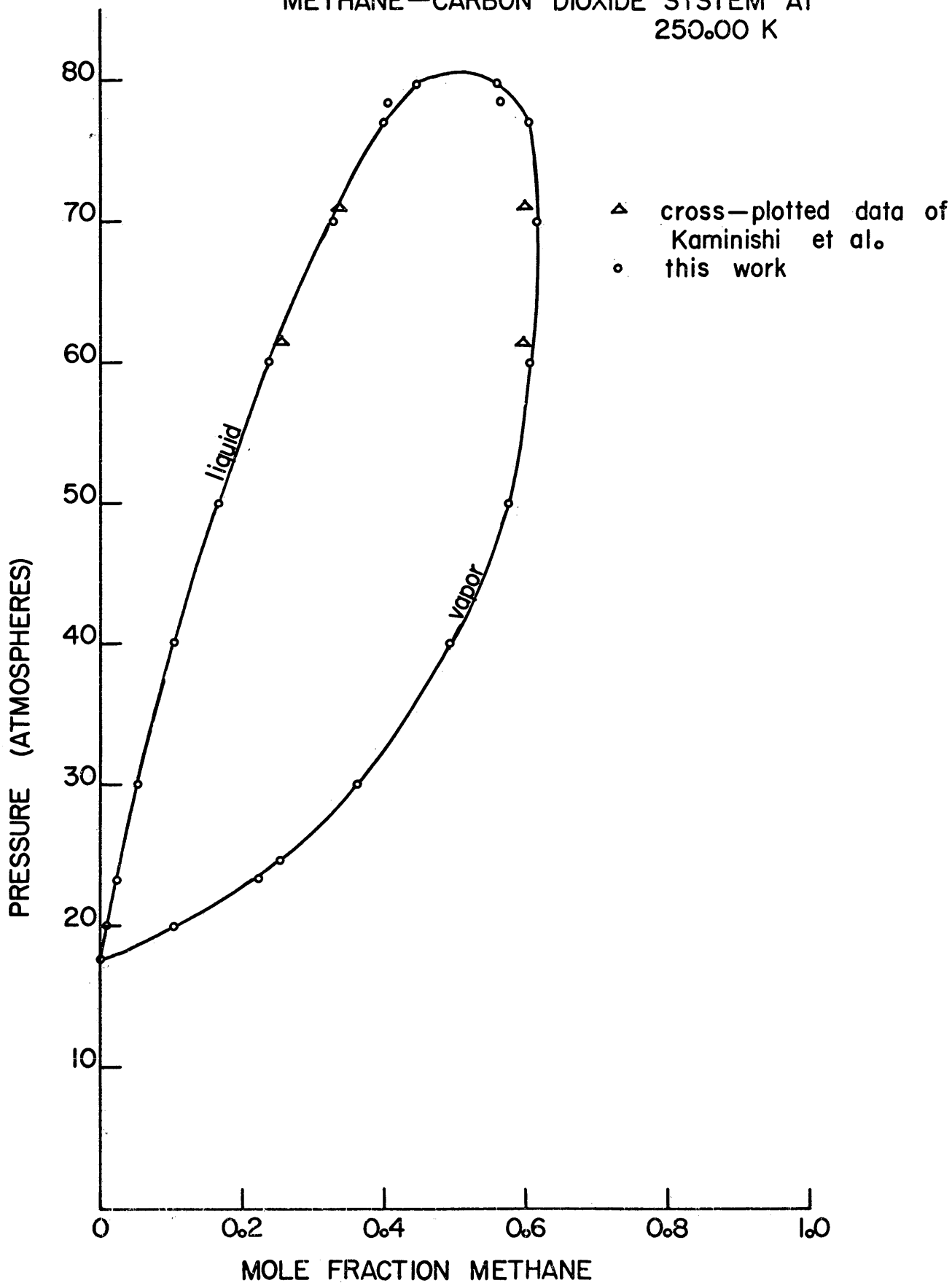


FIGURE 10  
METHANE-CARBON DIOXIDE SYSTEM  
AT 250.00 K

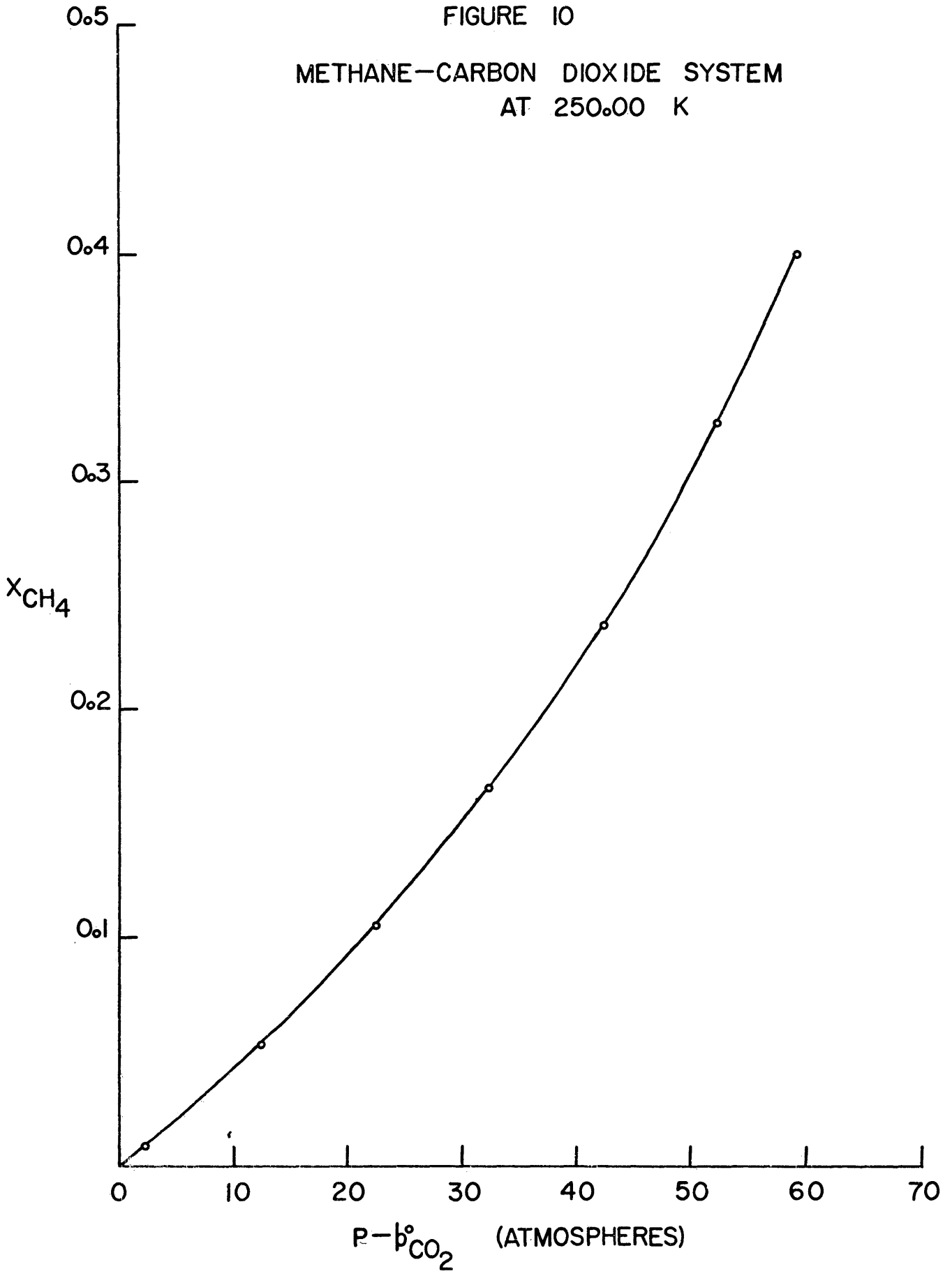
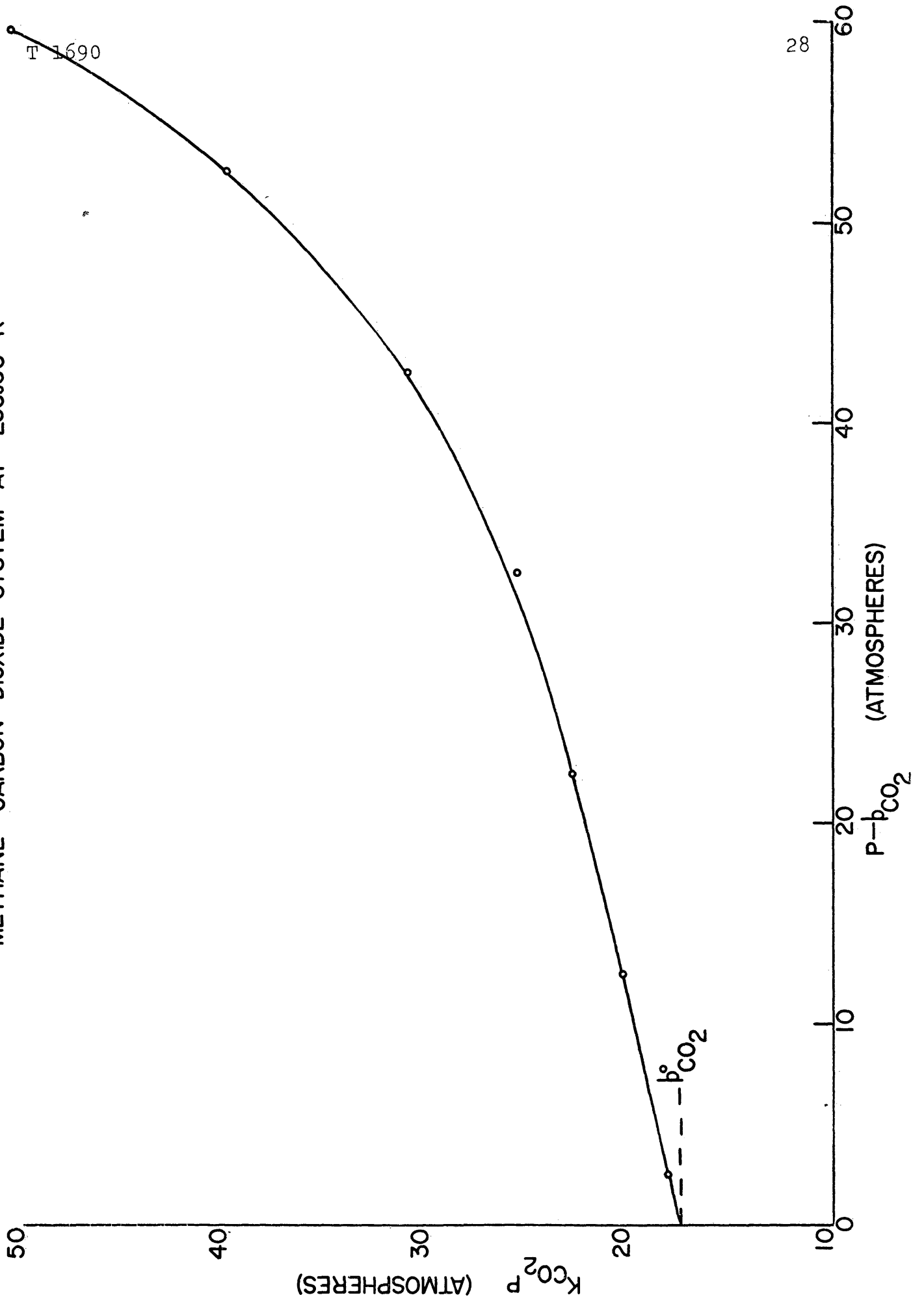
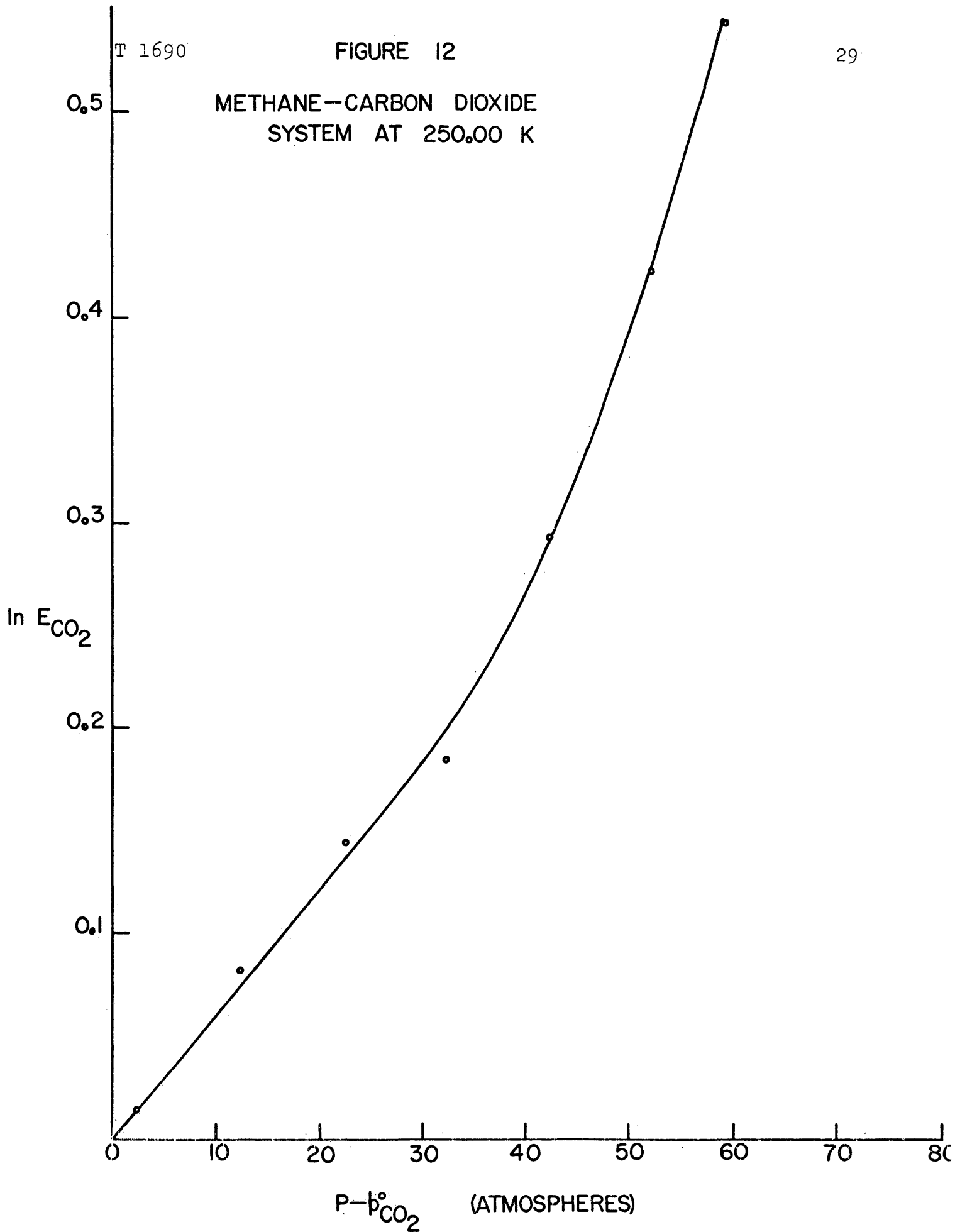


FIGURE 11  
METHANE-CARBON DIOXIDE SYSTEM AT 250.00 K



METHANE-CARBON DIOXIDE  
SYSTEM AT 250.00 K



$\text{CH}_4 + \text{CO}_2$  System at 270.00 K

The data for this system were obtained when the chromatograph was equipped with molecular sieve columns. These molecular sieves adsorbed the  $\text{CO}_2$  so strongly that it could not be measured. Therefore, the concentration of methane was measured and the concentration of  $\text{CO}_2$  was obtained as the difference.

The data for this system is presented in table 3 and in figure 13. Figure 13 shows all of the points lying on a smooth curve. The graphs of figure 14 and 15 also show good consistency of the data. The  $\ln E$  versus  $P-p^0$  graph (figure 16) shows some scatter to the data, but the scatter is slight when it is realized that this is a very sensitive check of the data. Figure 16 also, therefore, indicates good consistency in the data.



Table 3  
 $\text{CH}_4 + \text{CO}_2$  System at 270.00°K,  $P_{\text{CO}_2}^0 = 31.53$  atm

Date	System Pressure (atm)	$\frac{P-P_{\text{CO}_2}^0}{P_{\text{CO}_2}^0}$ (atm)	$\frac{Y_{\text{CH}_4}}{Y_{\text{CO}_2}}$	$\frac{X_{\text{CH}_4}}{X_{\text{CO}_2}}$	$\frac{Y_{\text{CO}_2}}{Y_{\text{CO}_2}}$	$\frac{X_{\text{CO}_2}}{X_{\text{CH}_4}}$	$\frac{K_{\text{CH}_4} P}{K_{\text{CH}_4}}$	$\frac{K_{\text{CO}_2} P}{K_{\text{CO}_2}}$	$\frac{K_{\text{CO}_2} P}{K_{\text{CO}_2}}$	$\frac{E_{\text{CO}_2}}{E_{\text{CO}_2}}$	$\frac{1n E_{\text{CO}_2}}{1n E_{\text{CO}_2}}$
6/4	31.53	0.00	0.00	0.00	1.00	indet.	indet.	1.00	31.53	1.00	0.00
6/4	35.09	3.56	0.083	0.014	0.917	6.09	213.7	0.930	32.61	1.020	0.0199
5/31	36.53	5.00	0.108	0.018	0.892	5.95	217.4	0.908	33.19	1.034	0.0334
6/4	39.75	8.22	0.162	0.032	0.838	5.09	202.3	0.866	34.42	1.057	0.0555
5/31	41.59	10.06	0.190	0.040	0.810	4.78	198.8	0.844	35.09	1.069	0.0668
5/31	49.97	18.44	0.282	0.077	0.718	3.68	183.9	0.778	38.86	1.138	0.1295
6/4	57.81	26.28	0.353	0.113	0.647	3.13	180.9	0.730	42.17	1.186	0.1710
5/31	69.29	37.76	0.405	0.166	0.595	2.43	168.4	0.714	49.45	1.307	0.2680
6/4	79.58	48.05	0.411	0.260	0.589	1.58	126.1	0.795	63.27	1.486	0.3958
6/5	84.08	52.55	0.375	0.319	0.625	1.17	98.71	0.919	77.24	1.668	0.5115
6/5	84.81	Single Phase Region									
6/5	85.71	Single Phase Region									

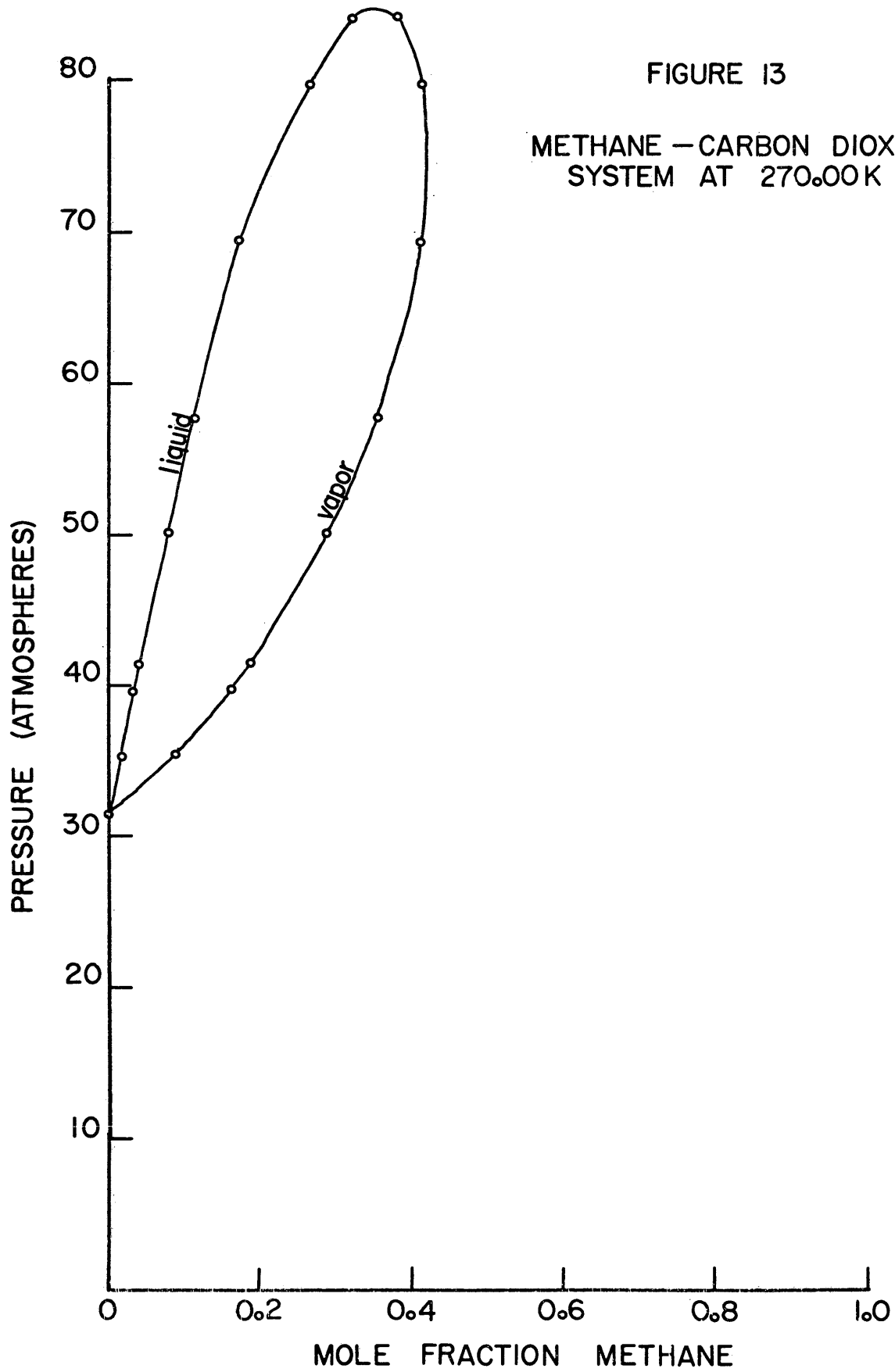


FIGURE 13

METHANE - CARBON DIOXIDE  
SYSTEM AT 270.00K

FIGURE 14

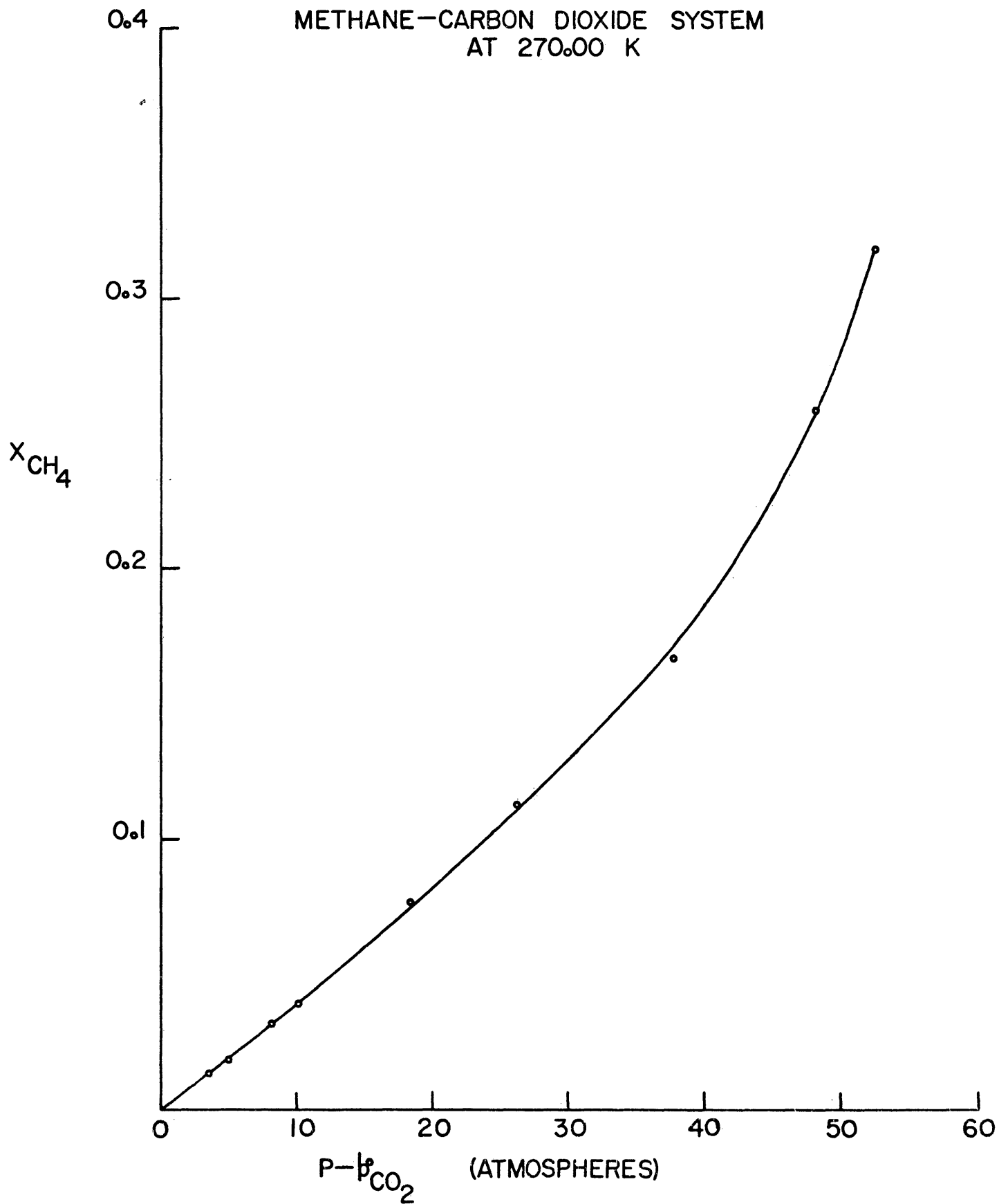
METHANE-CARBON DIOXIDE SYSTEM  
AT 270.00 K

FIGURE 15  
METHANE-CARBON DIOXIDE SYSTEM AT 270.00 K

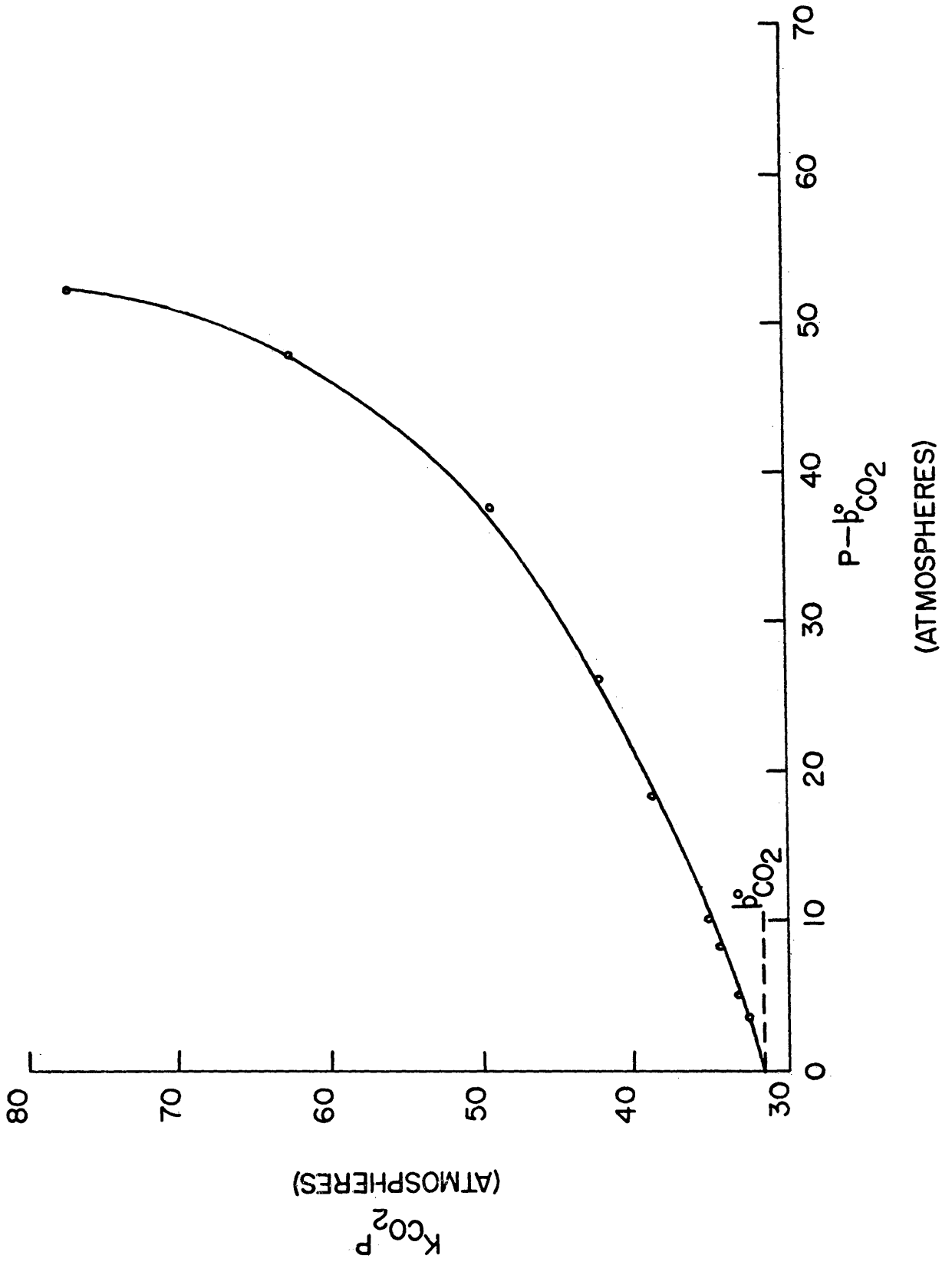
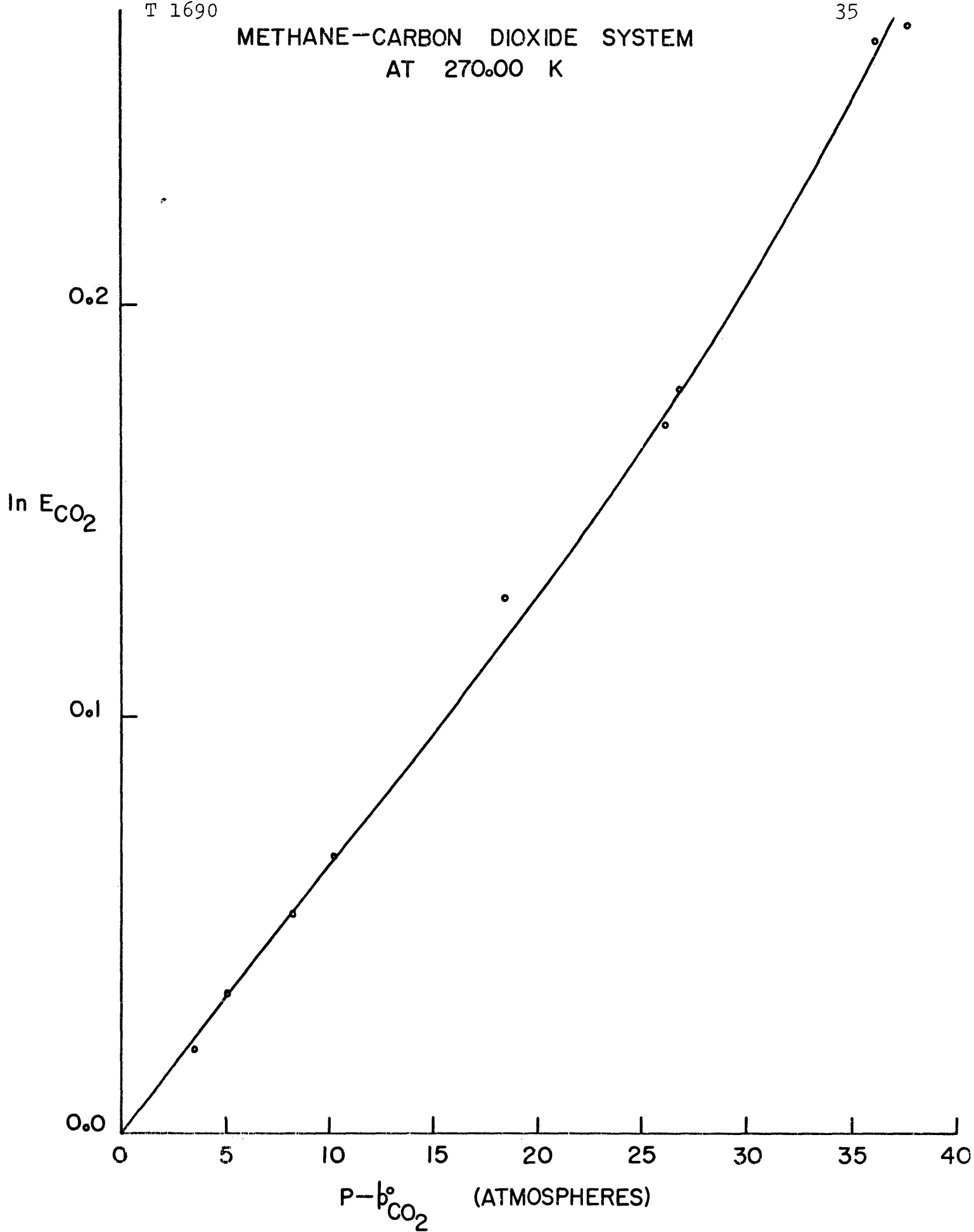


FIGURE 16

METHANE-CARBON DIOXIDE SYSTEM  
AT 270.00 K

T 1690

35



$\text{CH}_4 + \text{C}_2\text{H}_6$  System at 250.00 K

The data for this system were taken by Mr. Juan Davalos using the silica gel columns in the chromatograph. Both components could, therefore, be analyzed. All of the data for this system were normalized.

The data for this system are presented in table 4 and in figure 17. The graphical representation of the data shows all points on the smooth curve. Figures 18, 19, and 20 show that the data is consistent. Only 1 point on figure 20 is displaced from the straight line and this is a higher pressure point. Since the low pressure points in figure 20 are on a straight line through zero on the ordinate, the consistency is good.

Figures 21 and 22 show the data of this system plotted with the data of Ellington et al. (1959). These graphs show  $K$  of  $\text{CH}_4$  versus temperature (figure 21) and temperature versus composition of  $\text{CH}_4$  (figure 22). Both graphs show good agreement between the two sets of data.

Table 4

CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> System at 250.00°K

Date	System Pressure (atm)	P-P <sub>CO<sub>2</sub></sub> <sup>o</sup> (atm)	Y <sub>CH<sub>4</sub></sub>	X <sub>CH<sub>4</sub></sub>	Y <sub>C<sub>2</sub>H<sub>6</sub></sub>	X <sub>C<sub>2</sub>H<sub>6</sub></sub>	K <sub>CH<sub>4</sub></sub>	K <sub>CH<sub>4</sub></sub> <sup>P</sup>	K <sub>C<sub>2</sub>H<sub>6</sub></sub>	K <sub>C<sub>2</sub>H<sub>6</sub></sub> <sup>P</sup>	E <sub>C<sub>2</sub>H<sub>6</sub></sub>	ln E <sub>C<sub>2</sub>H<sub>6</sub></sub>
6/15	12.85	0.00	0.00	0.00	1.00	1.00	indet.	indet.	1.00	12.85	1.00	0.00
6/15	15.10	2.25	0.134	0.024	0.866	0.976	5.702	86.10	0.887	13.39	1.018	0.017
6/19	22.00*	9.15	0.369 0.365	0.092 0.089	0.643 0.635	0.941 0.911	4.101	90.22	0.697	15.33	1.087	0.084
6/15	22.50	9.65	0.383	0.097	0.617	0.903	3.948	88.83	0.683	15.37	1.080	0.077
6/15	32.50	19.65	0.540	0.196	0.460	0.804	2.755	89.54	0.572	18.59	1.163	0.151
6/15	34.00	21.15	0.554	--	0.446	--	--	--	--	--	1.180	0.166
6/15	45.00	32.15	0.643	0.320	0.357	0.680	2.009	90.40	0.525	23.63	1.250	0.223
6/15	55.20	42.35	0.673	0.426	0.327	0.574	1.580	87.22	0.570	31.45	1.405	0.340
6/15	65.70	52.85	0.673	0.546	0.327	0.454	1.233	81.01	0.720	47.32	1.672	0.514
6/15	67.50	Single Phase Region										

\*Chromatograph settings are much different for this point than for the others.

\*\*No liquid sample taken.

All data for this system are normalized.

T 1690

FIGURE 17  
METHANE-ETHANE SYSTEM  
AT 250.00

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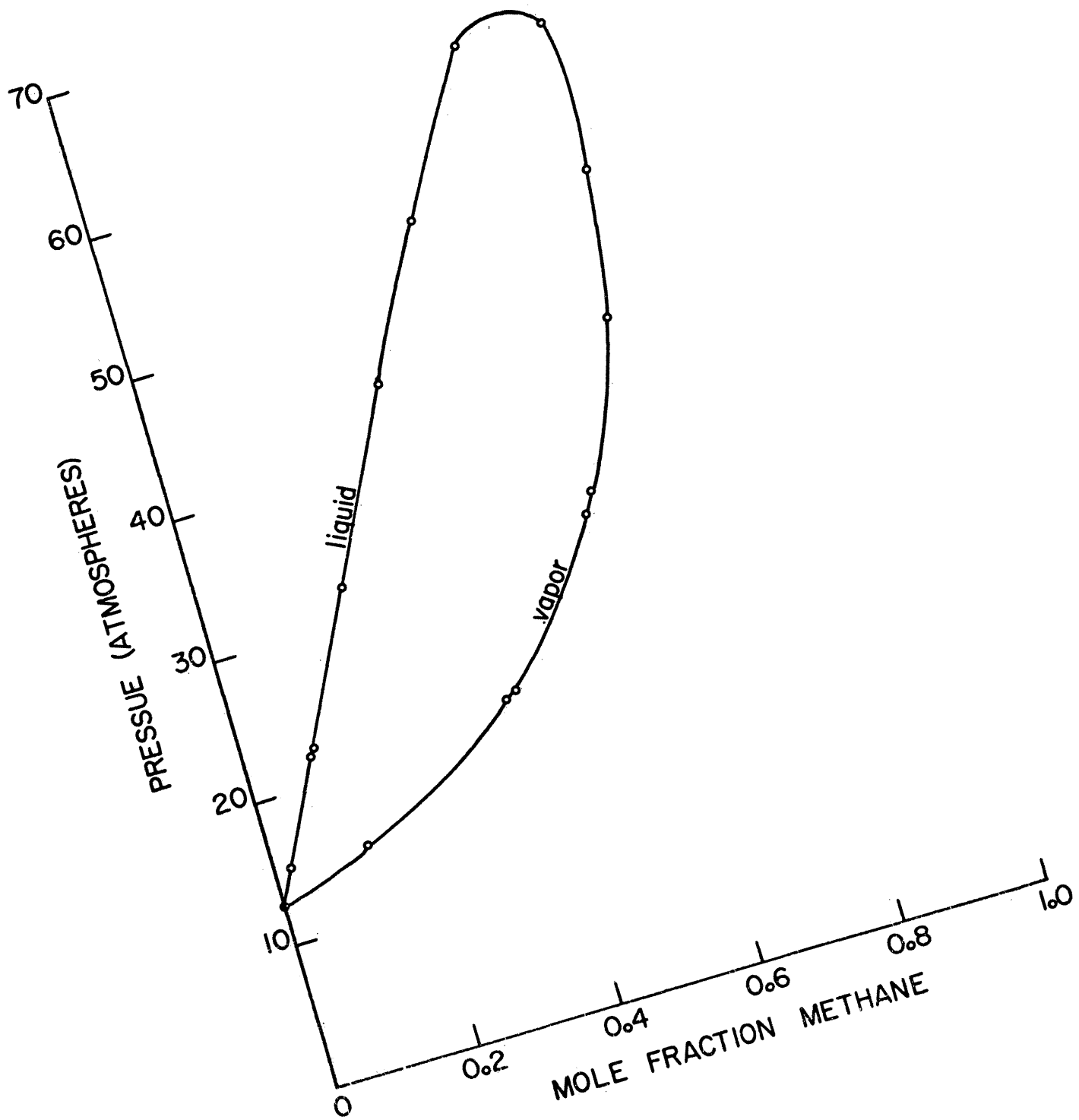




FIGURE 18

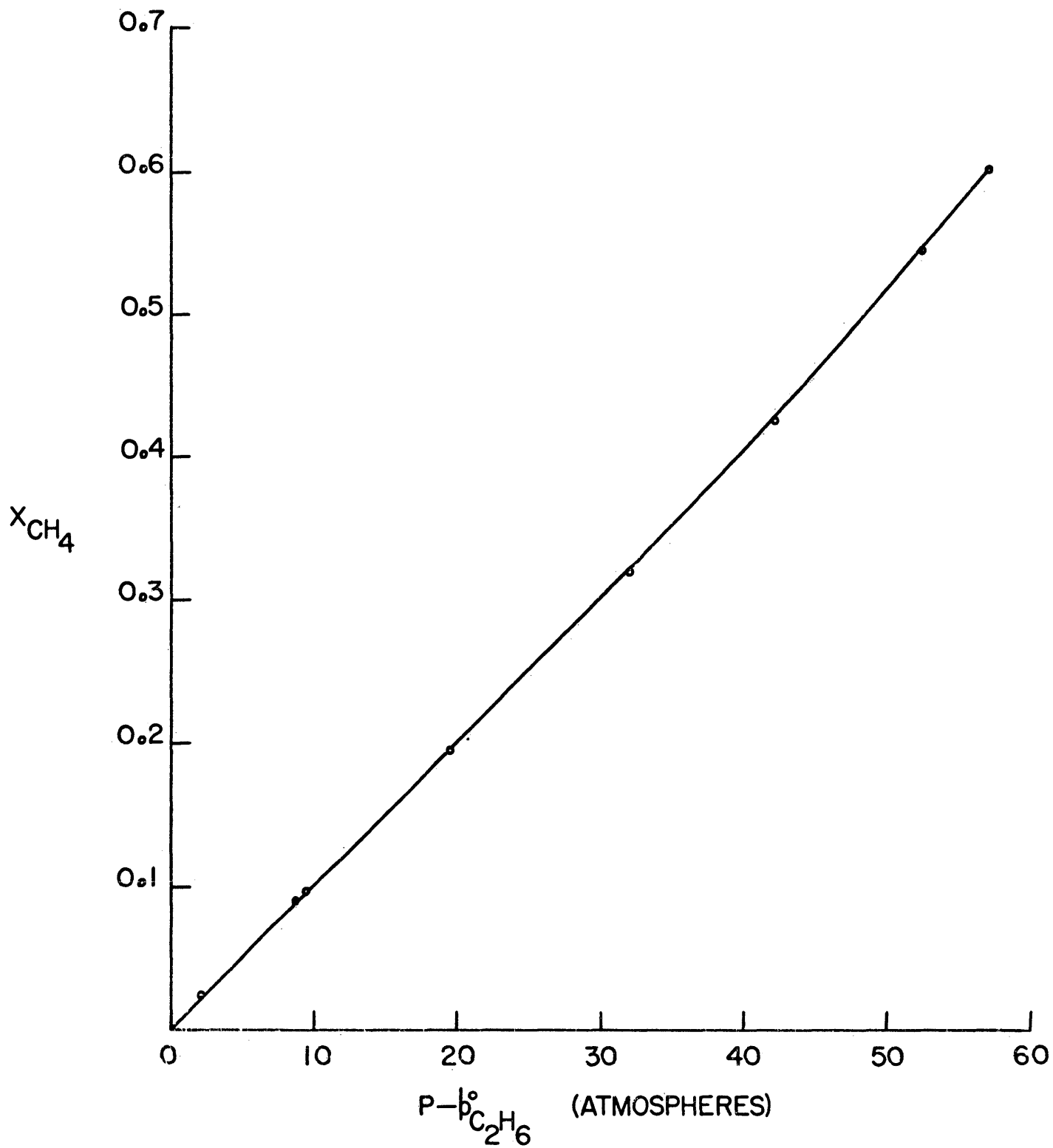
METHANE-ETHANE SYSTEM AT  
250.00 K

FIGURE 19  
METHANE-ETHANE SYSTEM AT 250.00 K

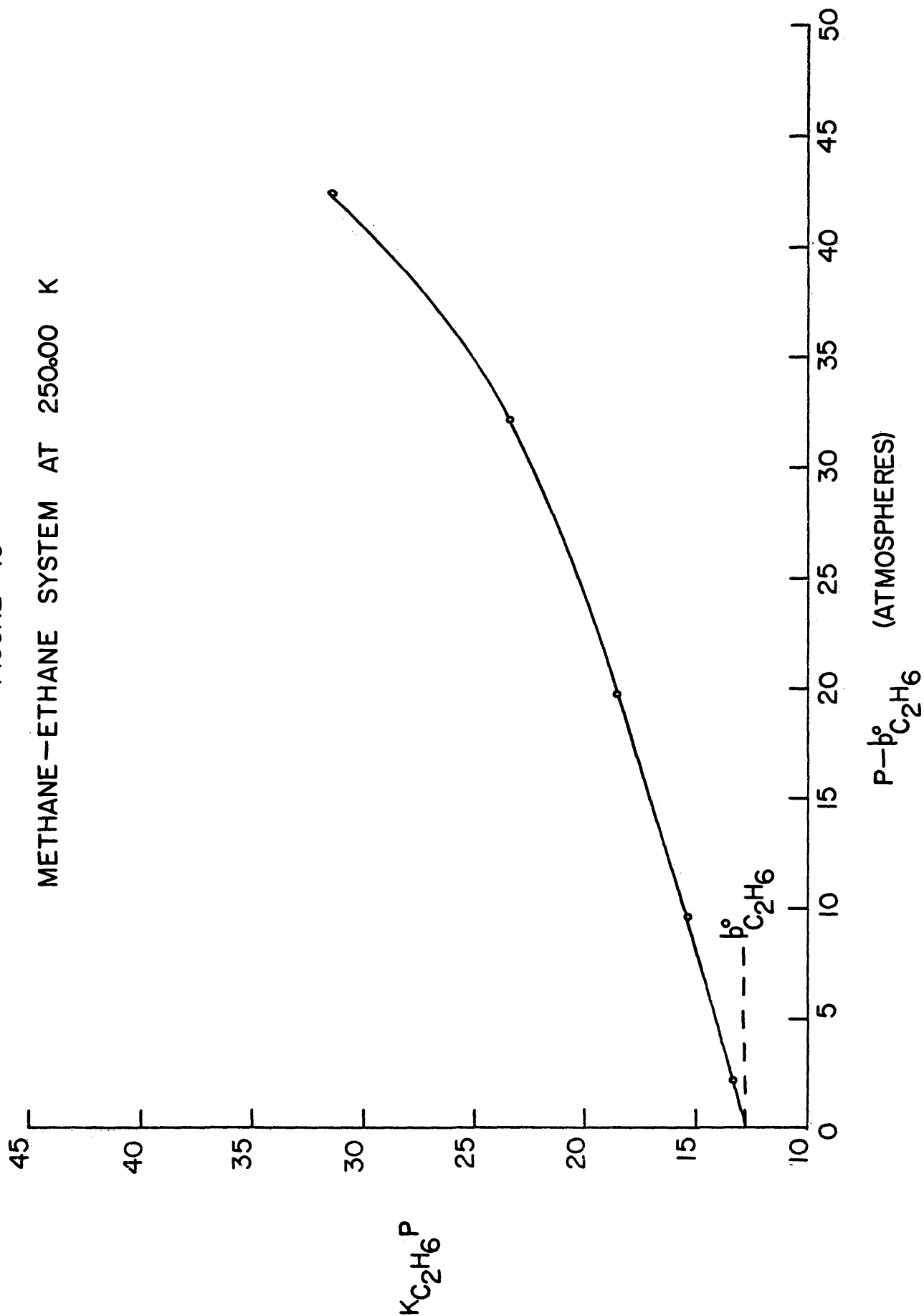


FIGURE 20  
METHANE-ETHANE SYSTEM AT 250.00 K

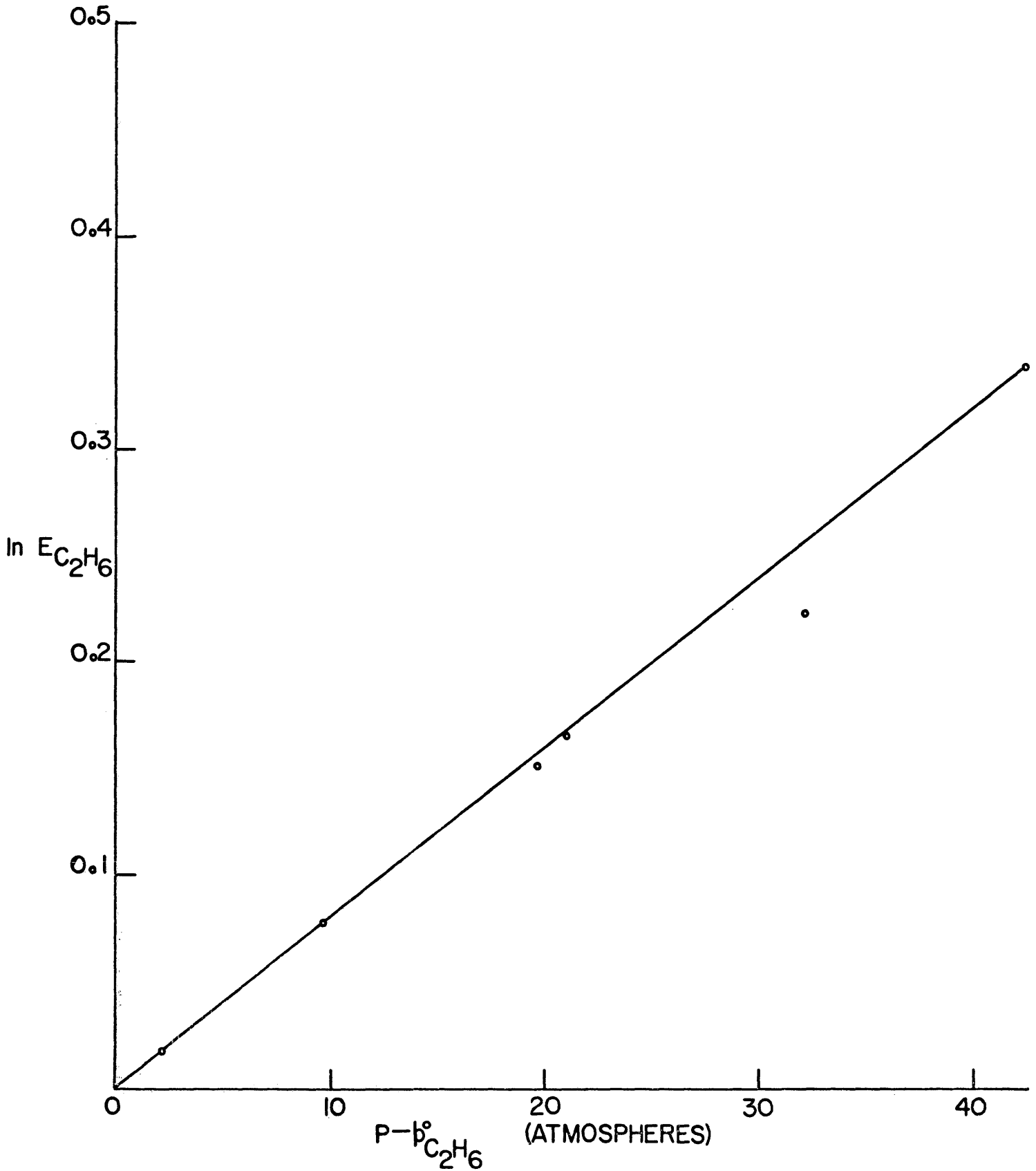


FIGURE 21  
METHANE-ETHANE SYSTEM

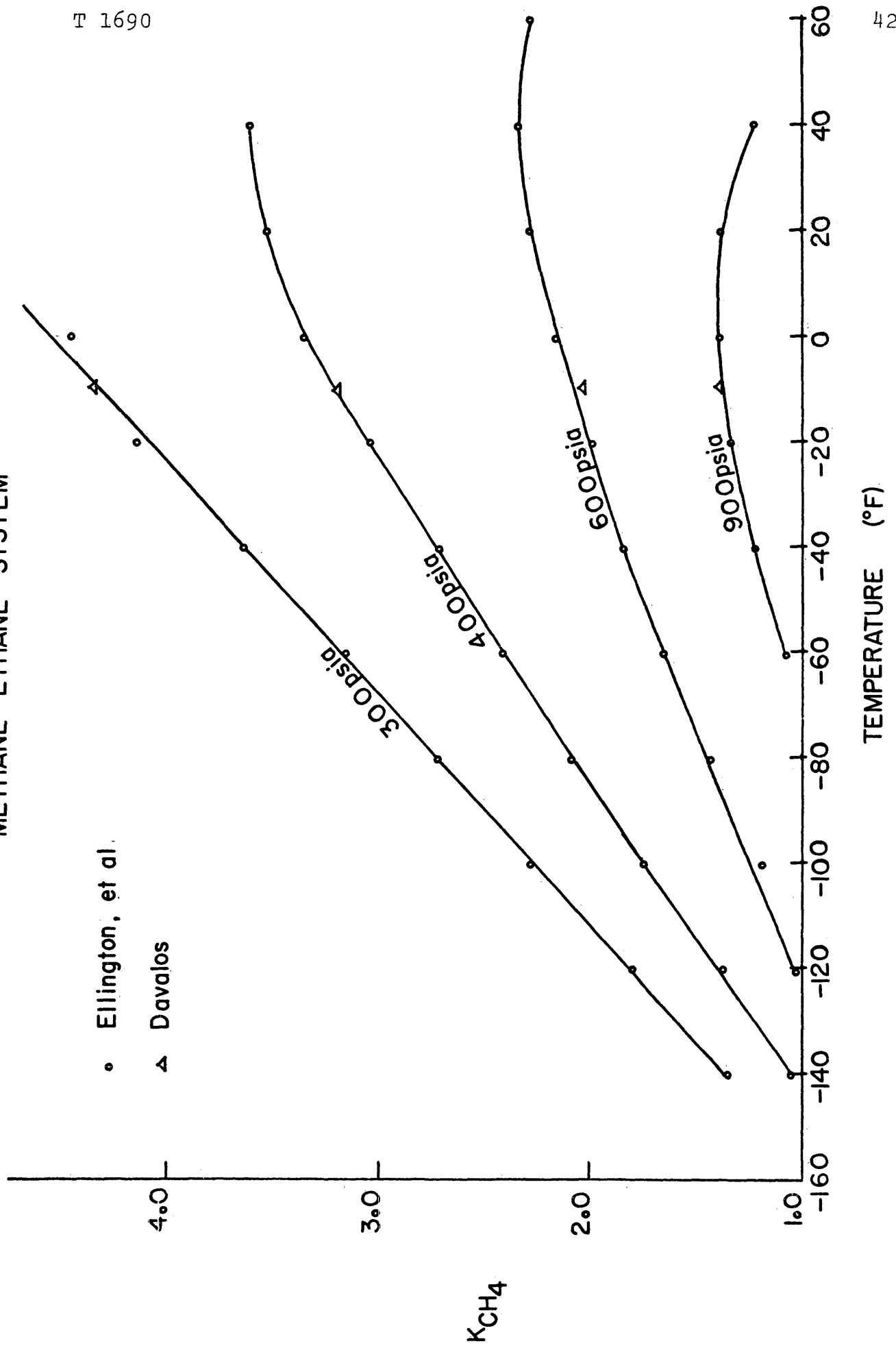
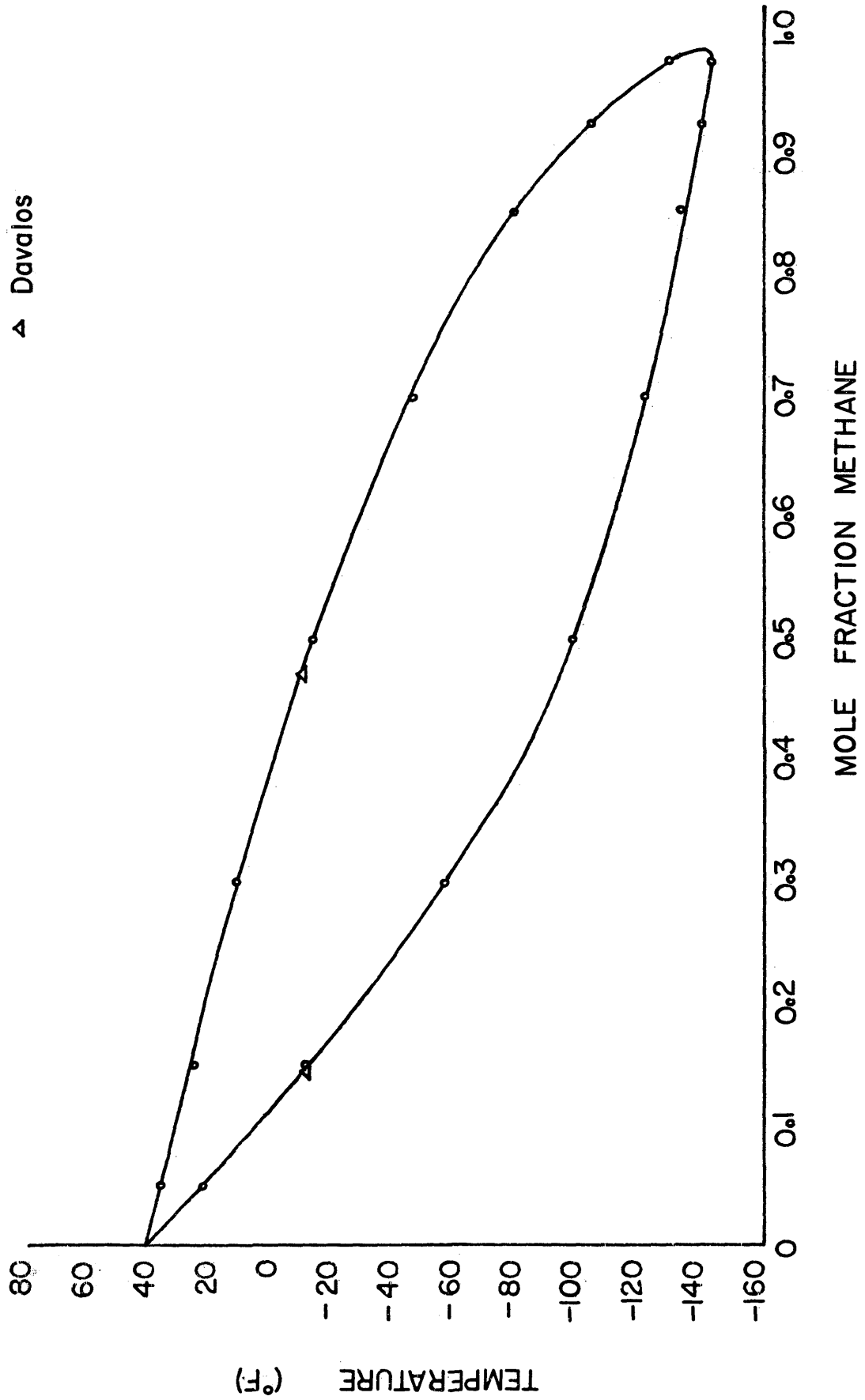


FIGURE 22  
METHANE-ETHANE SYSTEM AT 400 psia

• Ellington, et al.  
△ Davalos



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$\text{CO}_2 + \text{C}_2\text{H}_6$  System at 250.00 K

The data of this system were all taken with the chromatograph equipped with silica gel columns. Therefore, both components were analyzed and the data was normalized.

Table 5 and figure 23 show the data for this system. All of the data points fall nicely on the smooth curve as shown in figure 23. There is an azeotrope at about 65 mole percent  $\text{CO}_2$ .

Table 6 shows the derived values for this system. This table shows that all of the enhancement factors were 1 or less. The natural logarithm of those values less than 1 were negative and so the graph was hard to interpret and not included with the consistency graphs. However, KP versus P graphs for both components are included (figures 24 and 25), and they indicate good consistency of the data.

Figure 26 is a graph comparing the values of the azeotrope pressure versus temperature for this work and other earlier works. They are all in good agreement.

Table 5  
 $C_2H_6 + CO_2$  System at 250.00°K

Date	System Pressure (atm)	$Y_{C_2H_6}$	$Y_{CO_2}$	$\Sigma Y$	$\frac{Y_{C_2H_6}}{Y_{C_2H_6} + Y_{CO_2}}$	$\frac{Y_{CO_2}}{Y_{C_2H_6} + Y_{CO_2}}$	$X_{C_2H_6}$	$X_{CO_2}$	$\Sigma X$	$\frac{X_{C_2H_6}}{X_{C_2H_6} + X_{CO_2}}$	$\frac{X_{CO_2}}{X_{C_2H_6} + X_{CO_2}}$
7/3	12.85	1.00	0.00	1.00	1.00	0.00	1.00	0.00	1.00	1.00	0.00
7/3	14.23	0.8952	0.1123	1.0075	0.8885	0.1115	0.9624	0.0447	1.0071	0.9556	0.0444
7/3	15.68	0.7816	0.2238	1.0054	0.7774	0.2226	0.8870	0.1024	0.9894	0.8965	0.1035
7/3	16.93	0.6983	0.3006	0.9989	0.6991	0.3009	0.8254	0.1667	0.9921	0.8320	0.1680
7/3	18.04	0.6314	0.3704	1.0018	0.6303	0.3697	0.7825	0.2265	1.009	0.7755	0.2245
7/2	19.23	0.5579	0.4517	1.0096	0.5526	0.4447	0.6999	0.3120	1.0119	0.6917	0.3083
7/2	20.03	0.5025	0.5139	1.0164	0.4964	0.5056	0.6090	0.4027	1.0117	0.6020	0.3980
7/2	20.56	0.4522	0.5576	1.0098	0.4478	0.5522	0.5382	0.4757	1.0139	0.5308	0.4692
7/2	20.99	0.3787	0.6352	1.0139	0.3735	0.6265	0.4081	0.6095	1.0176	0.4010	0.5990
6/26	21.07	0.3211	0.6830	1.0041	0.3198	0.6802	0.3123	0.6951	1.0074	0.3100	0.6900
6/26	20.80	0.2550	0.7517	1.0067	0.2533	0.7467	0.2113	0.7985	1.0098	0.2092	0.7908
7/2	19.99	0.1798	0.8286	1.0084	0.1783	0.8217	0.1186	0.8938	1.0124	0.1171	0.8829
6/27	19.40	0.1322	0.8816	1.0138	0.1304	0.8696	0.0748	0.9364	1.0112	0.0740	0.9260
6/26	18.51	0.0623	0.9387	1.0010	0.0622	0.9378	0.0305	0.9880	1.0185	0.0299	0.9701
7/2	17.62	0.00	1.00	1.00	0.00	1.00	0.00	1.00	1.00	0.00	1.00

Table 6

 $C_2H_6 + CO_2$  System at 250.00°K

 $P_{C_2H_6} = 12.85 \text{ atm}, P_{CO_2}^0 = 17.62 \text{ atm}$ 

System Pressure (atm)	$P-P_{C_2H_6}^0$ (atm)	$P-P_{CO_2}^0$ (atm)	$K_{C_2H_6}$	$K_{C_2H_6}^P$	$K_{CO_2}$	$K_{CO_2}^P$	$E_{C_2H_6}$	$E_{CO_2}$
12.85	0.00	-4.77	1.00	12.85	indet.	indet.	1.00	0.00
14.23	1.38	-3.39	0.9298	13.23	2.511	35.74	0.9839	0.0900
15.68	2.85	-1.94	0.8672	13.60	2.151	33.72	0.9486	0.1981
16.93	4.08	-0.69	0.8403	14.23	1.791	30.32	0.9211	0.2891
18.04	5.19	0.42	0.8128	14.66	1.647	29.71	0.8849	0.3785
19.23	6.38	1.61	0.7989	15.36	1.451	27.91	0.8270	0.4883
20.03	7.18	2.41	0.8213	16.45	1.270	25.45	0.7706	0.5748
20.56	7.71	2.94	0.8436	17.35	1.177	24.20	0.7165	0.6443
20.99	8.14	3.37	0.9314	19.55	1.046	21.95	0.6101	0.7463
21.07	8.22	3.45	1.032	21.74	0.9858	20.77	0.5244	0.8134
20.80	7.95	3.18	1.211	25.18	0.9442	19.64	0.4100	0.8815
19.99	7.14	2.37	1.523	30.44	0.9307	18.60	0.2774	0.9322
19.40	6.55	1.78	1.762	34.19	0.9391	18.22	0.1969	0.9574
18.51	5.66	0.89	2.080	38.51	0.9667	17.89	0.0896	0.9852
17.62	4.77	0.00	indet.	indet.	1.000	17.62	0.00	1.00



FIGURE 23  
CARBON DIOXIDE-ETHANE SYSTEM AT 250.00 K

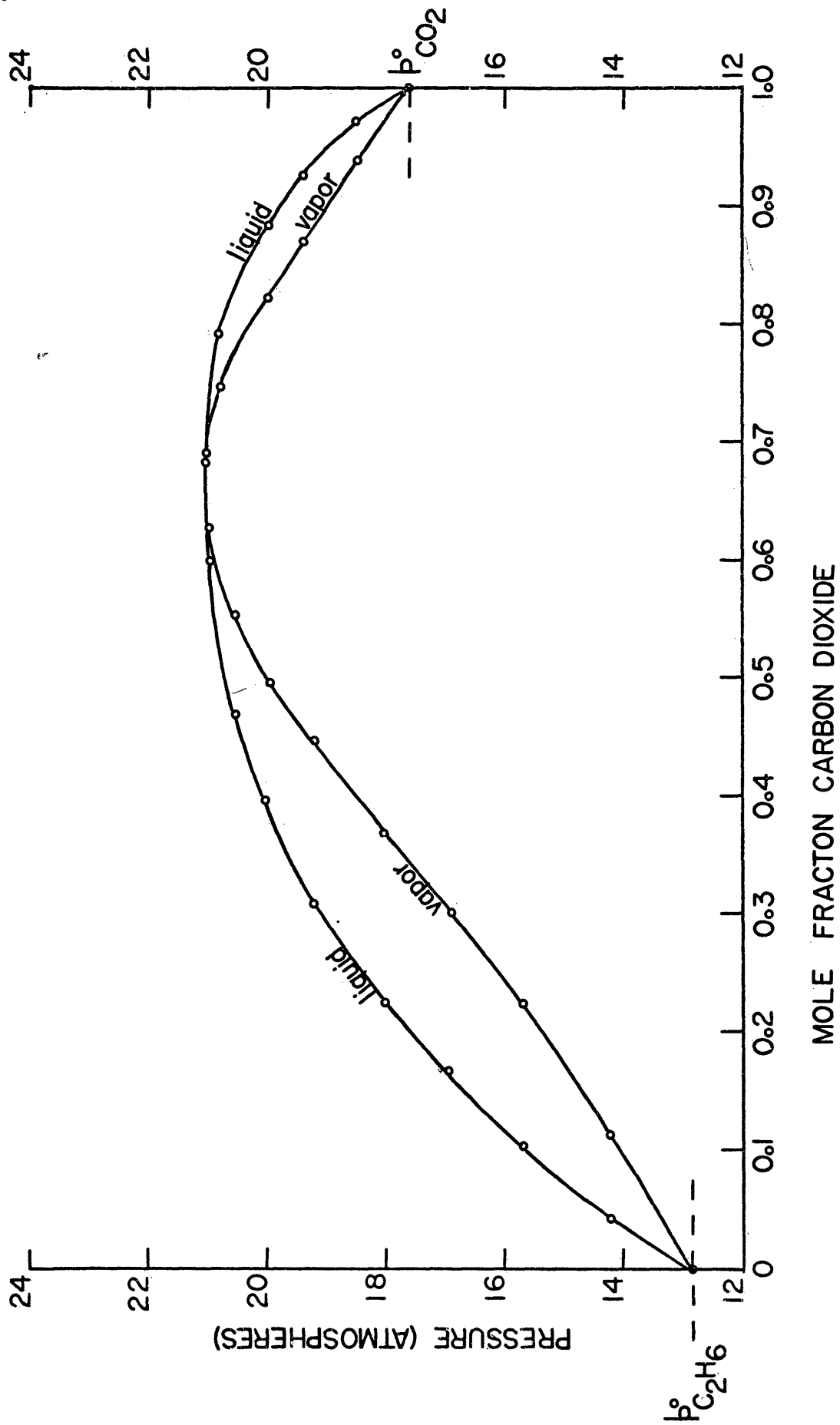


FIGURE 24  
ETHANE-CARBON DIOXIDE SYSTEM AT 250.00 K

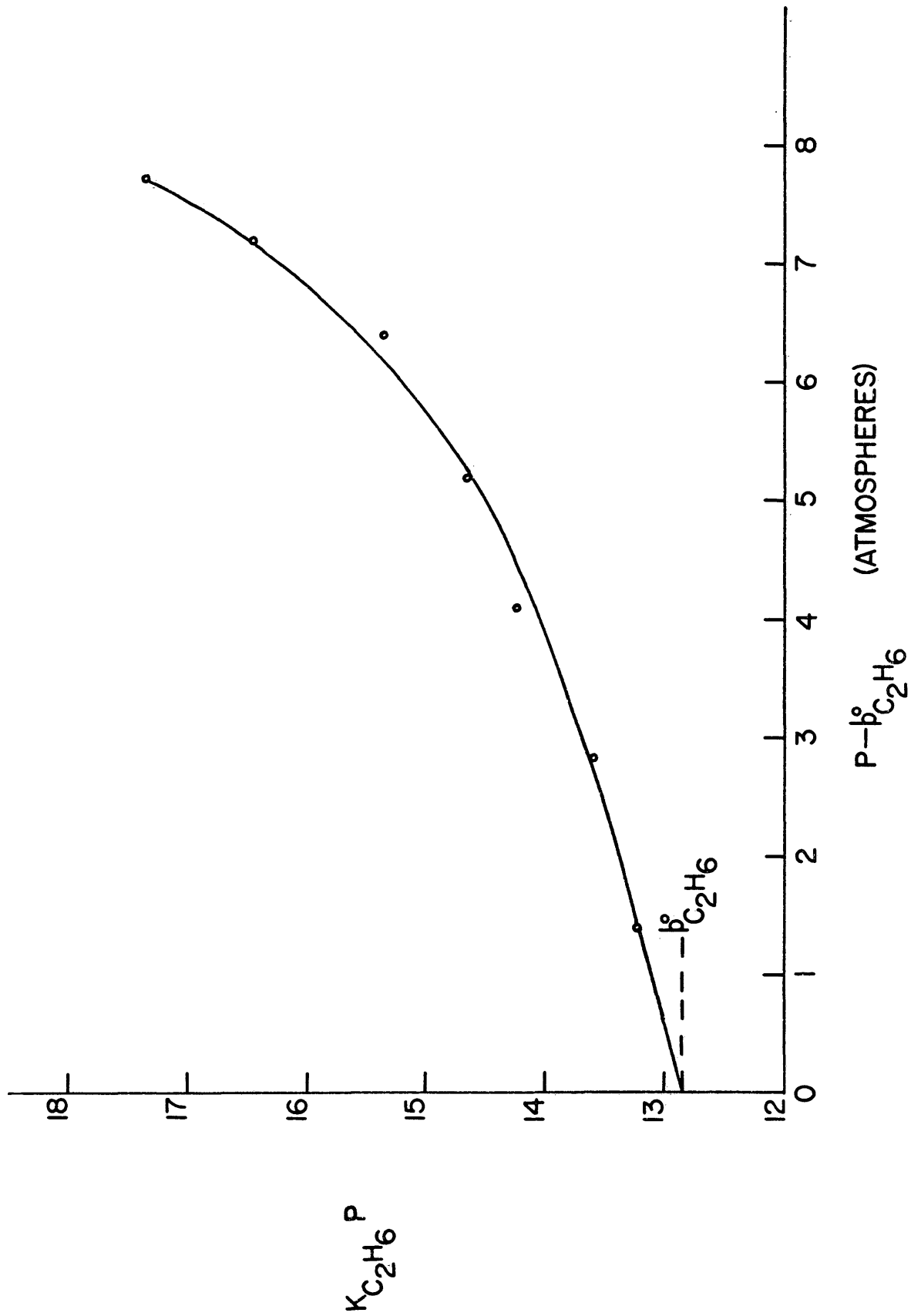
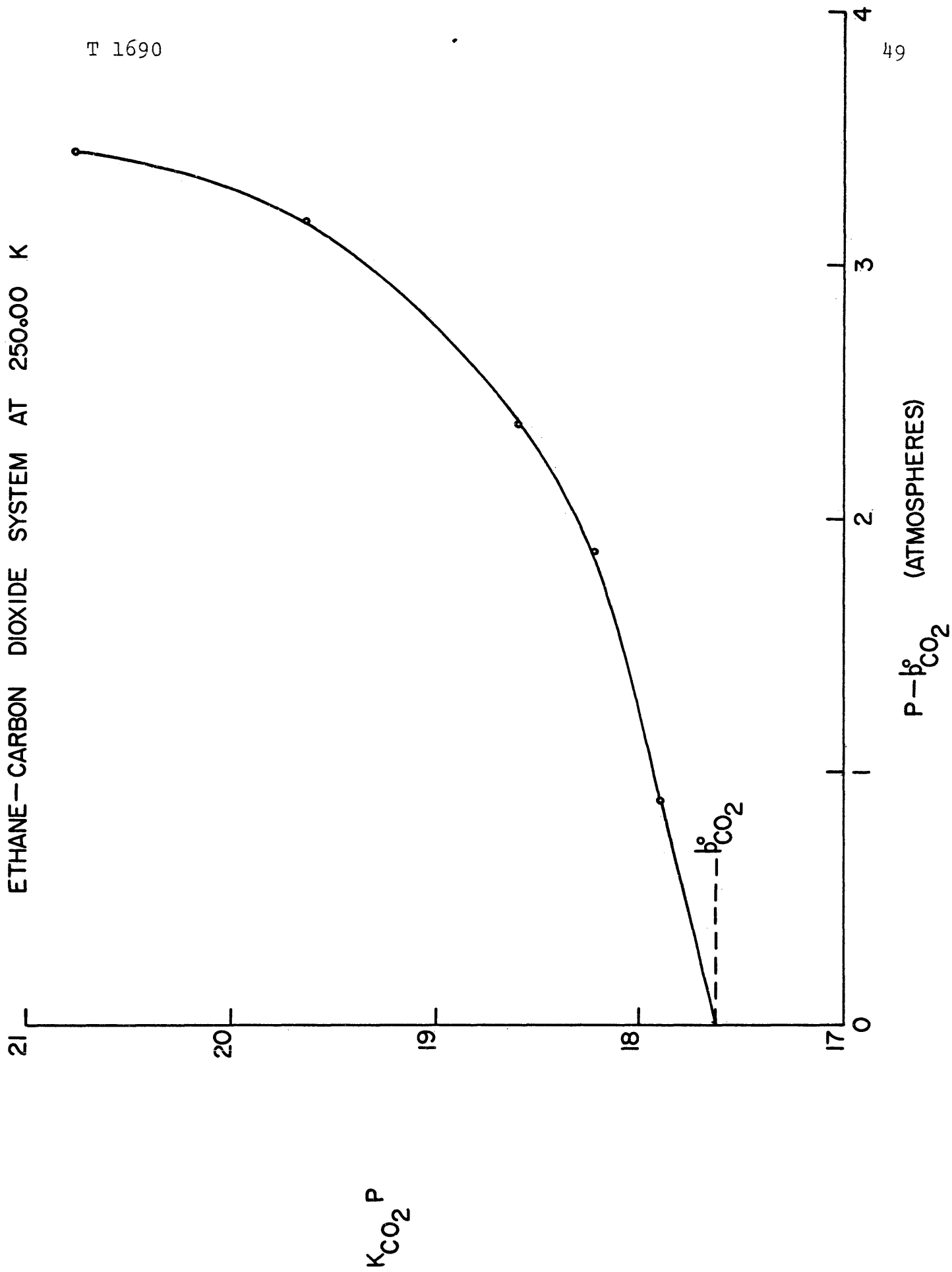
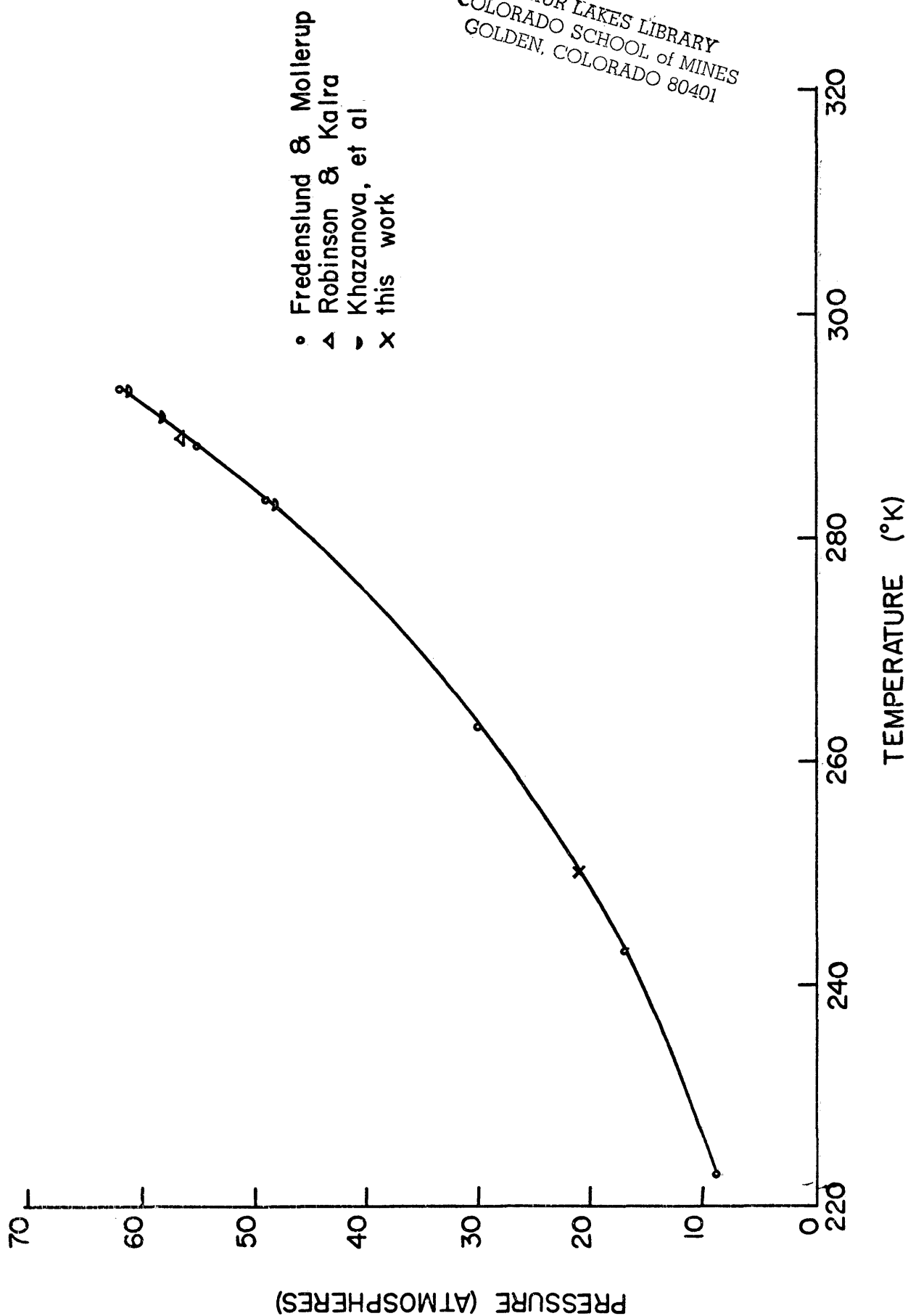


FIGURE 25  
ETHANE-CARBON DIOXIDE SYSTEM AT 250.00 K



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FIGURE 26  
ETHANE-CARBON DIOXIDE AZEOTROPE



## CONCLUSIONS

It can be concluded from the data that:

1. In the temperature range studied, the form of the system pressure versus composition graph for the  $\text{CH}_4 + \text{CO}_2$  system becomes more constricted at higher temperature and, of course, it is also shifted to a higher pressure range.

2. There is an azeotrope in the  $\text{C}_2\text{H}_6 + \text{CO}_2$  system at 250.00 K. This azeotrope peaks at a pressure of 21.07 atmospheres.

3. This apparatus is quite capable of giving measurements of composition and pressure that are consistent with previous data and also consistent with the real performance of the systems studied.

4. The recirculation pump can force the system to equilibrium in a fraction of the time that would be required to reach equilibrium without the pump.

## RECOMMENDATIONS

My experiences with this system lead me to make the following recommendations:

1. Calculate the points and plot them on the graph as soon as the data is taken. If the cell is too full of liquid or if all of the liquid has been exhausted, plotting the points is the easiest way to discover the problem.

2. Run gas into the system slowly or the gas may entrain droplets of liquid into the gas sampling lines and invalidate the results of the gas analysis.

3. Always begin a run by taking the vapor pressure of the condensible component. It is a valid point on the equilibrium curve and it demonstrates that the temperature and pressure measurements are valid.

4. It may be advisable to heat up the silica gel columns and purge them at the end of each run to clean the columns for the next run.

5. If a better barometer could be obtained the error in the concentrations could be about halved in all cases.

6. Longer silica gel columns would give better separation of  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$ . This could presently be the source of a slight error.

7. If possible the valves should only be opened slightly to avoid wear to the packing which can lead to leaks.

8. When a run is started, begin the analysis by vacuuming out the analysis system lines and injecting a sample of this vacuum into the chromatograph. A peak on the recorder as a result of this vacuum indicates a leak in the system or a foul up of the chromatograph or the recorder.

9. Before zeroing the gauges at the start of a run, vacuum out all of the adjoining high pressure lines so there is no leakage to the cell to alter the zero setting of the gauges.

10. The inverse slope of the calibration curve should be used instead of reading the curve itself. This is to avoid large errors in the low pressure section of the graph where the values are hard to read directly.

11. When the ethane peak requires a higher attenuation than the carbon dioxide peak, adjust the recorder zero with the attenuation set at the value used for carbon dioxide and switch to the value of attenuation used for ethane just as the chromatograph starts to detect ethane. This should be done because there is no chance to change the zero setting between these two peaks.

## 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. More 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 P.
- 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 (figure 1)



$p^{\circ}$  = The vapor pressure of a component.

$E$  = Enhancement factor and is the system pressure times the vapor-phase composition divided by the vapor pressure of the component.

$x$  = The concentration of a particular component in the liquid phase.

$y$  = The concentration of a particular component in the vapor phase.

Subscripts indicate the component to which the value refers.

APPENDIX A  
CALIBRATION CURVE USING MOLECULAR SIEVE COLUMNS

All of the data that is not normalized were taken by analyzing the gas mixture for methane. The concentration of the other component was obtained by difference. At the time this unnormalized data was taken, the chromatograph was equipped with molecular sieve columns. The heavy component would hang up on these molecular sieve columns because it is so strongly adsorbed. This component then comes off the columns slowly as time goes by. The columns would have to be heated when the recorder would become hard to zero. This heating would purge the columns of the heavier gas in about the time it would take to set the system for the next sample.

Methane is present as the minor constituent in most cases, so the calibration curve was created using an 8.6-mole-percent methane in helium mixture of gases. This standardized gas was previously prepared and analyzed by us. This 8.6 percent was multiplied by the injection pressure for each point to give a partial pressure which is plotted on the abscissa of the calibration curve versus peak height, corrected for attenuation, on the ordinate. The data taken for the calibration curve using the 8.6-mole-percent methane mixture is as follows:

Chromatograph settings -

columns = 12 foot molecular sieve columns

column temperature = 130 C

column flow rate = 40 percent flow

chromatograph current = 250 ma

carrier gas = helium

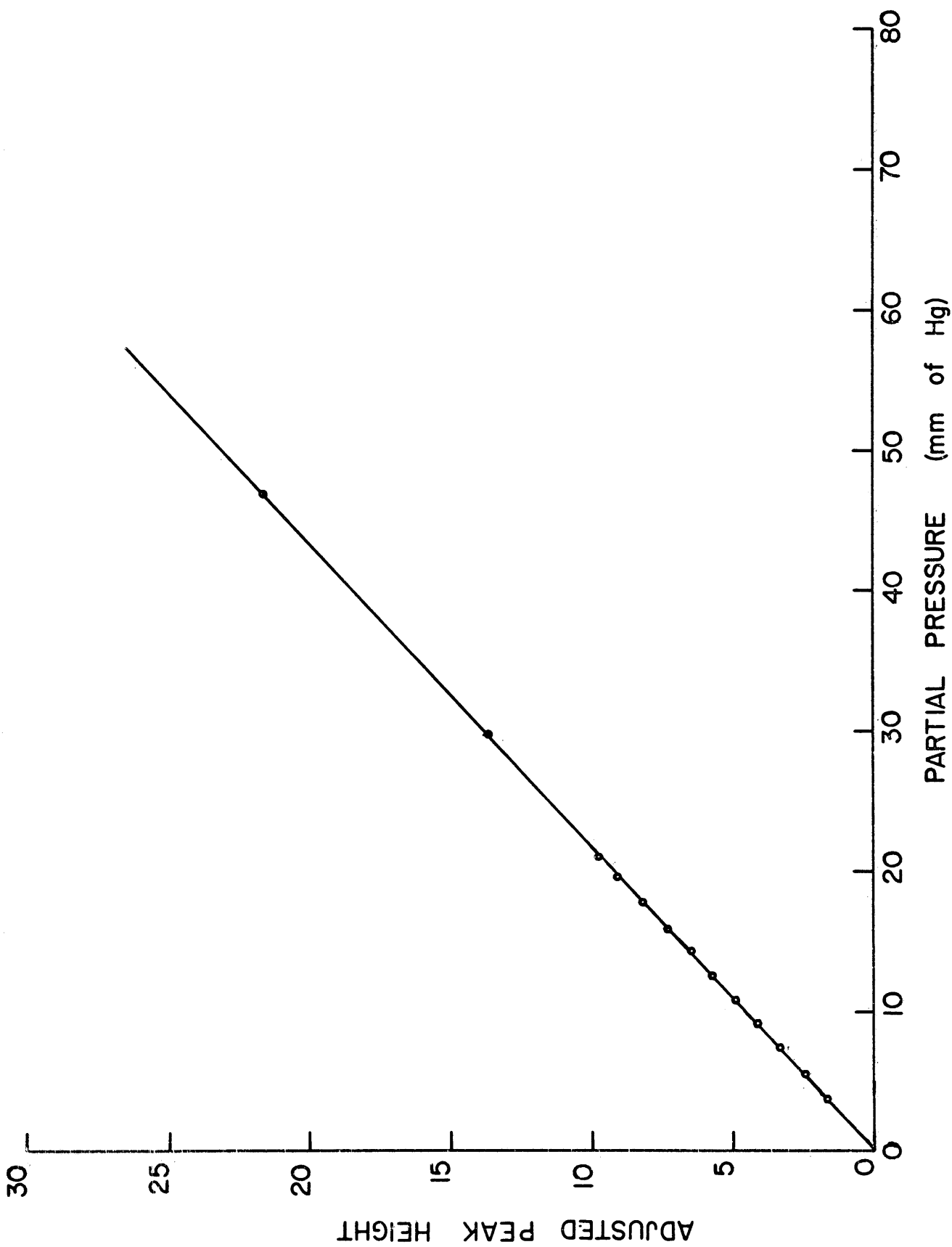
barometric pressure = 619.3 mm of mercury

base attenuation = 2

Table 7

RL	ATT	PH	IP	PP	CPH
30	16	4.23	844.3	72.61	33.76
45	8	5.39	544.3	46.81	21.56
55	4	6.80	344.7	29.64	13.60
60	4	4.86	245.1	21.08	9.70
61	4	4.48	225.3	19.38	8.96
62	4	4.10	205.3	17.66	8.20
63	4	3.68	185.3	15.94	7.36
64	4	3.27	165.3	14.22	6.54
65	2	5.75	145.3	12.50	5.75
66	2	4.94	125.3	10.78	4.94
67	2	4.15	105.3	9.06	4.15
68	2	3.37	85.3	7.34	3.37
69	2	2.46	65.3	5.62	2.46
70	1	3.52	45.3	3.90	1.76

FIGURE 27  
CALIBRATION CURVE FOR MOLECULAR SIEVE COLUMNS



APPENDIX B  
CALIBRATION CURVE FOR SILICA GEL COLUMNS

When the silica gel columns were obtained, methane, ethane and carbon dioxide could all be analyzed since the chromatograph gave distinct and separate peaks for each component. However, the chromatograph settings had to be changed considerably to obtain a good separation of the ethane peak and the carbon dioxide peak. The pure gases are used for these calibration curves so the injection pressure is also the partial pressure of the gas. These calibration curves were used to obtain the data where both components were analyzed and the results were normalized. The data for these calibration curves are as follows:

Chromatograph settings -

columns = 6 foot silica gel columns

column temperature = 65 C

column flow rate = 75 percent flow

chromatograph current = 250 ma

carrier gas = helium

barometric pressure = 616 mm of mercury

Methane (base attenuation) = 64

Table 8

RL	ATT	PH	IP	CPH
50	128	4.06	439.8	8.12
56	64	5.95	320.8	5.95
58	64	5.20	280.3	5.20
60	64	4.47	240.3	4.47
62	64	3.79	200.3	3.79
64	64	3.03	160.3	3.03
66	32	4.59	120.4	2.30
68	32	3.13	80.5	1.57
70	32	1.55	41.0	0.78

Ethane (base attenuation = 16)

RL	ATT	PH	IP	CPH
45	128	2.01	540.5	16.08
56	64	2.44	320.8	9.76
58	64	2.12	280.3	8.48
60	32	3.70	240.3	7.40
62	32	3.00	200.3	6.00
64	32	2.46	160.3	4.92
66	16	3.74	120.4	3.74
68	16	2.47	80.5	2.47
70	8	2.41	41.0	1.20

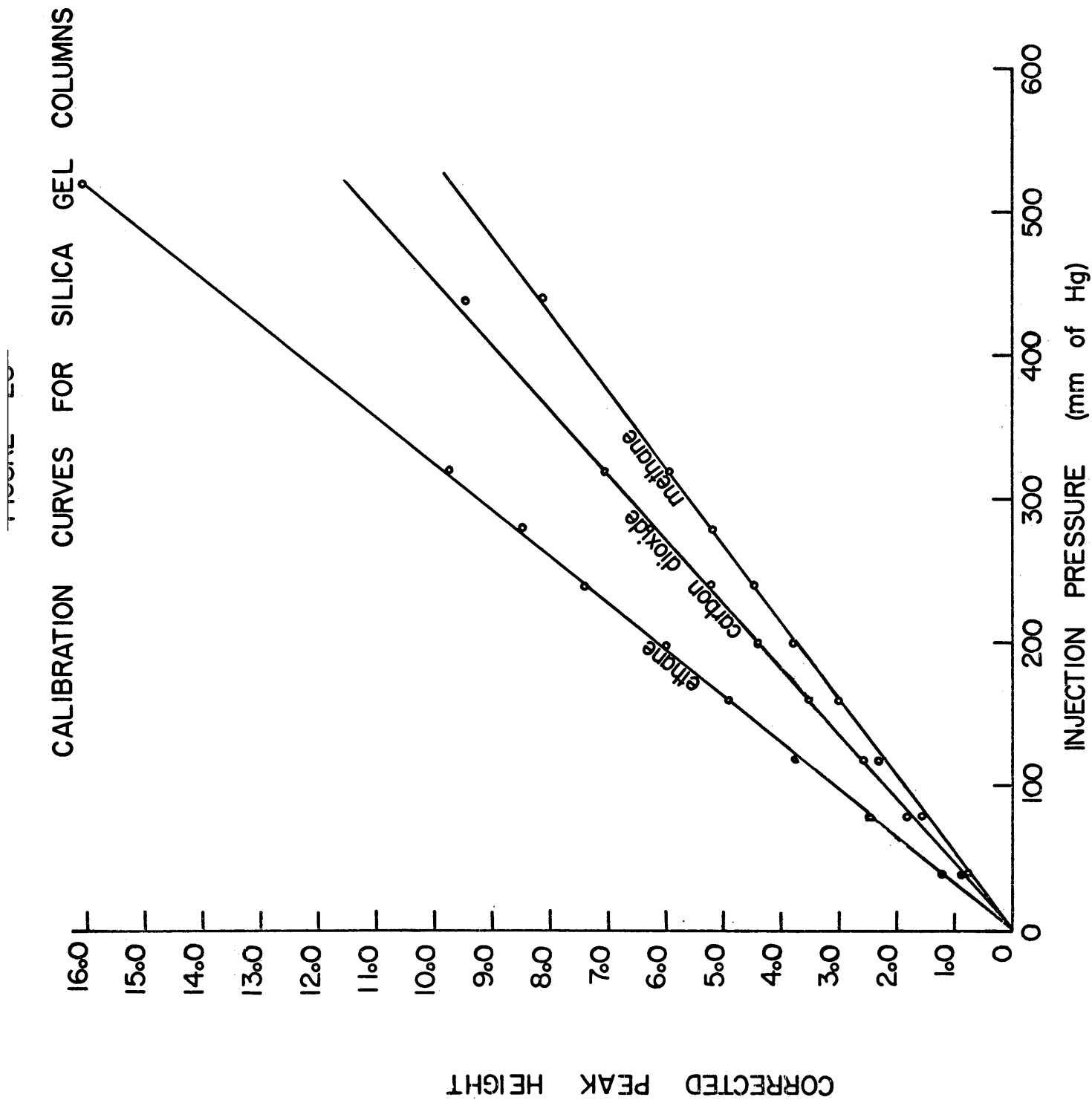
Carbon dioxide (base attenuation = 16)

RL	ATT	PH	IP	CPH
50	128	1.18	439.8	9.44
56	64	1.77	320.8	7.08
58	32	3.14	280.3	6.28
60	32	2.62	240.3	5.24
62	16	4.40	200.3	4.40
64	16	3.51	160.3	3.51
66	16	2.57	120.4	2.57
68	8	3.57	80.5	1.79
70	8	1.77	41.0	0.89

The calibration of the sensitivity gas was made at RL = 60 which is the injection pressure used for the sensitivity checks. Calibration of the sensitivity gas gives:

	RL	ATT	PH
CH <sub>4</sub>	60	64	1.41
C <sub>2</sub> H <sub>6</sub>	60	16	2.49
CO <sub>2</sub>	60	16	1.79

Since these calibration curves were all a straight line in their useful region, the inverse of the slope was calculated for each. This inverse of the slope could be multiplied by the corrected peak height for a particular point to give the corresponding partial pressure for that point. The ratio of this derived partial pressure to the injection pressure gives the concentration for the point.





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