

THE LIQUID VAPOR EQUILIBRIUM OF THE
HELIUM-CARBON DIOXIDE SYSTEM BETWEEN
250.15 K and 274.9 K.

BY

Juan Carlos Davalos

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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.

Signed

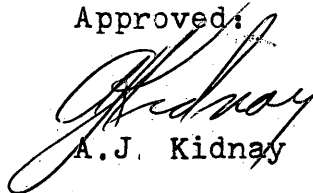


Juan Carlos Davalos

Golden, Colorado

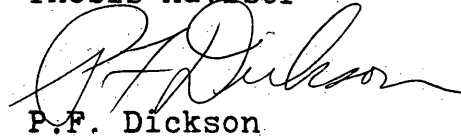
Date: March, 22 1974

Approved:



A.J. Kidnay

Thesis Advisor



P.F. Dickson

Head of Department

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Abstract

An experimental apparatus capable of measuring equilibrium pressures, temperatures and liquid + vapor phase compositions was developed, using as a base preexisting equipment.

To verify the precision and accuracy of this apparatus, several isotherms of the He + CO₂ system were measured and compared with literature values.

Helium-Carbon dioxide liquid + vapor phase compositions were determined between 250.15 K and 274.9 K, in the pressure range from 25 atm to 75 atm. The equilibrium values obtained experimentally were in excellent agreement with the data obtained by other investigators.

The accuracy of the equilibrium apparatus in use is believed to be $\pm 1.5\%$ of the reported equilibrium compositions.

The present work is a part of a larger program whose main objective is to examine the ability to predict mixed second virial coefficients using available mixing rules and generalized correlations for pure components.

DEDICATION

To my wife, Liliana,
and to my parents.

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ACKNOWLEDGMENTS

The Author wishes to express his appreciation for the guidance and encouragement of Dr. Arthur Kidnay as thesis advisor. Sincere thanks are extended to the Master of Science Committee members: Professors J.O. Golden and R. C. Robinson.

INTRODUCTION

During 1970-1971, an experimental apparatus capable of making accurate measurements of solid and liquid vapor pressures was constructed. It consisted basically of a constant temperature bath, a temperature controller, a platinum resistance thermometer and the necessary pressure gauges.

In 1972, a sampling system and a gas chromatograph were added allowing the measurement of solid + vapor phase equilibrium data.

Composition data on several systems (Nitrogen+Neopentane, Argon+Neopentane, Methane+Neopentane and Helium+Neopentane) were taken in the solid + vapor region, and interaction second virial coefficients were obtained from this data.

In 1973, several goals were set:

a. To recheck the accuracy and precision of the temperature, pressure and equilibrium composition analysis systems.

b. To rebuild the old equipment, putting all the different systems into one unit.

c. To add a recirculating pump so that equilibrium could be attained in a shorter time.

d. To design a liquid sampling system so that both gas and liquid compositions could be measured.

e. To verify the precision and accuracy of the modified equipment by measuring the vapor pressure of pure CO_2 and the $\text{He} + \text{CO}_2$ system in the liquid+vapor region and comparing this data with literature values.

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EXPERIMENTAL APPARATUS

The experimental apparatus consists of four separate systems working together. These systems will be called the refrigeration system, the equilibrium system, the pressure and temperature system and the analysis system.

The Refrigeration System

The refrigeration system has not been modified and has been discussed in detail by D. Duston (1971, p. 11, 12, 13, 14.) and G. Baughman (1972, p. 26, 27).

The Equilibrium System

A brief description of the operation of this system will be presented here.

The component with its critical point below 150 K, in this case He, was passed through a pressure reducing valve, a vernier throttle valve, and a 1/8 - inch coil about 3 ft. long placed in the constant temperature bath. The He was bubbled through liquid CO₂ contained in the equilibrium cell. The CO₂ was the component with its critical point above room temperature.

The gas mixture from the coil exited through the top of the cell, passed through what will be called the gas sampling coil where samples of the mixture could be kept for com-

position analysis, and was then pumped back to the cell by a recirculation pump or vented. See figures 1,2,3.

Liquid samples could be taken directly from the cell by means of a capillary tube, 115 cm. long. The capillary tube ended in a 10-ml cylinder equipped with the necessary valving. The liquid sample was flashed very rapidly into this cylinder and kept there for two or three minutes until an homogeneous mixture was obtained. The composition was then measured with a gas chromatograph.

The 10-ml. cylinder has a pressure gauge to monitor the pressure in this cylinder. Measuring the pressure insures that conditions in the sample cylinder are such that no liquid phase is present. See figure 3.

In addition, the 10 ml cylinder has been covered with a heating tape, which keeps the cylinder temperature above room temperature

Initially, a magnetically operated recirculating pump was placed in the system. The pump was similar to that of Street and Erickson (1972)

Low pressure He + CO₂, liquid + vapor equilibrium compositions were measured with this pump, but at higher pressures because of the limited power of the electromagnetic coil, the functioning of this pump became uncertain.

Because of the high cost of obtaining a new magnet, the magnetic pump was replaced with a diaphragm pump having the following specifications:

Type: Lapp, pulsafeeder, diaphragm metering pump

Model: LS-20

Flow rate: 1500 cc/hr

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Figure 1
Equilibrium Cell Assembly

material:
stainless steel

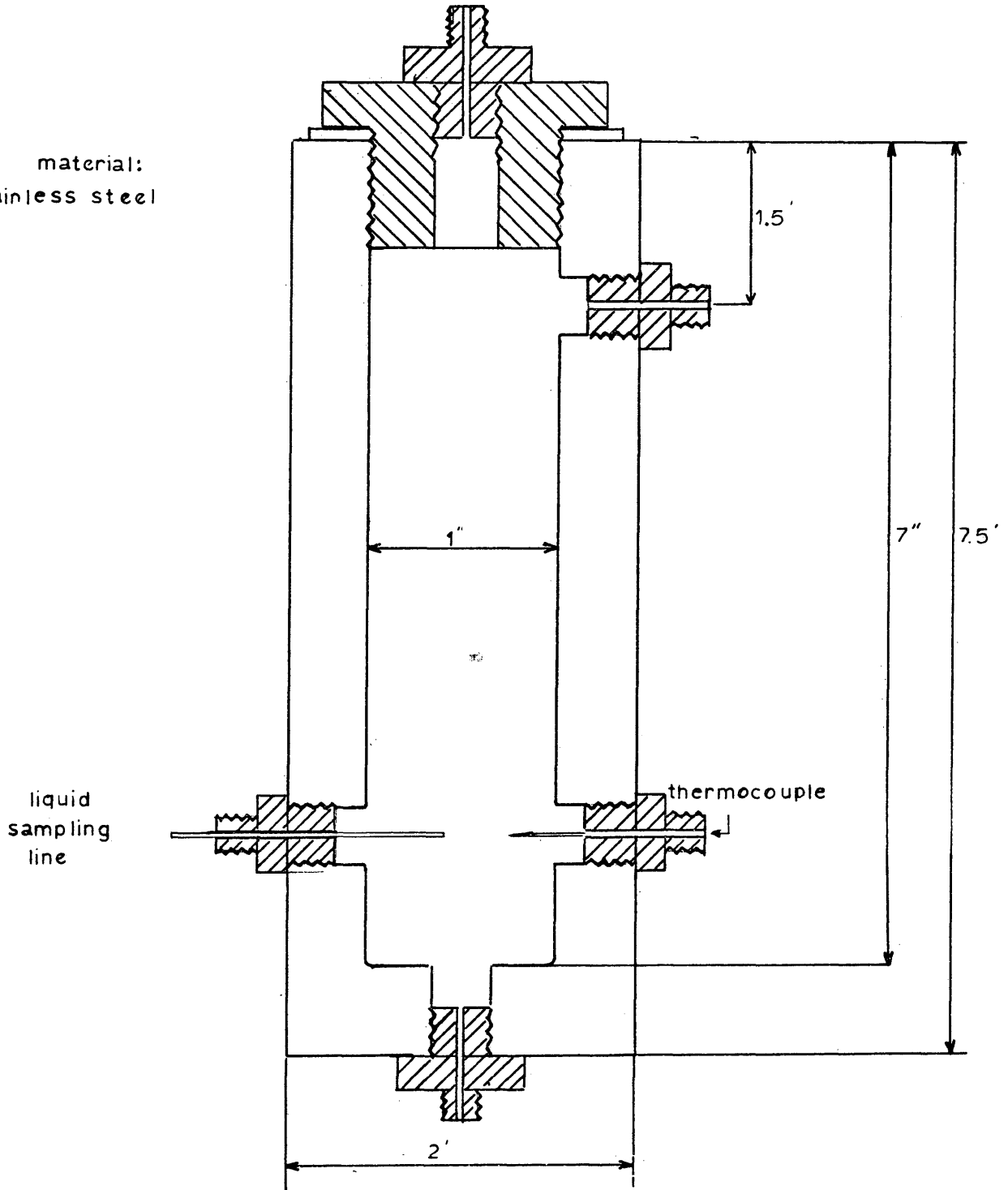
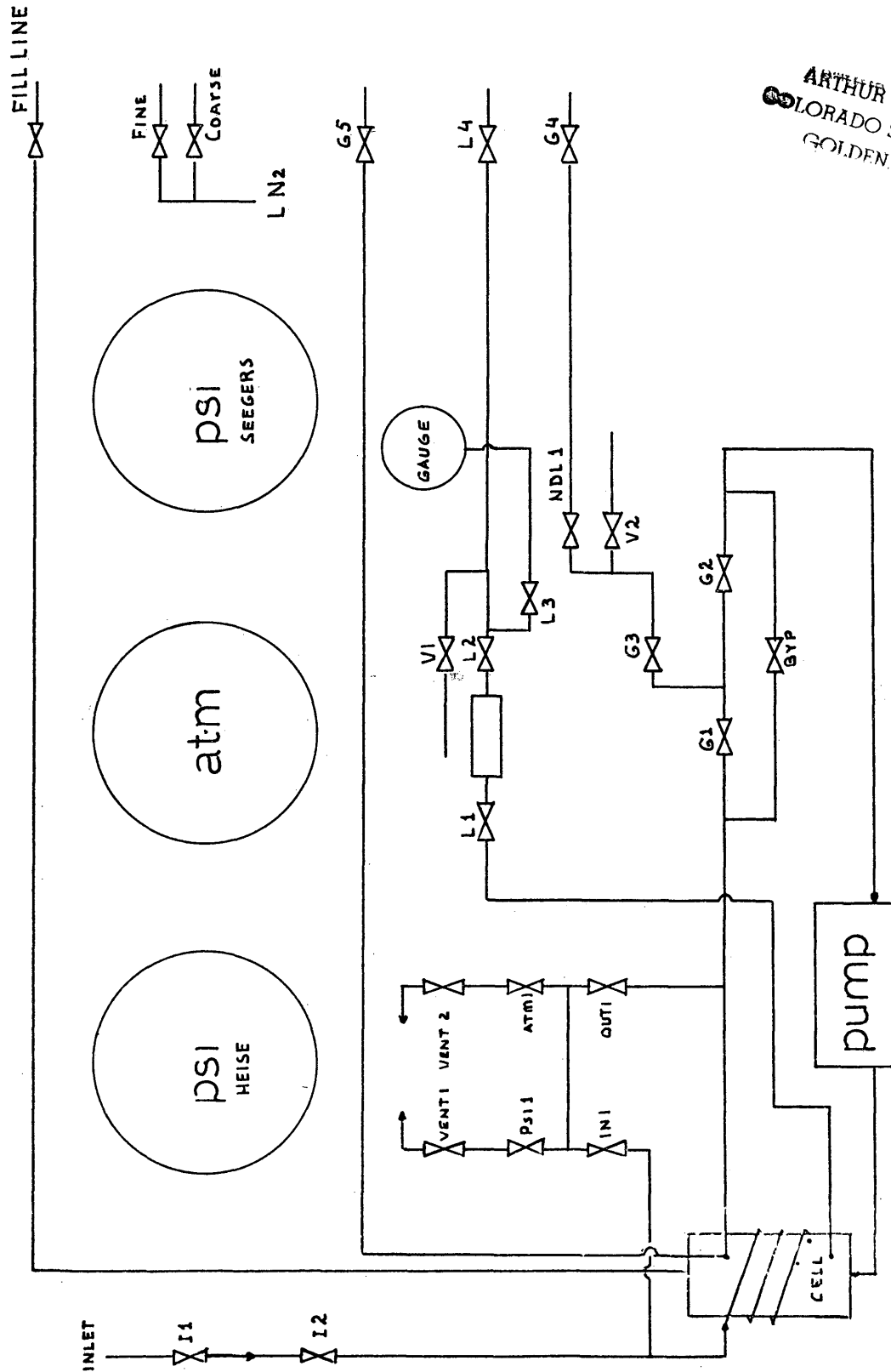


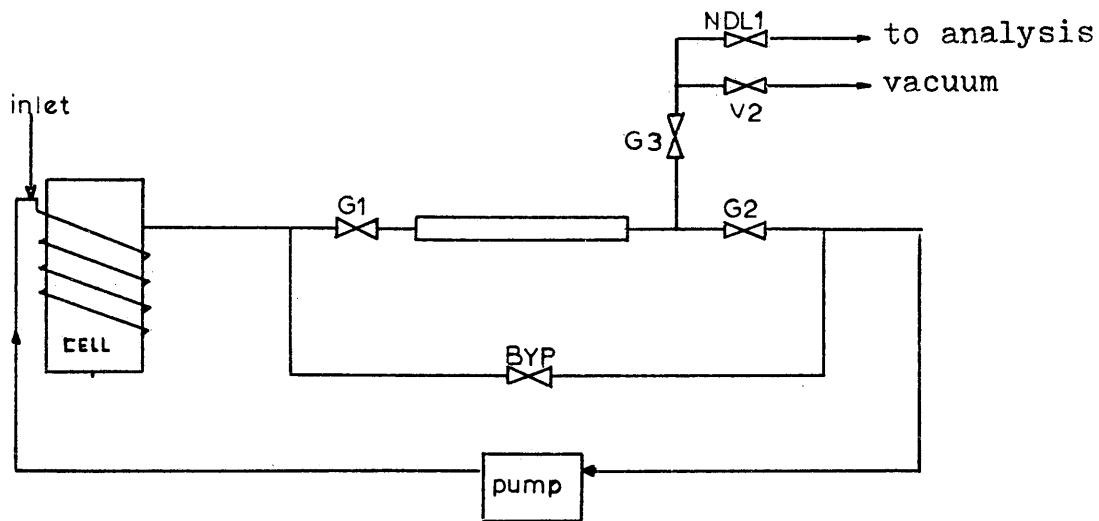
Figure 2
Sketch Of The Instrument Board



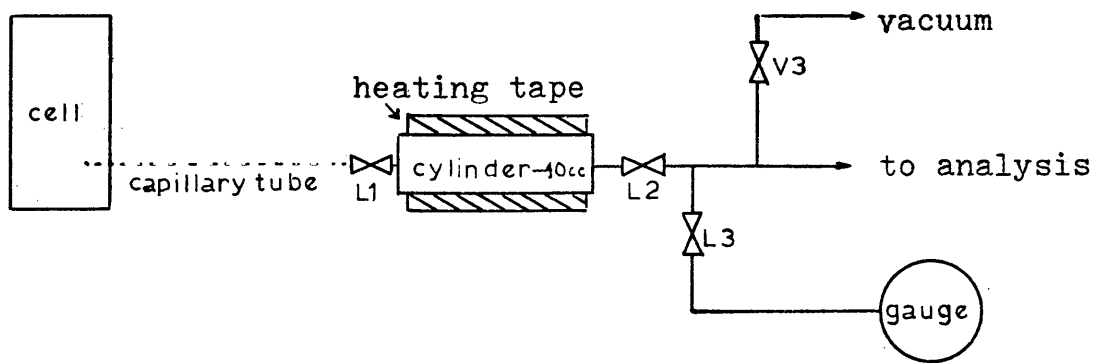
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Figure 3

Schematic Of The Sampling Systems



Gas Phase Sampling Loop



Liquid Phase Sampling System

The Pressure and Temperature System

Temperature and pressure measurement have been treated in detail by G. Baughman (1972, p. 31, 32, 33).

The Analysis System

Samples taken directly from the equilibrium cell were analyzed in a Beckman GC 72-5 gas chromatograph with liquid partition columns and a thermal conductivity detector.

With the chromatograph variables used, the recorded peak was very sharp, so the peak heights were used to compare compositions rather than peak areas.

To relate the peak heights obtained in the recorder with composition, calibration curves were constructed. Basically, either CO₂ or He was injected into the chromatograph at a number of pressures and the peak heights recorded.

In the present work, two calibration curves were constructed, one for He using CO₂ carrier gas and the other for CO₂ using He carrier gas.

In some runs, only the component CO₂ was analyzed and in others, only the component He was analyzed. The objective was to compare how well the data taken using different carrier gases agreed and to find out how the chromatograph sensitivity changed when carrier gases other than He were used.

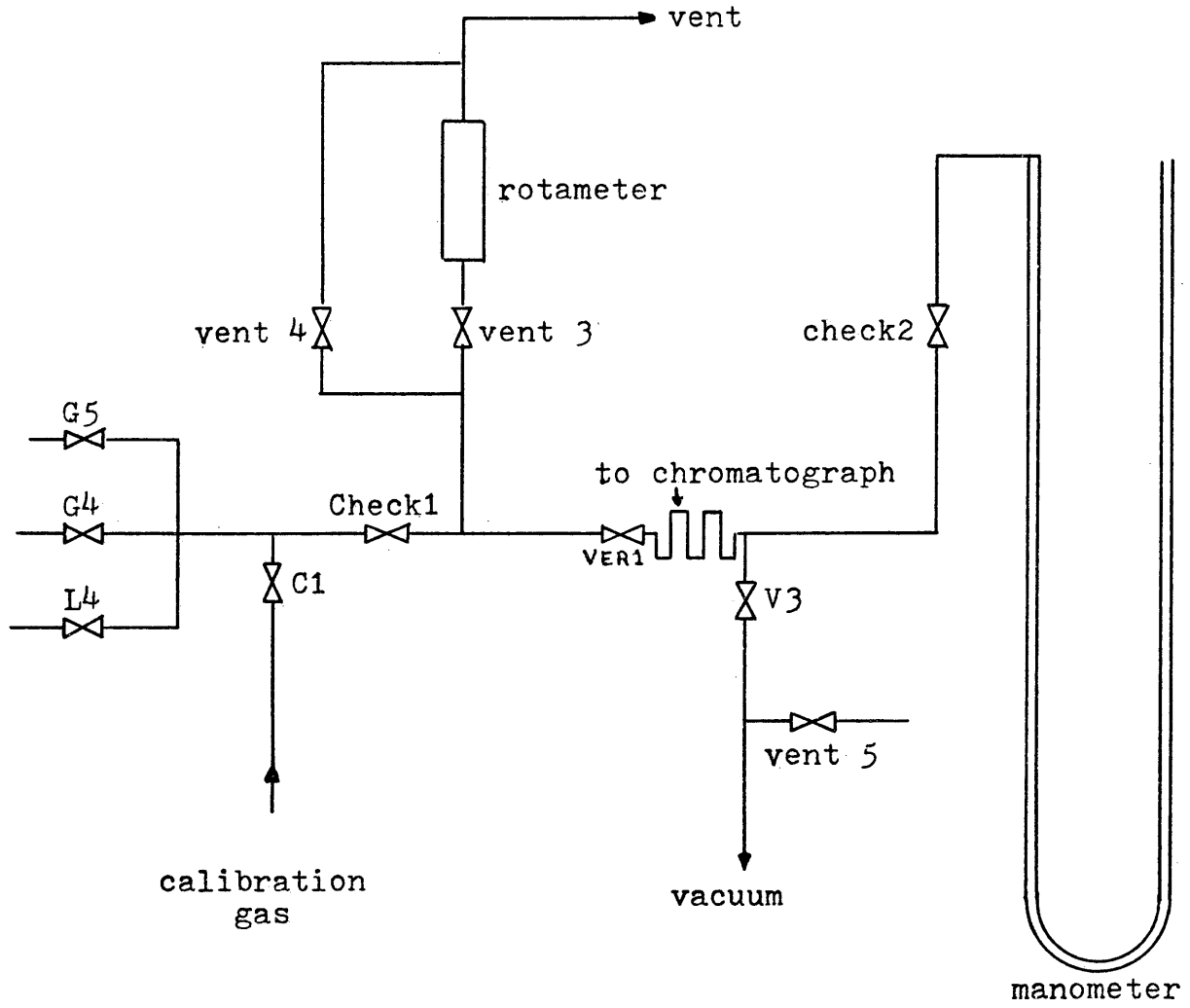
Very few changes were made in the analysis system.

The operating procedure is discussed in detail in

G. Baughman (1972, p.9,10,11) and G. Baughman(1973, p. 42,43, 44)

A schematic of the analysis system is shown in Figure 4.

Figure 4
Schematic Of The Analysis System



Operating Procedures

A. Vapor Pressure Measurements

a. Temperature Measurement

See G. Baughman (1972, p. 55, 56)

b. Cool Down Procedure

See G. Baughman (1972, p. 45, 46, 48)

c. Equilibrium System Preparation and Setting Gauges1. Evacuation

-Turn on vacuum pump

-Close I1, I2, Psi 1, Vent 1, Vent 2, G5, L4, G4

-Open In1, Out 1, Atm 1, G1, G2, G3, L1, L2, L3,
V1, V2

-Evacuate for 5 minutes

-Adjust Atm Gauge to zero

-Close V1, V2

-Open Vent 2

-Open Psi 1 and set Psi gauges to zero

-Close Psi 1

-Open V1 and V2 until atm. gauge reads 0

-Close V1, V2, L1, L3, G1, G2, G3 and NDL 1

2. CO₂ Injection

-Open fill line valve and inject 40-45 gr of CO₂

-Close fill line and allow the system to reach
equilibrium

-Read the system pressure

B. Liquid + Vapor Measurement

a. Chromatograph warm up

See G. Baughman (1972, p. 40, 41)

b. Mueller Bridge balancing

See G. Baughman (1972, p. 55, 56)

c. Cool down procedure

See G. Baughman (1972, p. 45, 46, 48)

d. System Evacuation and Setting Gauges

See page 13

e. CO₂ Injection

-Open G1 and G2

-Open I1 and I2 until desired pressure is reached

-Turn on recirculation pump

-Close G1 for several minutes to make sure that the
by pass line is purged completely.

-Close BYP and allow system to attain equilibrium

f. Gas Phase Sampling

-Open BYP

-Close G1, G2, G3, V2, NDL1 and G4

-Open 63 and NDL 1

-Open 64 and the gas will be injected into the Gas
Chromatograph Analysis System

g. Liquid Phase Sampling

-Close L1, V1, L2, L3 and L4

-Open L1

-Close L1

-Wait several minutes and open L2

-Open L4 and the gasified liquid sample will be
injected into the gas chromatograph analysis system

h. Analysis System1. Evacuation

- Close G5, G4, L4, vent 31, vent 41, vent 51, C1 and Ver 1
- Open check 1 and V3
- Wait for 2-2.5 minutes and close V3

2. Injecting samples into the chromatograph

- Open either G5 or G4 for gas samples
- Open L4 for liquid samples
- Using VER 1, inject the sample at the chosen manometric pressure
- Close VER 1 and inject sample into the chromatograph

3. Sensitivity Check

- After taken each data point:
- Evacuate analysis system
 - Open C1
 - Using VER 1, inject calibration gas into the chromatograph

Carbon Dioxide Vapor Pressure Measurement

Carbon dioxide was chosen because it is recommended as a test substance for vapor pressure measurements and its vapor pressure is accurately known in the temperature range 200 K to room temperature.

The observed vapor pressures were compared with the National Bureau of Standards data (Meyers and Van Dusen, 1933). The Meyers and Van Dusen is the most accurate vapor pressure data for CO₂.

To compare the experimental values obtained in this experiment with that of Meyers and Van Dusen, it was necessary to convert the data to a common temperature scale, because the Meyers and Van Dusen data was based on the 1927 International Temperature Scale and the platinum resistance thermometer used in this experiment is calibrated on the 1968 International Practical Temperature Scale.

The Literature values used for comparison in the present work, consist then of the Meyers and Van Dusen data adjusted to the International Practical Temperature Scale of 1968 (IPTS - 68) (A.J. Kidnay (Private Communication)). See appendix A.

Three Bourdon - tube pressure gauges are presently mounted:

- a. Atmosphere gauge (Heise 0 - 100 atm)

It is a temperature compensated gauge. The manufacturers started accuracy of the Heise gauge is ± 0.1 percent of the full scale, which corresponds to an error of ± 0.10 atm.

It can be seen from table 1, that errors for all data points did not deviate more than ± 0.08 atm.

b. Psi gauge (Heise 0 - 100 Psi)

It is also a temperature compensated, and the stated accuracy of this gauge is ± 0.1 percent of the full scale, which corresponds to an error of 0.10 Psi.

The maximum observed error for this gauge was ± 0.05 Psi. See table 1.

c. Psi gauge (Seegers 0 - 100 Psi)

It is not a temperature compensated gauge, however, the readings were as good as the Heise 0 - 100 Psi. The maximum error observed was ± 0.05 Psi. See table 1.

Experimental Procedure

- Evacuate system
- Set gauges
- Adjust system temperature
- Inject 30 - 40 gr of CO₂
- Let the system attain equilibrium and measure the pressure.

Operating procedures have been explained in detail on page 13, also see D. Duston (1971, p. 25, 26, 27, 28)

Vapor Pressure Data Comparison

Table 1 shows the experimental results obtained with the equipment before modification and the comparison of these results with Meyers and Van Dusen. Table 1 assumes that the temperature measurements are exact and that all of the error is in the pressure measurement.

Assuming that the experimental vapor pressures were 100 percent accurate and the errors could have been caused only by the system temperature, table 2 presents the temperatures corresponding to the vapor pressures measured by the gauges. Since the temperature measurements are much more accurate and precise than the pressure measurements in our system, table 2 is of limited interest.

Once the equipment was rebuilt and modified, more CO₂ vapor pressure data were taken in order to recheck the pressure and temperature systems. Table 3 presents the results.

Table 1

Experimental CO₂ Vapor Pressure and Data Comparison

t (C)	Experimental abs. pressure (1) (Atm. Heise)	Meyers and Van Dusen (2)	Deviation (1)-(2)
16.211	51.71	51.68	+0.03
15.659	50.93	51.00	-0.07
12.852	47.66	47.65	+0.01
9.455	43.91	43.83	+0.08
8.148	42.46	42.42	+0.04
4.649	38.81	38.82	-0.01
2.060	36.31	36.31	0.00
-4.991	30.11	30.07	+0.04
-10.212	26.01	30.07	+0.03
-13.000	24.00	23.98	+0.02
-14.000	23.31	23.29	+0.02
-18.903	20.11	20.11	0.00
-23.000	17.71	17.70	+0.01
-28.998	14.58	14.58	0.00
-38.079	10.63	10.64	-0.01
-50.438	6.62	6.62	+0.00
-52.915	6.03	5.98	+0.05
-54.053	5.73	5.70	+0.03
-57.234	4.96	*4.97	-0.01
	(Psia Heise)		
-50.438	97.3	97.28	+0.02
-52.915	87.85	87.88	-0.03
-54.053	83.82	83.77	+0.05
-57.234	73.03	73.77	+0.00
-62.177	50.92	50.87	+0.05

Table 1 (continued)

Experimental CO₂ Vapor Pressure and Data Comparison

t (C)	Experimental abs. pressure (1) (Psia Heise)	Meyers and Van Dusen (2)	Deviation (1)-(2)
-65.476	40.13	40.13	+0.00
-73.397	22.09	22.07	+0.02
	(Psia Seegers)		
-50.438	97.30	97.28	+0.02
-52.915	87.85	87.88	-0.03
-54.053	83.82	83.77	+0.05
-57.234	73.03	73.03	0.00
-62.177	50.92	50.87	+0.05
-65.476	40.13	40.13	0.00
-73.397	22.11	22.07	+0.04

*undercooled liquid

Table 2

Temperature Comparison			
Experimental Vapor Pressure	Experimental Temperature (1)	Ideal Temp. (2)	Deviation (2)-(1)
51.71	16.234	16.211	-0.023
50.93	15.599	15.659	-0.060
47.66	12.859	12.852	-0.007
43.91	9.529	9.455	-0.074
42.46	8.184	8.148	-0.036
38.81	4.636	4.649	+0.013
36.31	2.060	2.060	0.000
34.36	-0.039	0.000	+0.039
30.11	-4.938	-4.991	-0.053
26.01	-10.177	-10.212	-0.035
24.00	-12.969	-13.000	-0.031
23.31	-13.969	-14.000	-0.031
20.11	-18.897	-18.903	-0.006
17.71	-22.988	-23.000	-0.012
14.58	-28.987	-28.998	-0.011
10.63	-38.101	-38.079	+0.022
6.62	-50.434	-50.438	-0.004

Table 3

Vapor Pressure Measurements With the Modified Equipment

T (K)	Experimental Pressure (atm)	Meyers and Van Dusen (atm)
274.00	36.00	36.02
273.15	34.45	34.40
260.15	24.00	23.98
253.15	19.45	19.44
250.15	17.70	17.70
244.90	15.00	14.95

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The Helium + Carbon Dioxide System

The He + CO₂ System has been studied in the range 0-200 atm, 229.9-293.15 K by the following authors:

R.F. Mackendrick, C.K. Heck and P.L. Barrick, Department of Chemical Eng. University of Colorado, 1968.

D. W. Burfield, H.P. Richardson and R A Guereca, U.S. Department of Interior, Bureau of Mines, Helium Research Center, Amarillo, Texas, 1970.

According to Mackendrick, Heck and Barrick, their data were the first equilibrium values obtained for He + CO₂.

Burfield, Richardson and Guereca were testing a new type of equilibrium apparatus, which eliminated equilibrium disturbances upon sampling. Capacitors were used to monitor both liquid and vapor phase compositions.

In order to compare the data of Mackendrick et al, and Burfield et al. with the experimental data of this investigation, it was necessary to cross-plot and interpolate the data of the above mentioned authors.

See appendices D. and E and figures 8 and 9.

A. Experimental vapor-phase equilibrium data

Because in the following tables and figures, the terms original and modified equipment will be use extensively, a definition of the terms is necessary and therefore is presented below:

original equipment: This term refers to the equipment used by

S. Westhoff (1972), G. Baughman (1972), S. Dincer (1973) and G. Baughman (1973). It was a straight flow system, capable of making only gas-phase composition measurements.

modified equipment: The original equipment was rebuilt, and the gas-phase sampling system was modified in such a way that a recirculating pump could be added to the equipment without difficulty. A new equilibrium cell was installed in the system (figure 1) and a liquid sampling system was added to the experimental apparatus (figure 3).

Three isotherms of the He + CO₂ system were measured with this modified equipment. See Table 3 and Figure 5.

Afterwards, two recirculating pumps were tried. The first was a magnetic pump similar to that of Street and Erickson. Three isotherms were measured with the modified equipment plus the magnetic pump. See table 6-7. This magnetic pump was suitable only at low pressures.

The second pump used in the system was a high-pressure Lapp metering pump. One isotherm at 274.9 was run to verify its correct functioning. See tables 6-7.

a. Vapor-phase equilibrium data taken with the original equipment and He as the chromatograph carrier gas.

Table 4

T(K)	P(atm)	Vapor Composition (CO ₂ mole fraction)		
		<u>This Investigation</u>	<u>Mackendrick et al</u>	<u>Burfield et al</u>
273.15	34.41	1.000		
	40.81	0.898	0.895	0.898

Table 4 (Continued)

T(K)	P(atm)	Vapor Composition (CO ₂ mole fraction)		
		<u>This Investigation</u>	<u>Mackendrick et al</u>	<u>Burfield et al</u>
	45.81	0.848	0.825	0.831
	50.81	0.781	0.770	0.777
	60.81	0.689	0.680	0.680
	40.81	0.905	0.895	0.898
260.15	24.00	1.000		
	40.81	0.675	0.665	0.666
	50.81	0.570	0.553	0.565
	60.81	0.469	0.475	0.485
	40.81	0.684	0.665	0.660
250.15	17.70	1.000		
	25.81	0.755	0.739	0.739
	30.81	0.647	0.640	0.639
	40.81	0.511	0.495	0.496
	50.81	0.415	0.402	0.402
	60.81	0.357	0.340	0.336

b. Vapor-phase equilibrium data taken with the modified equipment and He as the chromatograph carrier gas.

Table 5

T(K)	P(atm)	Vapor Composition (CO ₂ mole fraction)		
		<u>This Investigation</u>	<u>Mackendrick et al</u>	<u>Burfield et al</u>
273.15	34.45	1.000		
	40.00	0.914	0.910	0.900
	45.00	0.847	0.840	0.835
	50.00	0.783	0.785	0.780

Table 5 (Continued)

T(K)	P(atm)	Vapor Composition (CO ₂ mole fraction)		
		<u>This</u>	<u>Mackendrick</u>	<u>Burfield</u>
		<u>Investigation</u>	<u>et al</u>	<u>et al</u>
	60.00	0.687	0.625	0.685
	70.00	0.600	0.613	0.610
260.15	24.00	1.000		
	35.00	0.760	0.751	0.752
	41.00	0.670	0.665	0.665
	50.00	0.567	0.560	0.570
	54.00	0.534	0.525	0.538
	60.00	0.478	0.480	0.489
	70.00	0.415	0.420	0.430
250.15	17.70	1.000		
	26.00	0.744	0.74	0.740
	30.00	0.658	0.655	0.655
	40.00	0.513	0.510	0.507
	50.00	0.419	0.412	0.412
	60.00	0.352	0.350	0.340
	70.00	0.308	0.305	0.290

c. Vapor-phase equilibrium data taken with the modified equipment and CO₂ as the chromatograph carrier gas.

Table 6

T(K)	P(atm)	Vapor Composition (CO ₂ mole fraction)		
		<u>This</u>	<u>Mackendrick</u>	<u>Burfield</u>
		<u>Investigation</u>	<u>et al</u>	<u>et al</u>
	34.45	1.000		
273.15	(p)40.00	0.907	0.900	0.910
	(s)50.00	0.784	0.780	0.785
	(s)60.00	0.687	0.655	0.685
	(s)70.00	0.612	0.610	0.613

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Table 6 (continued)

T(K)	P(atm)	Vapor Composition (CO ₂ mole fraction)		
		<u>This</u> <u>Investigation</u>	<u>Mackendrick</u> <u>et al</u>	<u>Burfield</u> <u>et al</u>
253.15	19.45	1.000		
	(p)29.45	0.727	0.719	0.730
	(p)35.00	0.639	0.628	0.636
	(p)46.74	0.500	0.492	0.493
	(s)54.60	0.422	0.427	0.428
	(s)63.20	0.374	0.371	0.370
	(s)74.00	0.327	0.323	0.320
274.9	36.00	1.000		
	(p)42.60	0.896	0.898	0.900
	(p)45.70	0.854	0.856	0.860
	(s)55.30	0.753	0.750	0.760
	(s)58.00	0.731	0.725	0.731
274.9	25.95	1.000		
	(m)45.00	0.860	0.865	0.869
	(m)55.30	0.748	0.750	0.760
	(m)62.00	0.693	0.690	0.697
	(m)71.00	0.626	0.623	0.627

(p)= with the magnetic recirculating pump

(m)= with the Lapp diaphragm pump

(s)= straight flow

Figure 5

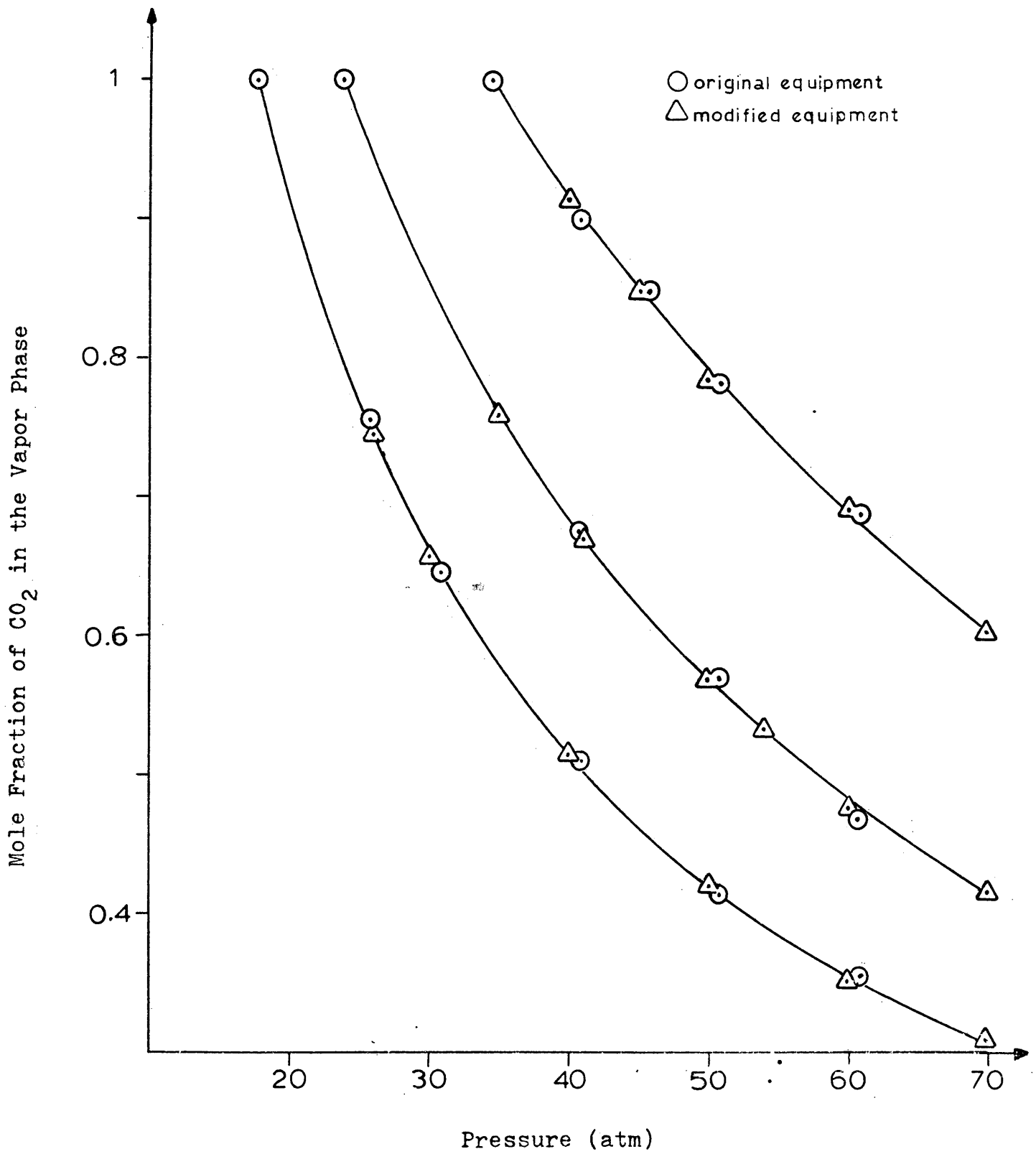
Experimental Vapor Phase Equilibrium Data

Figure 6

Experimental Vapor Phase Equilibrium Data

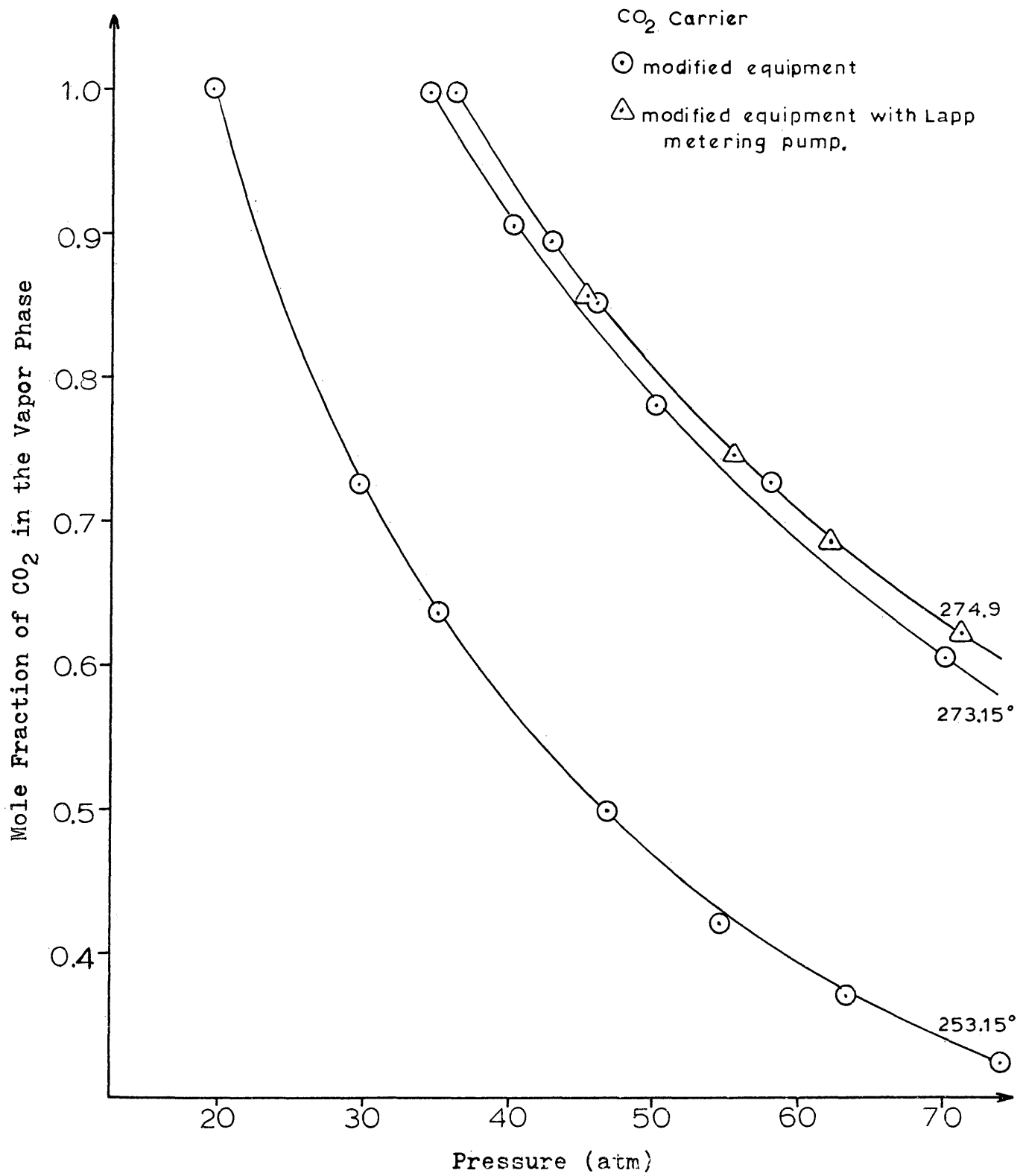
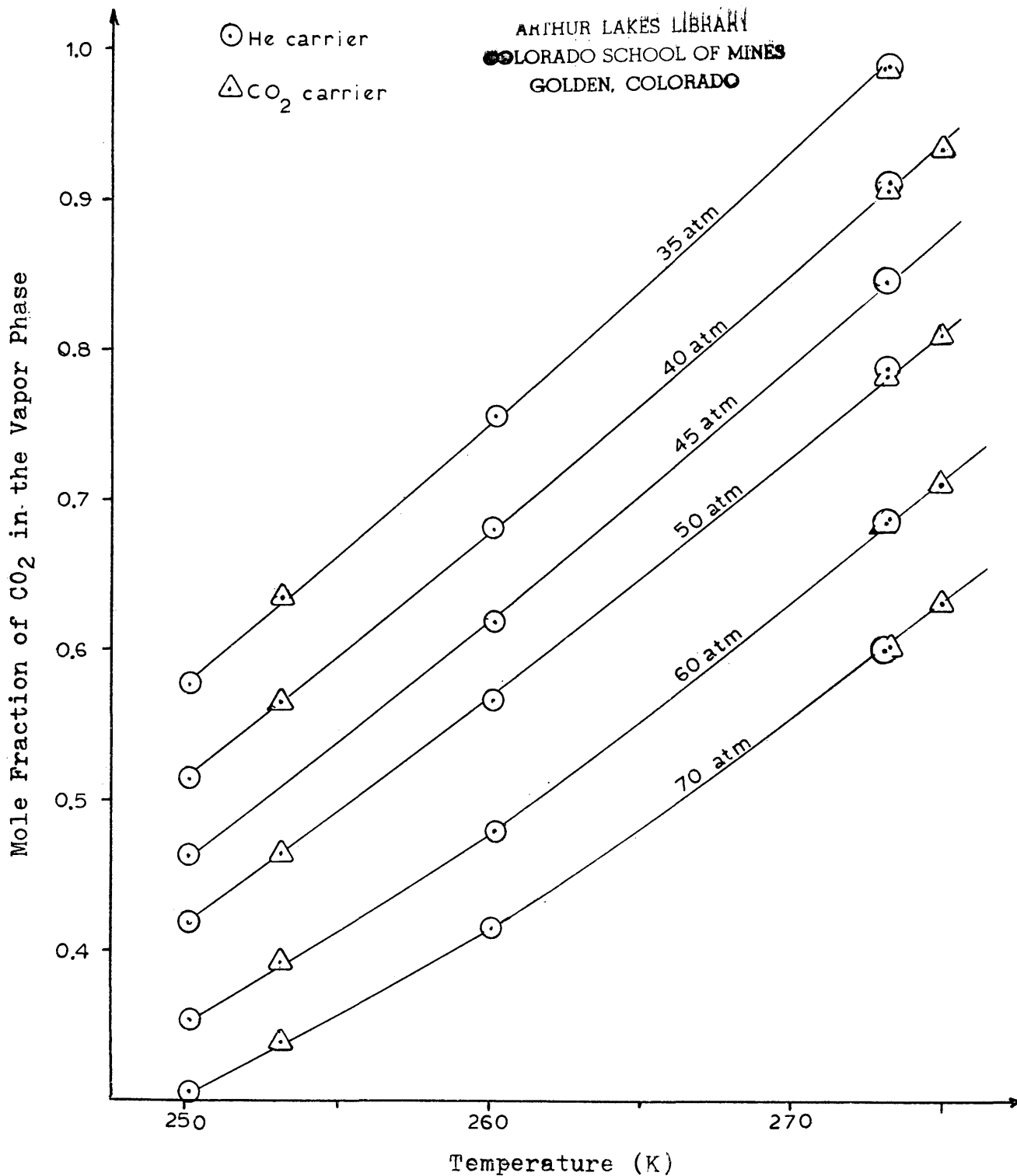


Figure 7

Cross-Plot of Experimental Vapor-Phase Equilibrium Data



Vapor Phase Equilibrium Values Reported
by Mackendrick et al. and Burfield et al.

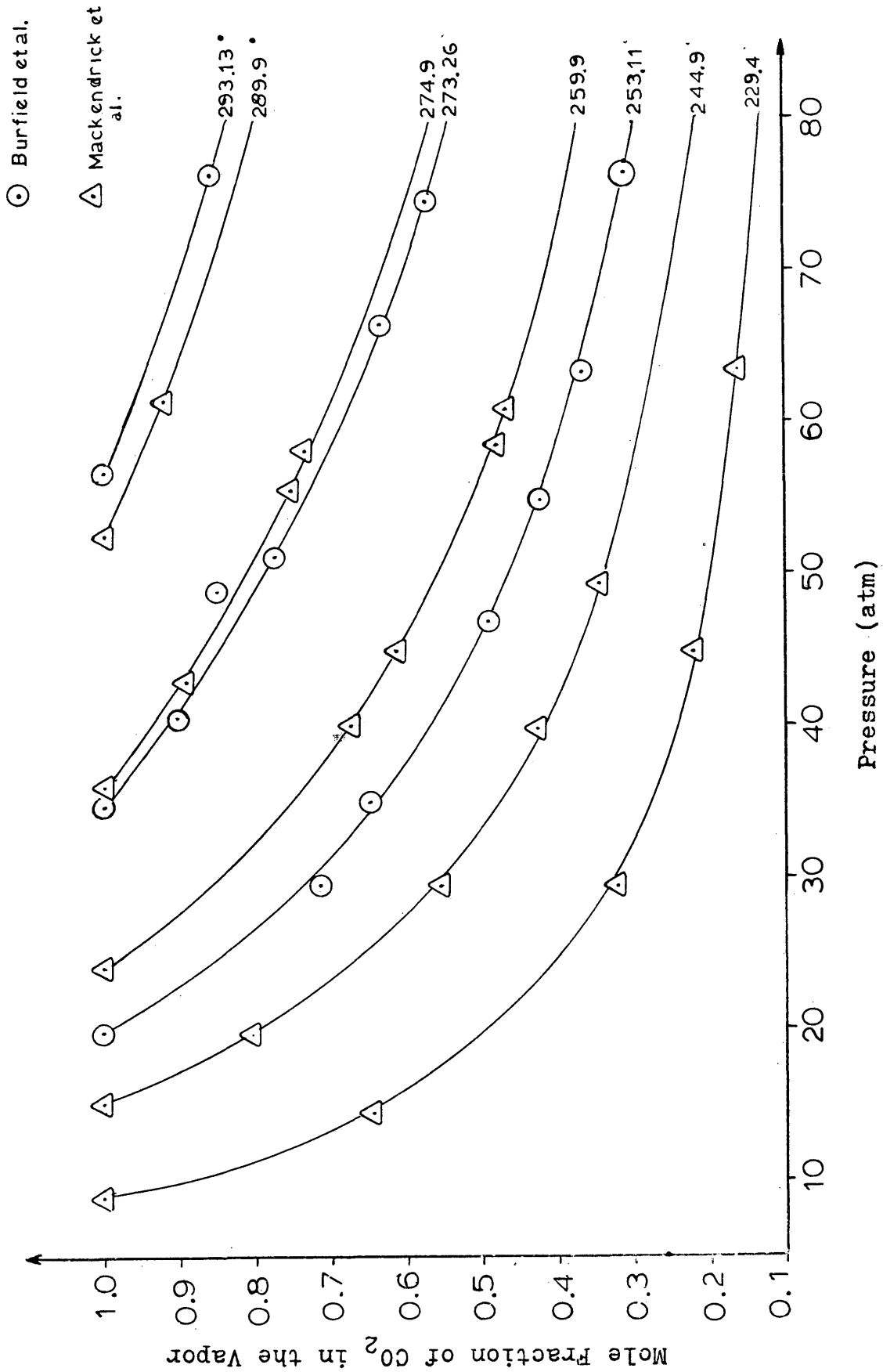
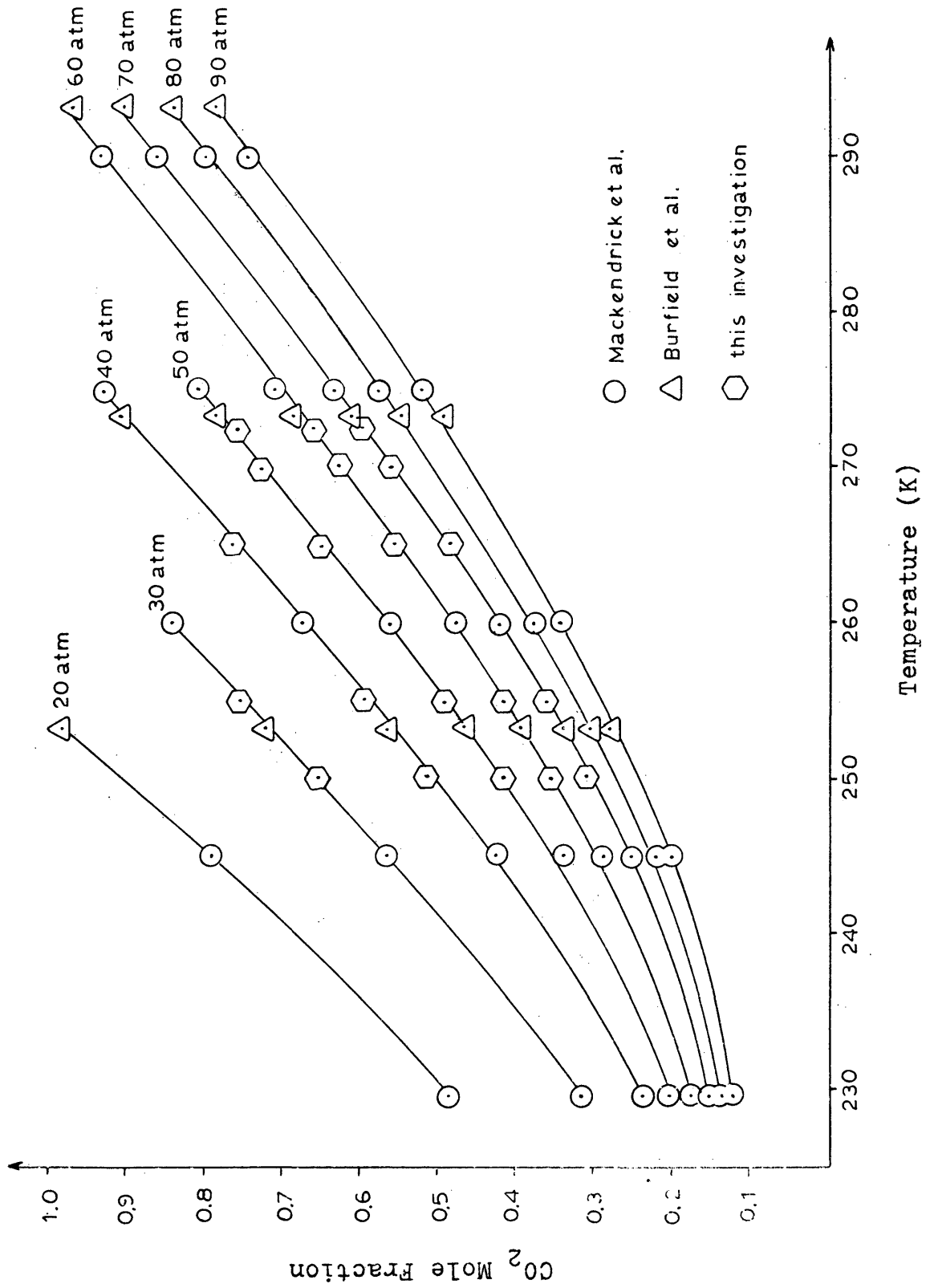


Figure 9

Cross-Plot of the Vapor Phase Equilibrium Data

B. Experimental Liquid-Phase Equilibrium Data

The following data were collected with the modified equipment using CO₂ as the chromatograph carrier gas.

Table 7

Experimental Liquid Phase Equilibrium Data

<u>T(K)</u>	<u>P (atm)</u>	<u>P-po</u>	<u>Composition(mole % of He)</u>
273.15	34.40	0.00	0.000
	(p) 40.00	5.60	0.201
	(s) 50.00	15.60	0.600
	(s) 60.00	25.60	0.980
	(s) 70.00	25.60	1.370
253.15	19.44	0.00	0.000
	(p) 29.45	10.01	0.196
	(p) 35.00	15.56	0.302
	(p) 46.74	27.30	0.556
	(s) 54.60	35.16	0.680
	(s) 63.20	43.76	0.828
274.90	36.02	0.00	0.000
	(p) 42.60	6.58	0.259
	(p) 45.70	9.68	0.373
	(s) 55.30	19.28	0.725
	(s) 58.00	21.98	0.832
274.90	35.95	0.00	0.000

Table 7 (continuation)

Experimental Liquid Phase Equilibrium Data

<u>T(K)</u>	<u>P (atm)</u>	<u>P-po</u>	<u>Composition (mole % of He)</u>
	(m) 45.00	9.05	0.364
	(m) 55.30	19.35	0.736
	(m) 62.00	26.05	1.005
	(m) 71.00	35.05	1.340

po= CO2 vapor pressure

(p)= with the magnetic recirculating pump

(m)= with the lapp metering pump

(s)= straight flow

Table 8

Liquid-Phase Equilibrium Data Comparison

<u>T(K)</u>	<u>P-po (atm)</u>	<u>Liquid Composition (He mole percent)</u>		
		<u>This Investigation</u>	<u>Mackendrick et al</u>	<u>Burfield et al</u>
273.15	5.6	0.201	0.220	0.220
	15.6	0.600	0.560	0.585
	25.6	0.980	0.960	0.980
	35.6	1.370	1.330	1.360
153.15	10.01	0.196	0.220	0.200
	15.56	0.302	0.330	0.300
	27.3	0.556	0.595	0.535
	35.16	0.680	0.770	0.680
	43.76	0.828	0.955	0.850
274.90	6.58	0.259	0.260	0.280
	9.68	0.373	0.380	0.400
	19.28	0.735	0.740	0.780
	21.98	0.832	0.850	0.890
274.90	9.05	0.364	0.360	0.370
	19.35	0.736	0.743	0.782
	26.05	1.005	1.020	1.050
	35.05	1.340	1.375	1.410

Figure 10

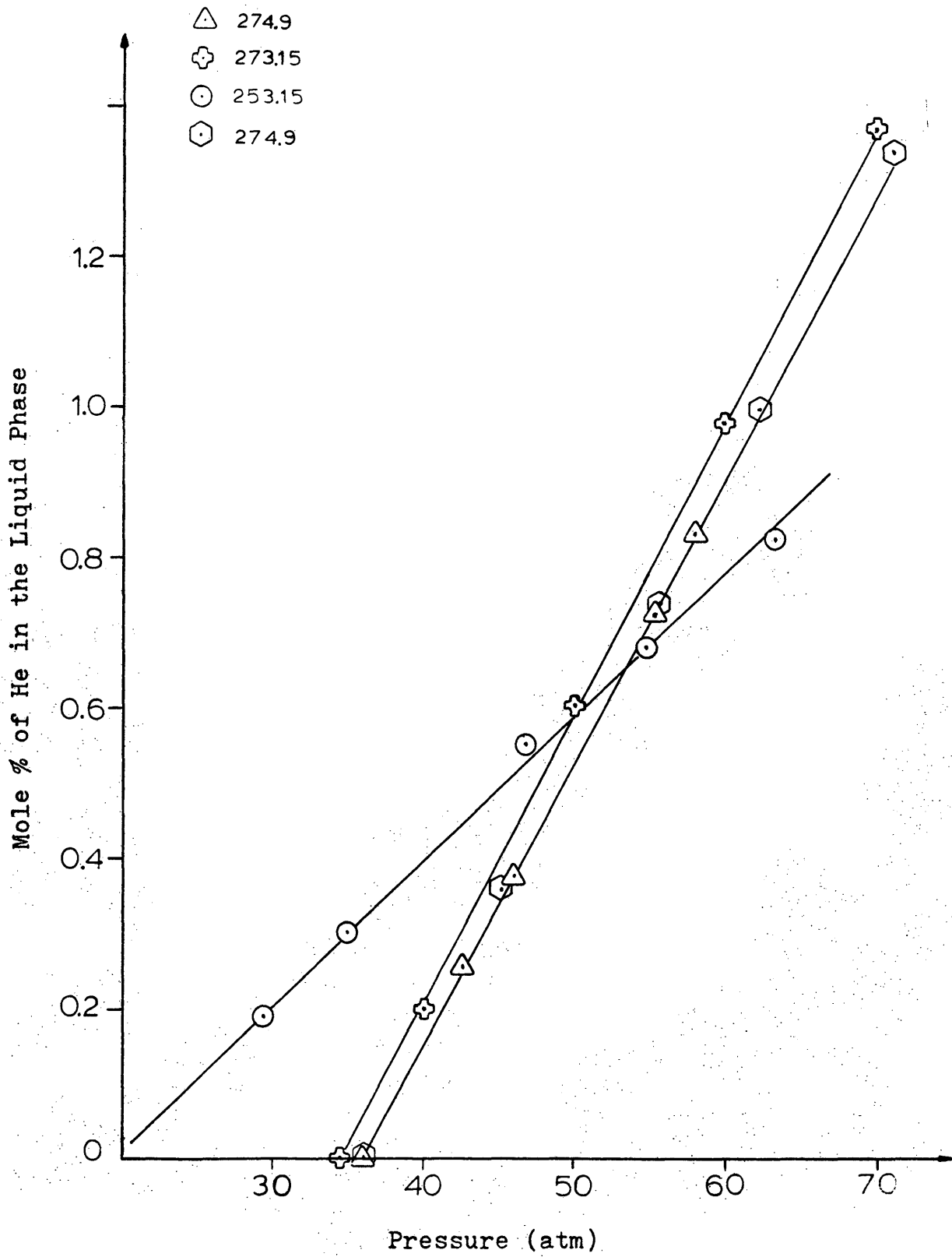
Experimental Liquid Phase Equilibrium Data (P vs comp.)

Figure 11

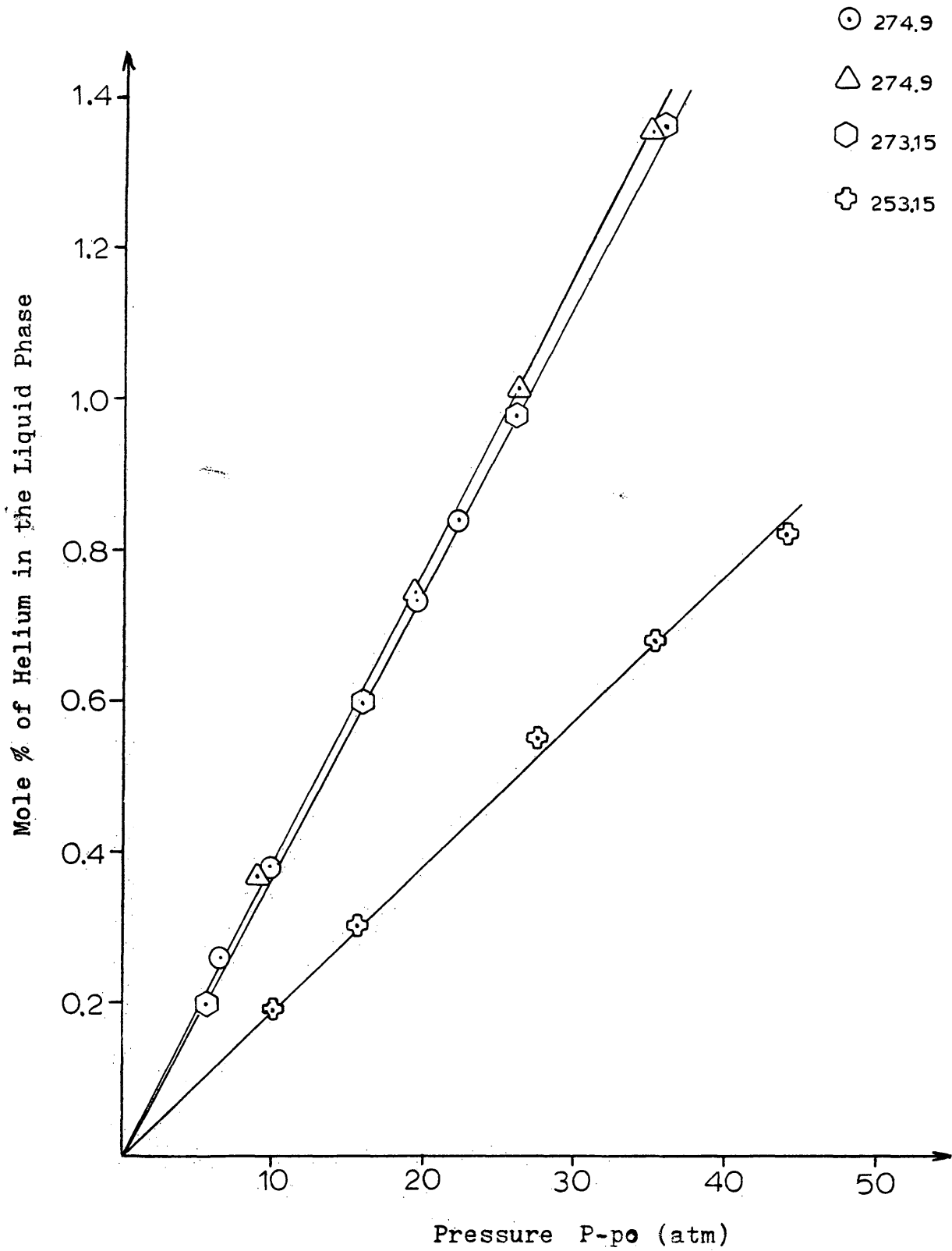
Experimental Liquid Phase Equilibrium Data (P-po vs composition)

Figure 12

Cross-Plot of the Experimental Liquid Phase Equilibrium Data

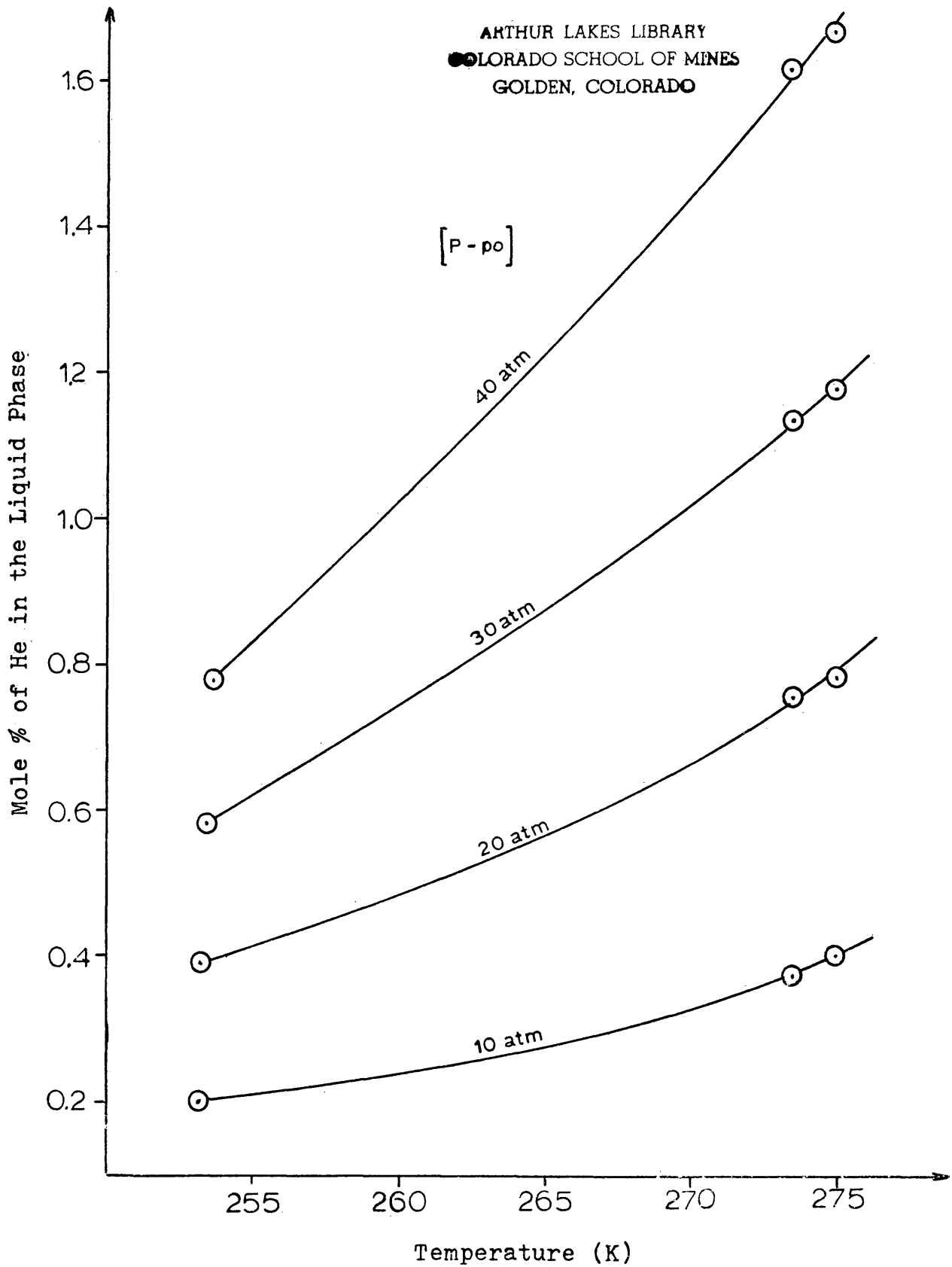


Figure 13

Liquid Phase Equilibrium Data Reported by Mackendrick et al.

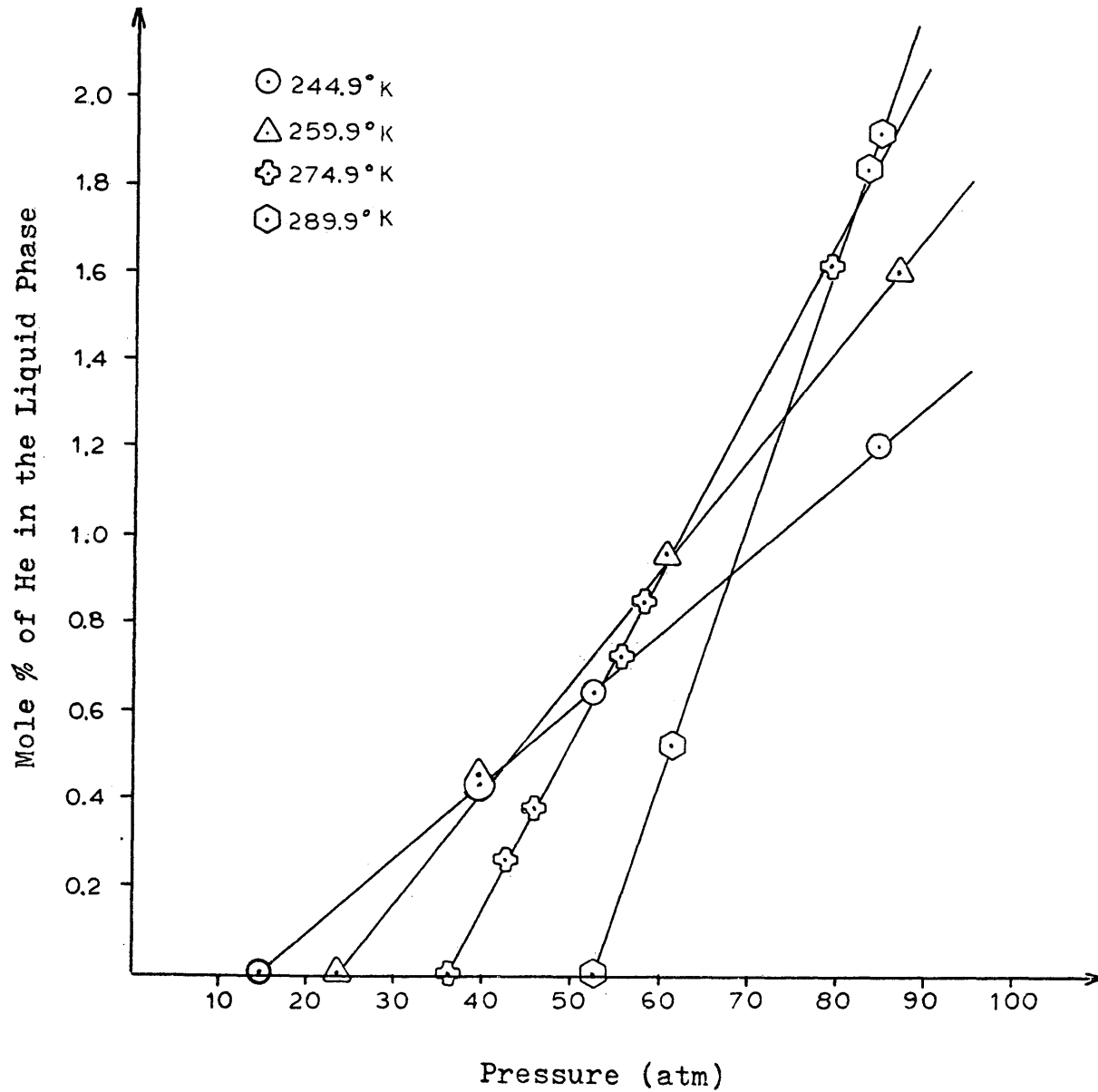


Figure 14

Liquid Phase Equilibrium Data Reported by Burfield et al.

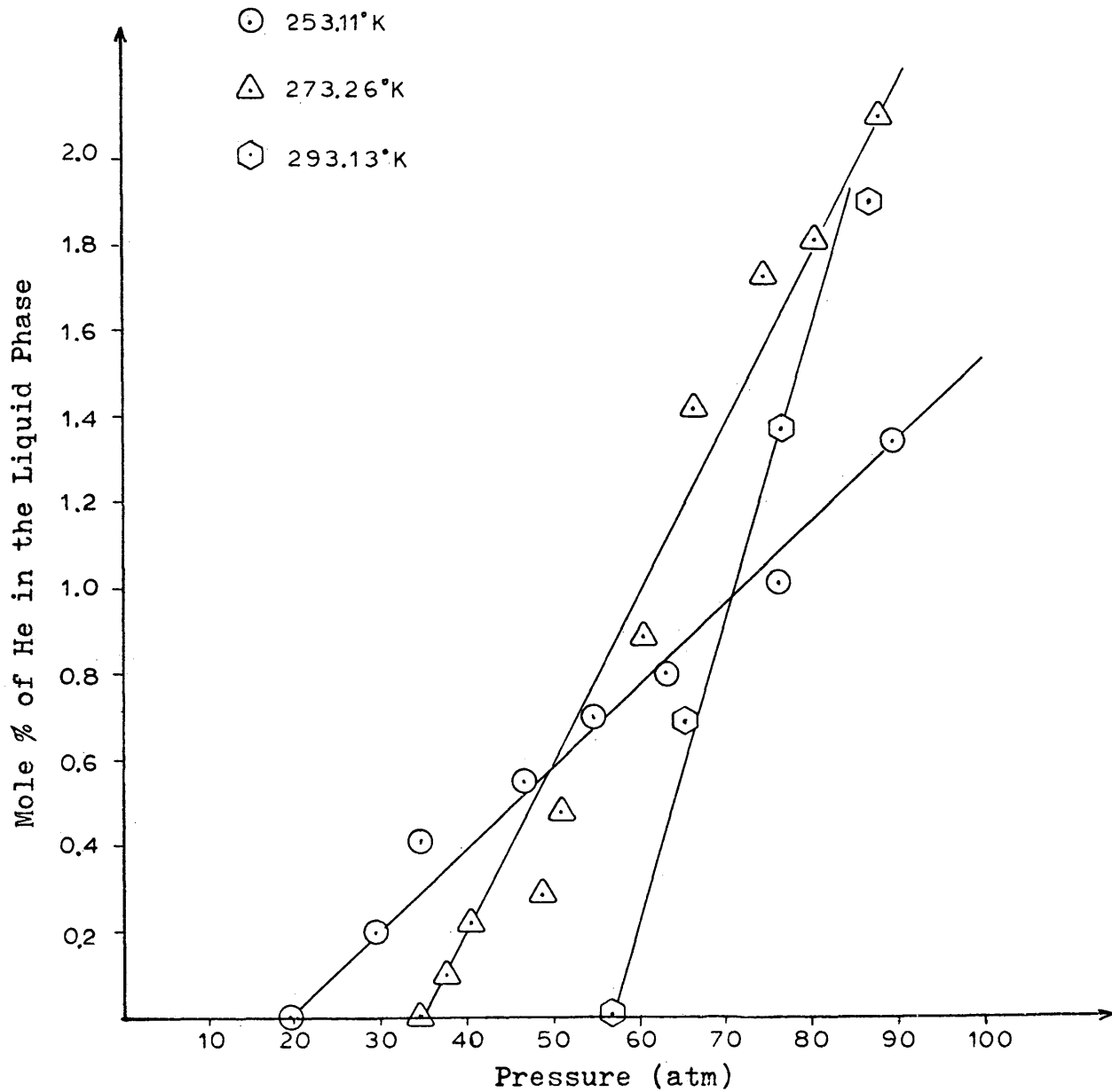
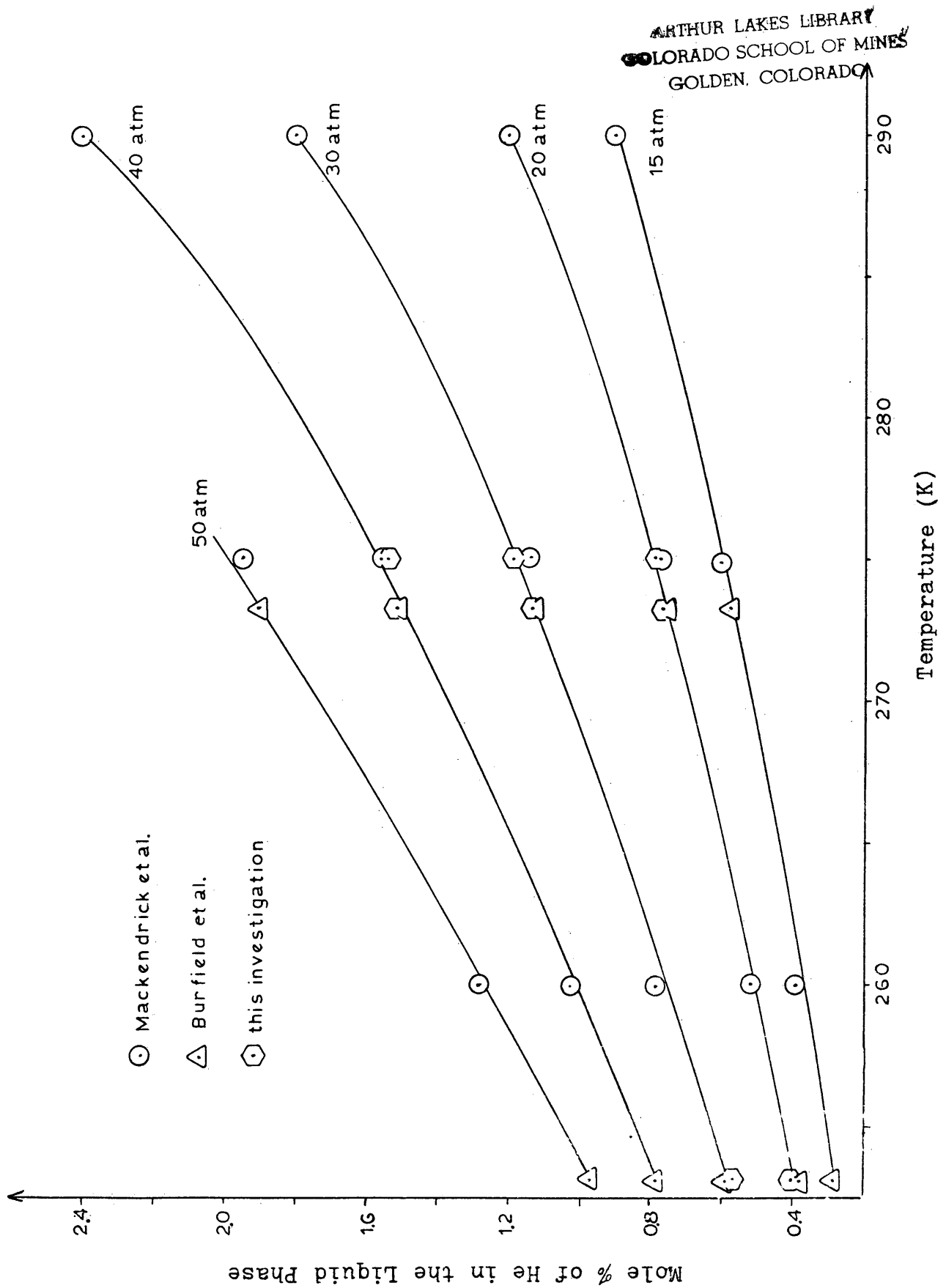


Figure 15

Cross-Plot of the Liquid Phase Equilibrium Data



OPERATIONAL CALCULATIONS

The purpose of this section is to illustrate and explain the procedures and calculations that were made before, during and after the raw data were taken.

A more detailed explanation of the various steps can be found in G. Baughman (1972) and S. Westhoff (1972)

Determination of the Calibration Curves

It was decided to measure two calibration curves: one using He as the chromatograph carrier gas, and the other using CO₂ as the carrier gas.

The sensitivity of the thermal conductivity of the chromatograph depends on the filament current, the carrier gas, the difference in thermal conductivity between the carrier gas and the material being analyzed, and the detector temperature.

The filament current used with He (250 ma) was much larger than the filament current used with CO₂ (100 ma) and therefore the sensitivity of the chromatograph when He was the carrier gas increased significantly.

It was decided to construct two calibration curves because in that way gas-phase composition data could be analyzed using two different carrier gases and a sensitivity comparison between He and CO₂ as carrier gases could be estimated. This was desirable because when measuring the composition of the liquid phase, the calibration curve using CO₂ as the chromatograph carrier gas had to be used to the small amounts of He

in this phase.

To construct the calibration curve with CO_2 as the carrier gas, a 35 mole percent He in CO_2 mixture was used. In a small high-pressure cylinder containing CO_2 , a certain amount of He was injected, and the resultant mixture was analyzed in the gas chromatograph. See appendices C and B.

For the He as a carrier calibration curve, it was not necessary to use a calibration mixture, because of the high sensitivity of the chromatograph. Thus the entire calibration curve was developed using samples of pure CO_2 injected into the chromatograph at different pressures.

The two calibration curves are presented in figures 16 and 17.

Checking the Calibration Curves

At various times, the calibration curves were checked to make sure that no shifts in chromatographic sensitivity were introduced, thus affecting the accuracy of the composition measurements.

The general procedures are discussed by G. Baughman (1972, p. 106-114), by S. Westhoff (1972, p. 117-148) and G. Baughman (1973, p. 45-55)

In this experimental work, the calibration curves were checked immediately after each data point was taken. See appendix F.

Taking Experimental Data

In order to convert raw data into values, a series of

calculations were performed. See appendix F.

A detailed explanation is presented elsewhere (Baughman, 1972) however a general listing of the steps to follow is presented below:

- 1 Record barometric pressure
- 2 Record system pressure
3. Record system temperature
- 4 Record manometer pressure
5. Record peak heights and chromatograph attenuation
6. Record machine sensitivity
- 7 Calculate injection pressure
8. Calculate sensitivity corection
9. Calculate barometric pressure correction
10. Calculate corrected peak heights
11. Calculate partial pressures from the calibration curves
12. Calculate mole fractions

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CONCLUSIONS

In this section, all the work done is summarized and the main results are emphasized.

a. The CO_2 vapor pressure was measured with the original equipment, thus checking the correct functioning of the pressure and temperature systems.

b. Three isotherms of the $\text{He} + \text{CO}_2$ systems were measured with the original equipment, verifying the ability of the equipment to attain equilibrium and to accurately measure the vapor-phase compositions.

c. The original equipment was modified, the CO_2 vapor pressure was remeasured, and the same three isotherms, as in case b, were measured again.

Helium was used as the chromatograph carrier gas for both the original and the modified equipment.

The results obtained with the modified equipment are as good or better than the results obtained with the original equipment.

d. Two recirculating pumps were tried in the system, one was a magnetic pump, the other was a diaphragm pump. Low pressure points of the $\text{He} + \text{CO}_2$ system, in the liquid + vapor region, were taken with the use of the magnetic pump. See tables 6 and 7. When the diaphragm pump became available, an isotherm of the $\text{He} + \text{CO}_2$ system was measured with this pump, to verify its correct functioning.

Carbon dioxide was used as the carrier for the chromatograph in these series of runs.

e. Comparing the data taken with the original equipment, table 4, with the data obtained using the modified equipment, table 5, it is possible to conclude that there are no appreciable differences, figure 5.

f. Comparing the values obtained with the original equipment and the modified equipment using He as the chromatograph carrier gas, with the values obtained with the modified equipment and CO_2 as the chromatograph carrier gas (figure 6) it is possible to affirm that the equilibrium data closely agree, (figure 7) indicating the capability of using either carrier gas without effecting the accuracy of the composition measurements

g. The data taken with the recirculating pumps agree well with the data taken using straight flow, showing that the equipment is capable of functioning in either mode.

h. Comparison of the equilibrium data of Mackendrick et al and the data obtained in this investigation with the data presented by Burfield et al, indicated no significant difference in composition when samples are withdrawn from the system versus "in place" composition measurements, at values of $T_r = 0.9$ (273.15 K) and $P_r = 0.96$ (70 atm) for CO_2 .

i. The temperature of the liquid bath in which the cell is suspended can be controlled and measured accurately (± 0.001), and the pressure can be measured with a maximum error of

± 0.07 atm or ± 0.07 Psi, depending on the gauge in use.

See table 1.

j. Based on the calibrations and system comparisons, it is estimated that the overall accuracy of the data obtained is $\pm 1.5\%$ of the reported compositions.

APPENDIX A

CARBON DIOXIDE VAPOR PRESSURE DATA

The National Bureau of Standards data (Meyers and Van Dusen, 1933) is the most accurate vapor pressure data for CO₂. However their data is based on the 1927 International Temperature scale. The literature values used for comparison in the present work consisted of the Meyers and Van Dusen data adjusted to the 1968 International Practical Temperature Scale (IPTS-68). (A. J. Kidnay (Private Communication) See App.A)

Table 9

CO₂ Vapor Pressure Data

Solid CO ₂			
<u>T(K)</u>	<u>P(k Pa)</u>	<u>T(K)</u>	<u>P(k Pa)</u>
120	0.004	190	68.44
125	0.012	194.674	101.32
130	0.032	195	104.07
135	0.080	200	155.11
140	0.187	205	227.07
145	0.848	215	464.78
155	1.674	216.58	517.95
160	3.158		
165	5.721		
170	9.987		
175	16.86		
180	27.62		
185	44.02		

1 atm = k Pa/101 325

<u>Liquid CO₂</u>		
<u>T(K)</u>	<u>P (k Pa)</u>	<u>P (atm)</u>
216.58	517.95	5.112
200	599.60	5.918
225	735.60	7.260
230	893.50	8.818
235	1075.20	10.611
240	1282.90	12.661
245	1518.90	14.990
250	1785.30	17.620
255	2084.60	20.573
260	2419.00	23.874
265	2791.00	27.545
270	3203.00	31.611
275	3659.00	36.110
280	4160.00	41.056
285	4711.00	46.494
290	5317.00	52.475
279	5982.00	59.038
300	6713.00	66.252
**304.18	7380.00	72.835

*Triple point

**Critical temperature

In order to interpolate easily, the equation $P=A-\frac{B}{T}$ was applied and values of A and B were obtained for 5 degrees temperature intervals (Table 10)

Table 10

Values of the Constants A and B

<u>Temperature Interval (K)</u>	<u>Value of A and B (k Pa)</u>
270-297	A= 13.57868975 B= 1450.00732100
285-290	A= 15.47618735 B= 2000.28158600
280-285	A= 15.423221601 B= 1985.184752000
275-280	A= 15.39116276 B= 1976.20987400
270-275	A= 15.39245044 B= 1976.56397000
265-270	A= 15.3693029 B= 1970.3141340
260-265	A= 15.37253705 B= 1971.17116200
255-260	A= 15.37874689 B= 1972.78573000
250-255	A= 15.39185560 B= 1976.12846400
245-250	A= 15.40574109 B= 1979.59983800
240-245	A= 15.43117891 B= 1985.83211900
235-240	A= 15.4578941 B= 1992.2353990
220-225	A= 15.595330 B= 2023.794913

<u>Temperature Interval (k)</u>	<u>Value of A and B (k Pa)</u>
216.58-220	A= 15.66639194 B= 2039.42842000
215-216.58	A= 20.98887462 B= 3192.17174600
210-215	A= 20.88709924 B= 3170.29006000
205-210	A= 20.76456687 B= 3144.55825100

APPENDIX BCalibration Curves Data

Table 11

Base Attenuation.....128
 Barometric Pressure.....624.0 mm Hg.
 Carrier gas.....He
 Filament Current.....240 ma
 Calibration Gas.....CO₂

	<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>ΔP</u>	<u>Inj P.</u>	<u>Corrected PH.</u>
1.	55.00	256	7.00	-276	348.0	14.00
2.	55.50	256	6.80	-285.5	311.0	13.60
3.	56.90	246	6.20	-313	311.0	12.40
4.	58.60	256	5.60	-345	279.0	11.20
5.	59.60	256	5.12	-362	262.0	10.24
6.	60.00	256	5.00	-375	249.0	10.00
7.	62.00	128	8.35	-415	209.0	8.350
8.	62.00	256	4.18	-415	209.0	8.350
9.	63.00	138	7.57	-435	189.0	7.570
10.	64.10	178	6.70	-457	167.0	6.700
11.	65.00	128	5.95	-475	149.0	5.95
12.	67.00	128	4.40	-515	109.0	4.40
13.	68.00	64	7.17	-535	89.0	3.59
14.	68.80	64	5.15	-551	73.0	2.93
15.	68.90	64	5.60	-553	71.0	2.80
16.	68.90	128	2.80	-553	71.0	2.80
17.	69.00	64	5.57	-555	69.0	2.79

	<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>ΔP</u>	<u>Inj P.</u>	<u>Corrected PH.</u>
18.	70.60	32	5.95	-587	37.0	1.49
19.	71.40	16	7.20	-603	21.0	0.90
20.	71.50	16	6.45	-605	19.0	0.81
21.	71.50	16	6.45	-605	19.0	0.81
22.	71.58	16	5.93	-607	17.0	0.74
23.	71.80	32	0.17	-611	13.0	0.55
24.	71.92	8	7.47	-613	11.0	0.47
25.	72.00	8	6.45	-615	9.0	0.40

See symbols in appendix F.

Table 12

He Calibration Curve Data

Base Attenuation.....4
 Barometric Pressure.....619
 Carrier Gas.....CO₂
 Filament Current.....100 ma
 Calibration gas35% He in CO₂ Mixture

	<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>ΔP</u>	<u>Inj P.</u>	<u>Corrected PH.</u>
48.01	32	7.43	-133.5	485.5	59.44	
50.00	32	6.80	-173.5	445.5	54.40	
52.10	32	6.25	-215.0	404.0	50.00	
56.00	32	5.00	-292.5	326.5	40.00	
60.00	32	3.85	-372.5	246.5	30.80	
63.00	32	2.90	-432.5	186.5	23.20	
61.95	16	6.45	-412.0	207.5	25.80	
65.00	16	4.57	-473.0	146.0	18.30	
67.00	16	3.35	-512.5	106.5	13.40	

<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>P</u>	<u>Inj P.</u>	<u>Corrected PH.</u>
67.95	8	5.40	-531.5	87.5	10.80
68.60	8.	4.54	-545.0	74.0	9.10
59.20	8	3.80	-557.0	62.0	7.60
69.45	4	7.00	-562.0	57.0	7.00
69.80	4	6.19	-569.0	50.0	6.20
70.10	4	5.30	-574.5	44.5	5.30
70.40	4	4.76	-580.0	39.0	4.80
70.80	4	3.65	-588.0	31.0	3.70
71.30	4	2.43	-598.5	30.5	2.40
71.40	2	5.46	-60.05	18.5	2.70
71.55	2	3.60	-604.0	15.0	1.80
71.65	1	6.20	-605.5	13.5	1.60
71.80	1	4.60	-609.0	10.0	1.20
71.85	1	4.37	-609.5	9.5	1.10
72.00	1	2.90	-612.5	6.5	0.73
72.05	1	2.31	-614.0	5.0	0.58
73.00	1	0.00	-619.0	0.0	0.00

Figure 16
Carbon Dioxide Calibration Curve

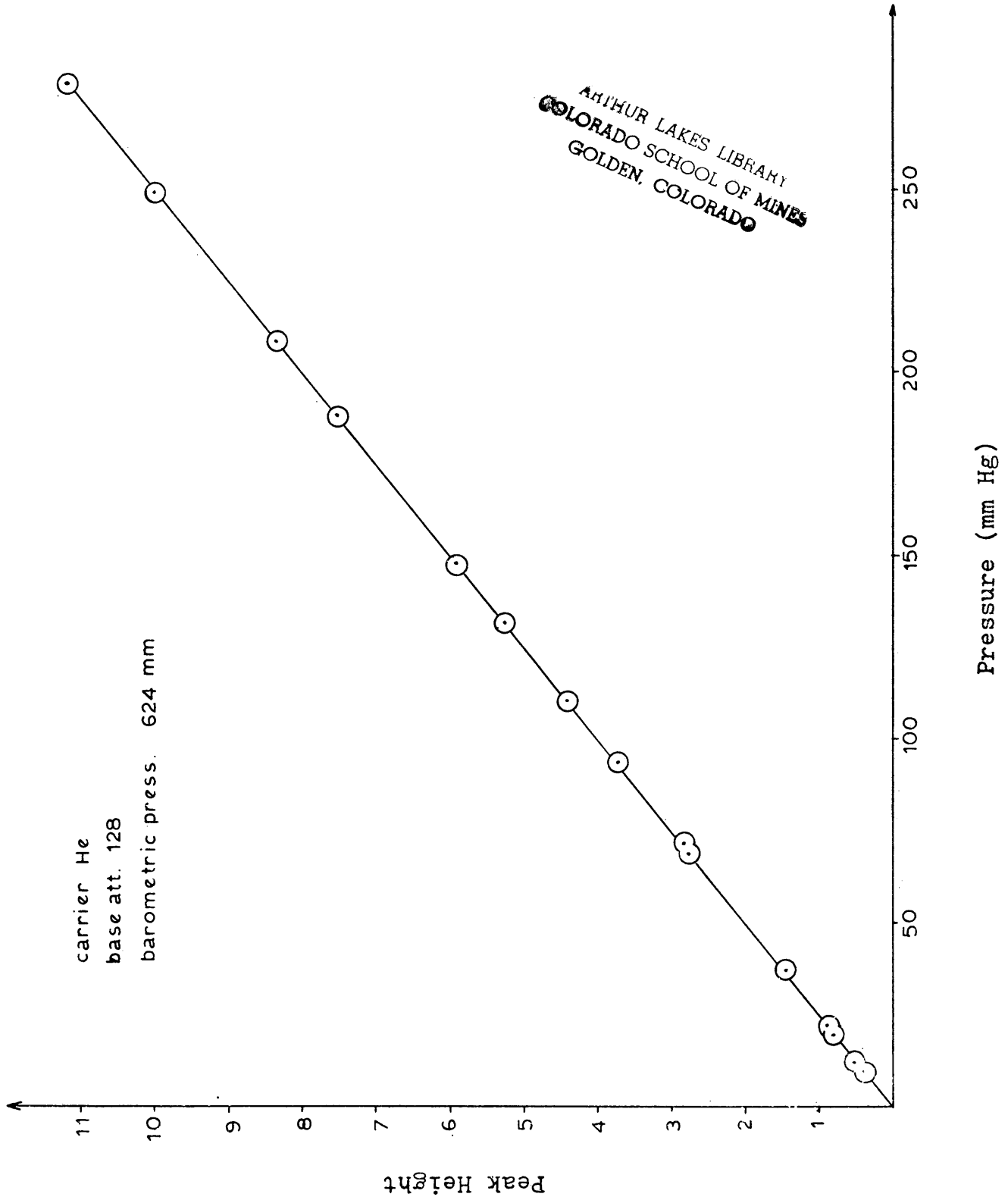
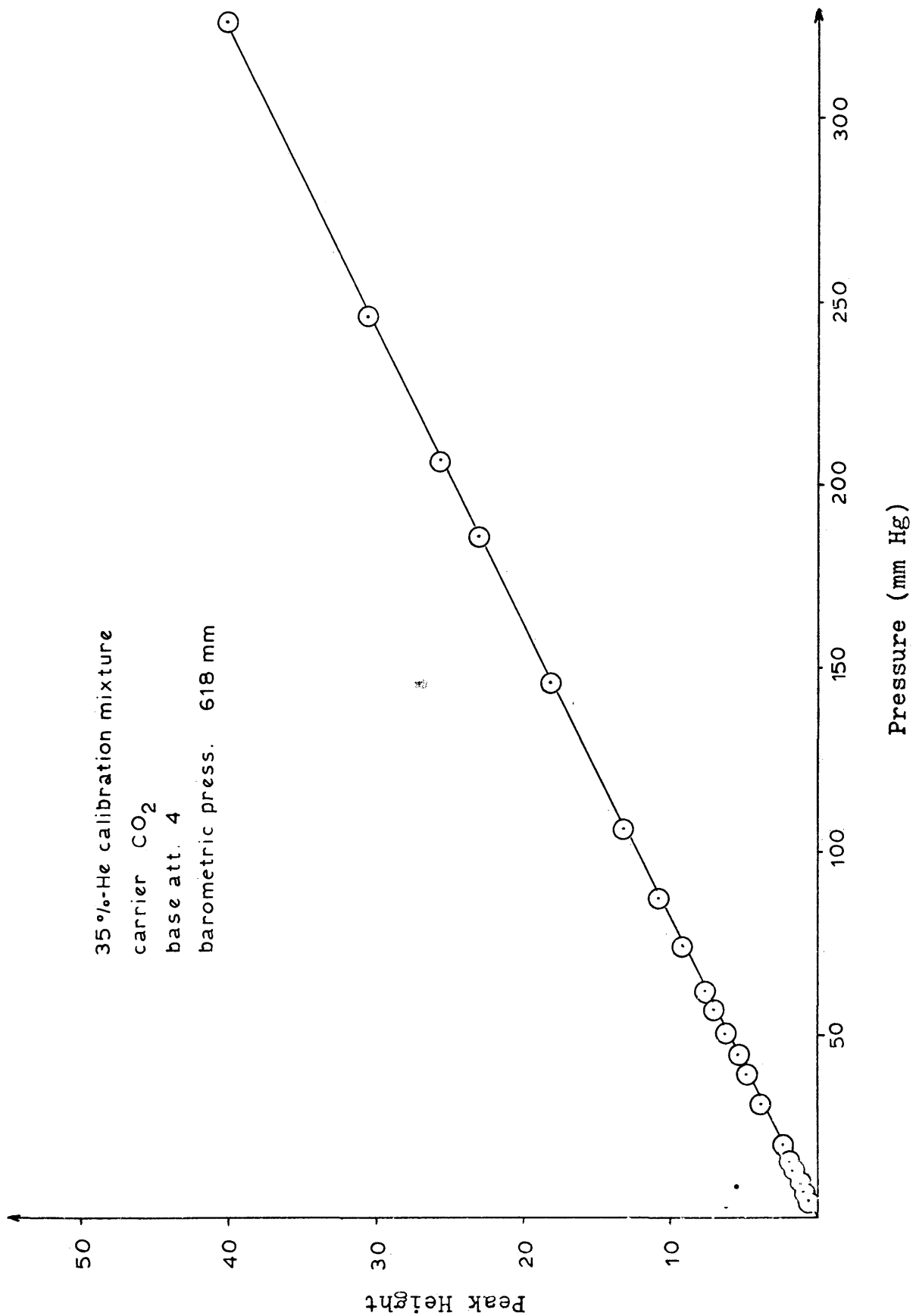


Figure 17

Helium Calibration Curve



APPENDIX C

Composition Analysis of the He-CO₂ Calibration Mixturea. Mixture Analysis

Table 13

Base Attenuation.....512
 Barometric Pressure.....615.0
 Carrier Gas.....He
 Filament Current.....250 ma

<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>Inj. Pressure</u>	<u>Corrected PH.</u>
45	256	7.27	541.0	3.64
35	512	5.00	741.0	5.00
30	512	5.65	840.0	5.65
26	512	6.17	920.0	6.17
50	256	5.93	441.5	2.96
55	256	4.55	341.5	2.28
60	256	3.20	242.5	1.60

b. Pure CO₂ Analysis

Table 14

Base Attenuation....512
 Barometric Pressure.....615.0
 Carrier Gas.....He
 Filament Current.....250 ma

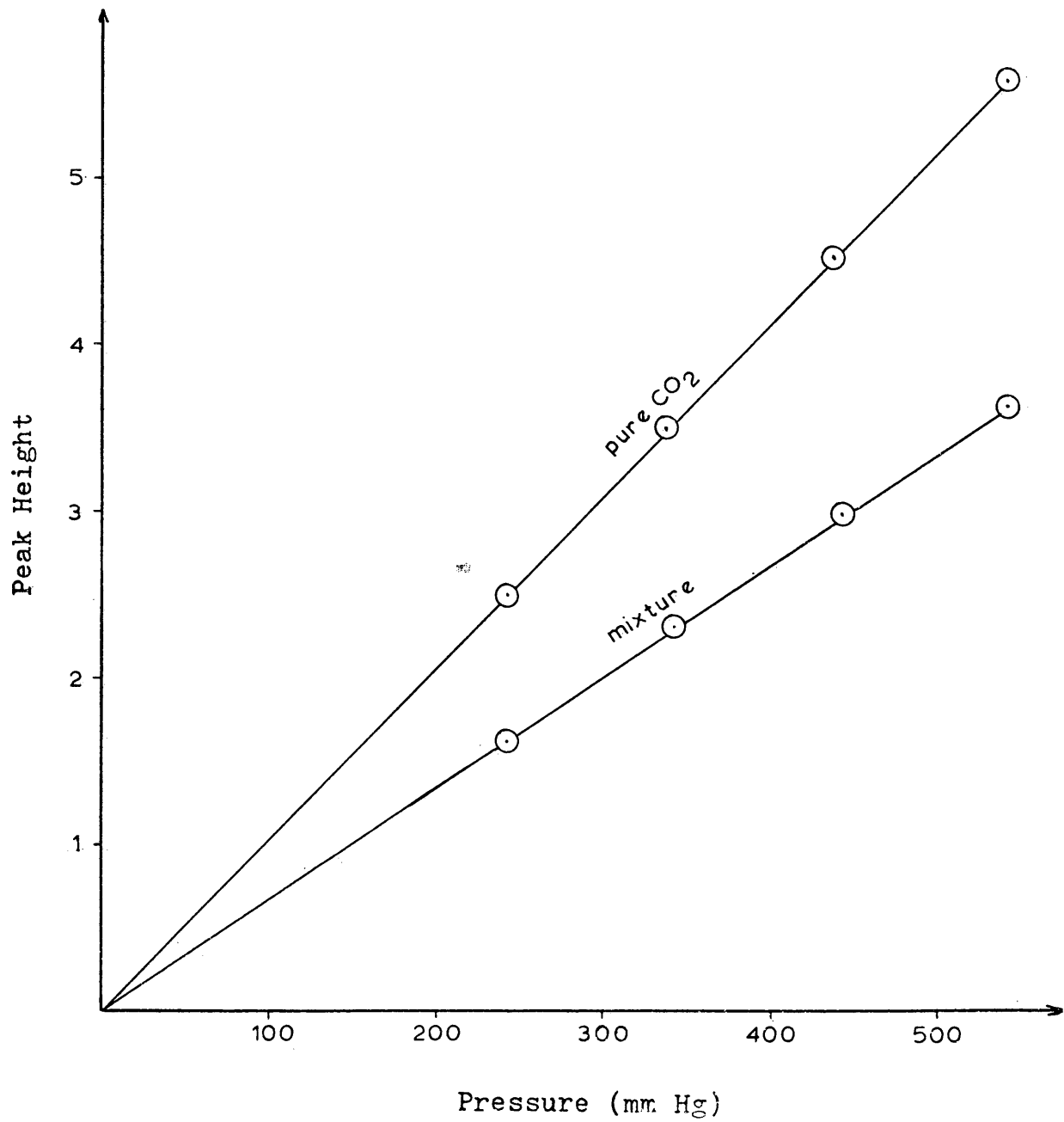
<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>Inj. Pressure</u>	<u>Corrected PH.</u>
26	1024	6.18	920.0	12.36
30	512	8.50	840.0	8.50
35	512	7.55	741.0	7.55

<u>LL</u>	<u>ATT</u>	<u>PH</u>	<u>Inj. Pressure</u>	<u>Corrected PH.</u>
45	512	5.57	541.0	5.57
50	512	4.55	441.5	4.55
55	256	6.98	341.5	3.49
60	256	4.93	242.5	2.47

Slope Ratio = 0.65 which means the mixture is 35% He and
65% CO₂ (from figure 18).

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Figure 18

Composition Analysis of the He-CO₂ Calibration Mixture

APPENDIX D

Gas Phase Equilibrium Data Reported by Mackendrick Et Al.

Table 15

<u>T(K)</u>	<u>P(atm)</u>	<u>Vapor Composition (mole fraction CO₂)</u>
229.9	14.4	0.646
	29.4	0.326
	44.8	0.221
	63.4	0.164
	89.8	0.120
244.9	19.5	0.802
	29.4	0.559
	39.6	0.430
	49.3	0.347
	84.2	0.216
259.9	39.7	0.678
	44.7	0.617
	58.3	0.485
	60.8	0.471
	87.1	0.347
274.9	42.6	0.891
	45.7	0.851
	55.3	0.753
	58.0	0.738
	86.1	0.539

<u>T(K)</u>	<u>P(atm)</u>	<u>Vapor Composition (mole fraction CO₂)</u>
289.9	61.2	0.924
	84.6	0.773

Table 16

Gas Phase Equilibrium Data Reported By Burfield Et Al.

<u>T(K)</u>	<u>P(atm)</u>	<u>Vapor Composition (mole fraction CO₂)</u>
253.11	19.58	1.000
	29.45	0.714
	34.91	0.650
	46.74	0.493
	54.64	0.428
253.11	63.23	0.370
	76.42	0.316
	89.51	0.267
273.26	34.53	1.000
	37.32	0.955
	40.31	0.906
	48.83	0.857
	51.02	0.778
	60.86	0.680
	66.42	0.637
	74.51	0.577
	80.91	0.541
	87.84	0.502
293.13	56.56	1.000
	65.20	0.930
	76.41	0.862
	86.89	0.814

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Figure 8 is a graphical representation of the values reported by Mackendrick et al and Burfield et al

APPENDIX E

Liquid Phase Equilibrium Values Reported By Mackendric Et Al.

Table 17

<u>T(K)</u>	<u>po (atm)</u>	<u>P(atm)</u>	<u>Composition (He mole%)</u>
244.9	14.95	39.6	0.440
		52.1	0.643
		84.2	1.210
259.9	23.80	39.7	0.428'
		60.8	0.960
		87.1	1.600
274.9	36.02	42.6	0.267
		45.7	0.384
		55.3	0.738
		58.00	0.857
		79.00	1.620
289.9	52.35	61.2	0.537
		83.0	1.840
		84.6	1.920

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Table 18

Liquid Phase Equilibrium Data Obtained by Burfield Et Al.

<u>T(K)</u>	<u>po(atm)</u>	<u>P(atm)</u>	<u>Composition (He mole%)</u>
293.13	55.35	56.56	0.00
		65.20	0.69
		76.41	1.37
		86.89	1.90

<u>T(K)</u>	<u>p₀ (atm)</u>	<u>P(atm)</u>	<u>Composition (He mole%)</u>
273.26	34.50	34.53	0.00
		37.32	0.10
		40.31	0.22
		48.83	0.29
		51.02	0.48
		60.86	0.89
		66.42	1.42
		74.51	1.73
		80.91	1.81
		87.84	2.10
253.11	19.42	19.58	0.00
		29.45	0.20
		34.91	0.41
		46.74	0.55
		54.64	0.70
		63.23	0.80
		76.42	0.02
		89.51	1.34

APPENDIX F

Raw Data and Calculations

Table 19

<u>Set</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Mole Fraction of CO₂ in Vapor</u>	<u>Mole % of He In the Liquid</u>	<u>Date</u>
1	273.15	45.81	0.848		7/1/73
	273.15	50.81	0.781		7/1/73
	273.15	60.81	0.689		7/1/73
	273.15	40.81	0.898		7/1/73
	273.15	40.81	0.905		7/2/73
	260.15	40.81	0.675		7/2/73
	260.15	50.81	0.570		7/2/73
	260.15	60.81	0.469		7/2/73
	260.15	40.81	0.684		7/16/73
	250.15	25.81	0.755		7/21/73
	250.15	30.81	0.647		7/21/73
	250.15	40.81	0.511		7/21/73
	250.15	50.81	0.415		7/21/73
	250.15	60.81	0.357		7/21/73
2.	273.15	40.00	0.914		11/4/73
	273.15	45.00	0.847		11/4/73
	273.15	50.00	0.783		11/4/73
	273.15	60.00	0.687		11/4/73
	273.15	70.00	0.600		11/5/73
	260.15	35.00	0.760		11/5/73
	260.15	41.00	0.670		11/5/73

<u>Set</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Mole Fraction</u> <u>of CO₂ in Vapor</u>	<u>Mole % of He</u> <u>In the Liquid</u>	<u>Date</u>
	260.15	50.00	0.567		11/5/73
	260.15	54.00	0.534		11/5/73
	260.15	60.00	0.478		11/5/73
	260.15	70.00	0.415		11/5/73
	250.15	26.00	0.744		11/7/73
	250.15	30.00	0.658		11/7/73
	250.15	40.00	0.513		11/7/73
	250.15	50.00	0.419		11/7/73
	250.15	60.00	0.352		11/7/73
	250.15	70.00	0.308		11/7/73
3.	273.15	*40.00	0.907	0.201	12/12/73
	273.15	50.00	0.784	0.600	12/12/73
	273.15	60.00	0.687	0.980	12/12/73
	273.15	70.00	0.612	1.370	12/12/73
	253.15	*29.45	0.727	0.196	12/13/73
	253.15	*35.00	0.639	0.302	12/13/73
	253.15	*46.74	0.500	0.556	12/13/73
	253.15	54.60	0.422	0.680	12/13/73
	253.15	63.20	0.374	0.828	12/13/73
	253.15	74.00	0.327	-----	12/13/73
	274.90	*42.60	0.896	0.259	12/17/73
	274.90	*45.70	0.854	0.373	12/17/73
	274.90	55.30	0.753	0.725	12/17/73
	274.90	58.00	0.731	0.832	12/17/73

<u>Set</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Mole Fraction</u> <u>of CO₂ in Vapor</u>	<u>Mole % of He</u> <u>In the Liquid</u>	<u>Date</u>
4.	274.9	45.00	0.860	0.364	13/11/74
	274.9	55.30	0.748	0.736	3/11/74
	274.9	62.00	0.693	1.005	3/11/74
	274.9	71.00	0.626	1.340	3/11/74

Set 1 Old equipment (He carrier gas)

Set 2 Modified equipment (He carrier gas)

Set 3 Modified Equipment (CO₂ carrier gas)

* Using the Magnetic pump.

Set 4 Modified Equipment (CO₂ carrier gas) plus the lapp diaphragm pump.

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Sample Calculation

Date: 7/1/73

Temperature: R= 25.527

N= 25.527

T= 273.15 K

Barometric Pressure: 0.81 atm = 620.0 mm

System Pressure: 45 + 0.81 = 45.81 atm

Chromatograph Attenuation: 128

Manometer Pressure: -475.00 mm

Absolute Injection Pressure: 620.0 mm - 475.0 mm = 145 mm

Peak height recorded: 5.00

Machine Sensitivity: 7.53

Correction Factor: $A = 7.57/7.53 = 1.0053$ $D = (620-435)/(624-435) = 0.9788$ $C = A \times D = 1.0053 \times 0.9788 = 0.9840$ $M = 128/128 = 1.0$ Corrected Peak Height: $M \times C \times \text{Peak Height} = 1 \times 0.984 \times 5.00 = 4.92$

Determine Partial Pressure: From the He calibration Curve at 4.92

p. pressure of $\text{CO}_2 = 123. \text{ mm Hg.}$ Mole Fraction: p. pressure / abs. injection pressure = $123.0 / 145.0 =$ 0.848. In this case 84.8% of CO_2 in the mixture.

For a more detailed explanation, see S. Wasthoff (1972, p. 153 - 157)

and G. Baughman (1972, p. 69 - 72)

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Symbols

LL	Manometer left leg
ATT.	Chromatograph attenuation
PH.	Peak Height
ΔP	Manometer left leg minus manometer right leg
Inj P	Injection pressure

APPENDIX G

Chromatograph Variables

Column Temperature	100° C
Detector Temperature	160° C
Line Temperature	125° C
Valve Temperature	103° C
Carrier Gas Flow Rate	30 cc/minute
Filament Current	100 ma (CO ₂) 250 ma (He)
Carrier Gas Pressure	80 Psig.
Recorder Range	1 mv.

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