

PHASE RELATIONSHIPS OF BINARY HYDROCARBON SYSTEMS
PROPANE-N-BUTANE

A Thesis


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for the Degree Master of Science

by

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SUMMARY

The propane-n-butane system was studied experimentally. A temperature range from 70°C to 155°C and pressure range from 190 to 625 psia were spanned in the work. Six mixtures were investigated to determine their P-V-T-X relationships. The method developed by Kay (12) was employed. Samples of n-butane and propane of the highest quality were deaerated by pumping under vacuum. The six mixtures of known compositions were confined over mercury in a calibrated glass tube. The tube was fastened to a mercury-filled compressor block with a means of controlling the pressure on the sample. The tube was then surrounded by a vacuum vapor jacket having a sidearm boiler which permitted refluxing with organic liquids with the desired boiling range. (7)

The P-T and T-X relationships for this system are presented in Figures 3 and 10 respectively; these graphs are similar to those for other binary n-paraffin hydrocarbon mixtures. The critical locus curve exhibits a maximum pressure point; this point of maximum critical pressure occurs at 624.7 psia and 82.62 mole per cent propane. The data taken in the study was used to further

test the various methods of correlating the critical properties of n-paraffin hydrocarbon mixtures.

STATEMENT OF PROBLEM

A sufficient number of mixtures of propane-n-butane to describe the critical locus curve of the system were to be investigated. Also, the critical point at the maximum pressure was to be determined for the system. In addition, the experimental data were to be correlated with data that had been taken in previous studies.

INTRODUCTION

In the chemical industry, as in every other industry, time is becoming a determining factor in developing new processes and products. Any reliable shortcut which will save time will enhance a company's chances of getting ahead of competition. This is one of the main reasons for such an intense interest in P-V-T studies.

These investigations are undertaken in the hopes that new and dependable correlations can be found for predicting the properties of pure substances and mixtures without having to resort to time-consuming laboratory work. The critical region is of special interest, because, although theoretical methods are available to predict P-V-T relations below this region, no such relations have been established for its prediction. Therefore, critical properties must be found experimentally.

Theoretically the P-T diagram can be calculated approximately only up to pressures and temperatures near the critical region of the mixture. Normally, in the critical region, P-T data have had to be determined experimentally. These data consisted of three unique points on the P-T envelope curve for each mixture. These

points are (1) the critical point, or the convergence point of the quality lines of the mixture, (2) the cricondenbar point, or the point of maximum pressure, and (3) the cricondentherm point, or point of maximum temperature." (7)

Several correlations of critical properties have been proposed. (4) One such correlation is the plot of average molecular weight versus critical pressure for binary systems of the n-paraffin homologous series containing both propane and butane as common components indicate that lines of constant mole fraction are approximately straight and converge to the critical pressure of pure propane and n-butane as the common points. Similar plots of average molecular weight versus cricondenbar pressure and cricondentherm pressure, respectively, yield the same general result.

If the above correlations prove valid for other, more complex systems, then it would be possible to predict critical properties of systems with a minimum amount of experimental data. It was for the purpose of establishing new correlations for critical data that a research project was started; several systems have already been studied as a part of the project, and the previously-mentioned correlations have been proposed. This thesis is a natural continuation of the project. Some of the objects of this

investigation will be to test the old correlations and try to propose new ones.

PHASE BEHAVIOR OF MIXTURES

A bubble point of a liquid mixture is the pressure at a given temperature, or vice versa, at which initial vaporization occurs; it is marked by the formation of an infinitesimal bubble in the liquid. The locus of all such points on a P-T plot is termed the bubble point curve of the mixture. A dew point is the pressure at a given temperature, or vice versa, at which the first drop-let appears in a vapor mixture; the locus of all such points on a P-T plot is termed the dew point curve of the mixture. If both of these curves were plotted on the same P-T plot, the resulting curve would be termed the P-T border curve, as shown in Figure 1. Line BDC represents the bubble point curve, and line HFC is the dew point curve. The border curve encloses the two-phase region of the mixture; outside the curve the mixture is a single phase. To the left of the bubble point curve the mixture is entirely liquid, and to the right of the dew point curve, the mixture is completely vapor. The point on the border curve where the dew point and bubble point curves meet is termed the critical point (C).

It is the point of convergence of the quality lines within the border curve, i.e., it is the point at which

liquid and vapor become indistinguishable. The critical point is of special interest because it is the point at which the properties of liquid phase and vapor phase of a mixture become identical. Two other points of interest in the critical region are the cricondenthem (F) and cricondenbar (E)--the point of maximum temperature and point of maximum pressure, respectively. The critical point may correspond to either of the other two, i.e., the critical point may be identical with the cricondenthem or cricondenbar.

The shape of the border curve depends on the pure components of the mixture. If the components differ greatly in their vapor pressures and are present in about equal amounts (on a weight basis) the border curve will be very wide; whereas, if the difference is small, the border curve will be narrow. It should be noted that, as long as the border curve is not crossed, the transition from one state to the other takes place so gradually that there is no visible change. Also, for a pure substance the bubble point curve and dew point curve are identical, and the resulting border curve is termed the vapor pressure curve.

In areas FJCM and EKCL a phenomenon occurs which is called retrograde condensation. If a mixture at the

condition of point 1 in the vapor phase is compressed at constant temperature, a liquid phase would appear at point G. The amount of liquid would increase until point J is reached; then the liquid would decrease in amount until it completely disappeared at point M. This is isothermal retrograde condensation (Type I); it occurs only when the dew point curve is crossed twice. Another type of retrograde condensation is isobaric retrograde condensation (Type II), which occurs in area EKCL. If the liquid mixture at point 3 is heated at constant pressure, the first bubble of vapor will appear at D. The amount of vapor will increase until point E is reached; then the amount will decrease until the sample becomes completely liquefied again at point L. Type II of retrograde condensation occurs only when the bubble point curve is crossed twice.

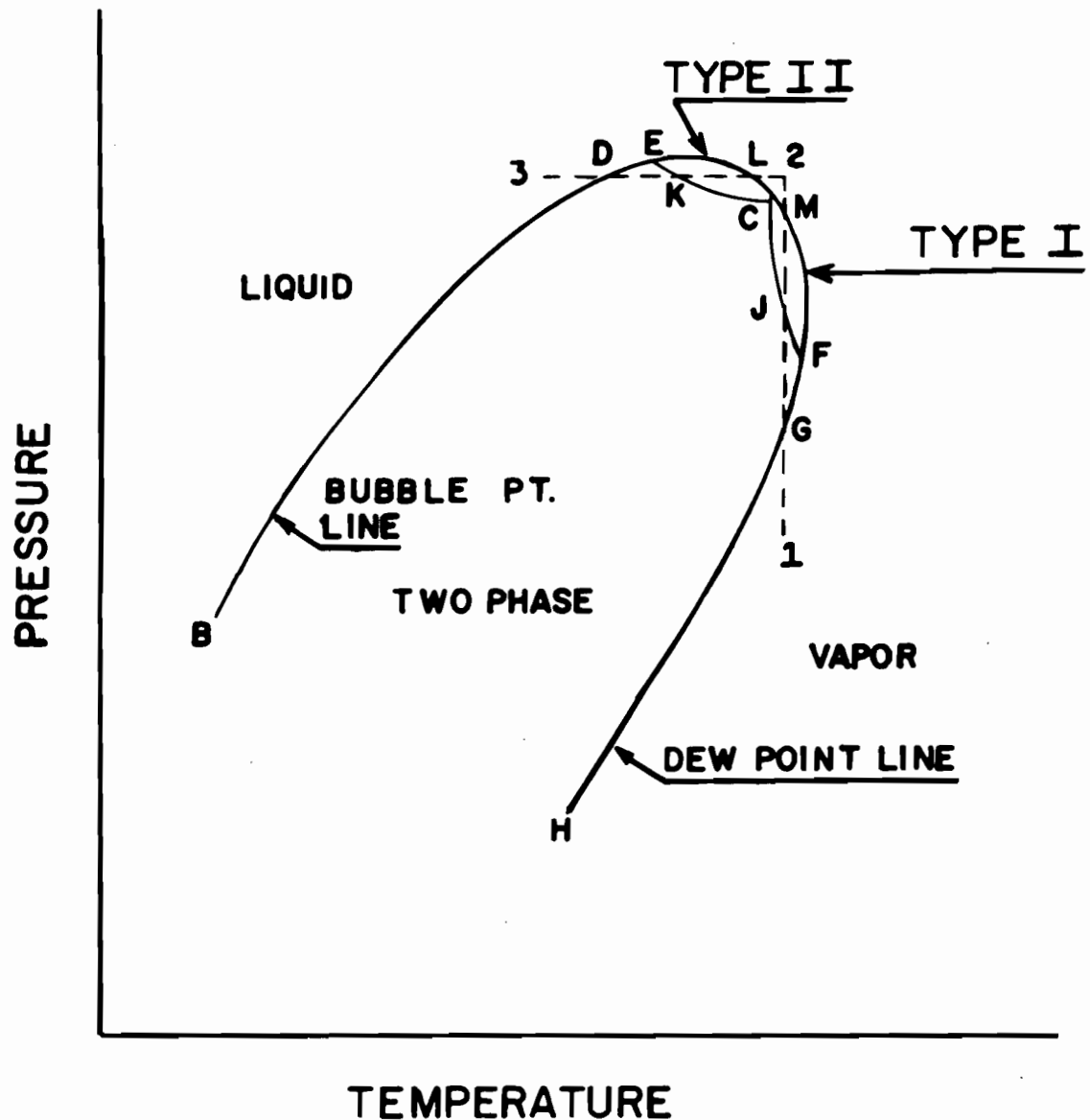


FIGURE I-TYPICAL P-T DIAGRAM

APPARATUS

General Description of P-V-T Experimental Apparatus

The experimental apparatus for the determination of the P-V-T relations was the same as that used in earlier studies. (10) A schematic diagram of the equipment is shown in Figure 2.

A small sample was contained in the glass tube (D) over the piston of mercury (C). The upper capillary portion of the tube had been calibrated so that its volume was known accurately as a function of the length. A small steel ball (B) was also contained in the experimental tube above the mercury. The movement of the ball by means of a strong magnet held outside the vapor jacket (E) agitated the sample, and brought it to equilibrium quickly. The experimental tube was held in the one leg of the compressor block (W) by means of a Bridgman type seal and was surrounded by a vacuum vapor jacket (E) as shown in Figure 2. The jacket had a side arm flask (F) which contained a pure boiling liquid; heat was supplied to this liquid by a rheostat-controlled electric heater (G). The temperature was controlled by varying the pressure in the vapor jacket; this was done either by removing air

from the system by means of the vacuum pump (Q) or by adding air by opening valves (NN). Three five-gallon bottles (R) were attached to the temperature-controlling system to increase its volume and make it more insensitive to small additions or extractions of gas. Small volumes of gas could be added or extracted through the use of the small surge vessels (N) and (P), making possible precise temperature control. The pressure in the vapor jacket was measured by the mercury manometer(M).

The water condenser (K) was used to insure that the boiling liquid vapors were condensed inside the jacket and did not reach the vacuum pump (Q). Actually, the use of this water condenser was a secondary safety measure because the vapors were condensed by blowing air across the top of the vacuum vapor jacket.

To prevent the contamination of the boiling liquid by contacting the rubber stopper (J), a mercury seal (H) was maintained in the bottom of the jacket as shown. The temperature was measured by means of the copper-constantan thermocouple (V) in conjunction with a sensitive Leeds-Northrup potentiometer (S). This arrangement allowed measurement of temperature within $\pm .05$ centigrade degree. The cold junction (T) was packed in an ice-filled dewar flask (U). Calibration of this thermocouple is described in the Appendix.

The sample was compressed by applying high pressure nitrogen gas from tank (GG) by way of the manifold (X) to the mercury in the compressor block (W). The pressure was regulated by either adding a small volume of high pressure gas to the system through (DD) or releasing a volume of gas (BB) from the system. Surge tank (FF) increased the volume of the system and acted as a stabilizer to prevent rapid changes of pressure.

A variable-zero Heise gage (Y) with a range of 0 to 2000 psig indicated the pressure on the sample. This gage was checked each operating day at a reference pressure of thirty psig by use of the open air manometer (CC); its movable dial allowed adjustment to exactly 30 psig. The accuracy of the pressure measurements were within ± 0.5 psig. The calibration of the Bourdon gage is described in the Appendix.

Because of their unique features and relative importance in the experimental systems a minute description of the compressor block (W) and the experimental tube (D) is given in the Appendix.

FIGURE 2-DIAGRAM OF P-V-T APPARATUS

EXPERIMENTAL PROCEDURE

A. General Procedure

Experimental data was taken on six mixtures of propane and n-butane. P-V-T border curves were determined for these mixtures by observing bubble, dew, and critical points. The vapor pressure curve for pure n-butane was determined experimentally; the data for pure propane was obtained through personal communication with Sun W. Chun, a candidate for a Ph.D. degree in chemical engineering at the Ohio State University.

After the experimental tube had been loaded with a mixture and secured in the compressor block, as explained previously, an organic liquid of suitable boiling range was put into the side-arm boiling flask, and the apparatus was assembled as shown in Figure 2.

Each operating day the Heise gage was checked and calibrated by the following method. The pressure was raised on the sample to liquefy it; then the valve between the compressor block and the manifold was closed to maintain the pressure on the sample. With the sample isolated from the manifold, the pressure in the manifold was reduced to 30 psig as measured by the open-end manometer (CC) and the pointer of the Heise gage (Y) was set exactly

on the 30 psig mark. After calibration, the pressure was raised in the manifold, and the valve between the compressor block and manifold was opened.

The temperature of the vapors surrounding the experimental tube was controlled by adjusting the pressure in the vapor jacket, as was previously described. Heat was supplied to the boiling liquid by a rheostat-controlled electric heater which was adjusted so that the line of condensation of the vapor was located at the top of the vacuum jacket. To make sure that it did not rise above this point, a stream of cool air was directed against the tube.

During the initial heating period, the pressure in the system was maintained at a value above the vapor pressure of the sample in order to prevent overexpansion and possible loss of the sample. When the desired steady-state temperature had been obtained, the pressure was lowered to obtain either dew points or bubble points as desired.

In the critical region of the border curve of a mixture, it was often found advantageous to alter the above procedure. Sometimes in this region it was best to hold pressure constant and vary the temperature; this was true especially when searching for the cricondentherm

point of a border curve. Also, in the search for the critical point of a mixture, it was necessary to change both the temperature and pressure since the critical point is a unique point on the border curve.

After the desired experimental point had been reached and steady state assured, the following observations were made: Pressure was read directly from the Heise gage; temperature was indicated by a reading of the potentiometer; volume was indicated by the length of tube containing the sample, as measured by the cathetometer; and the barometric pressure was obtained from a reading of the standard barometer located in the laboratory.

B. Bubble Point Observations

The bubble point was determined in the following manner: First, a desired steady-state temperature was obtained. The pressure was then raised on the sample until it was completely liquefied. The pressure was incrementally decreased until an infinitesimal bubble formed and remained at the top of the tube. After each incremental pressure change the sample was stirred vigorously by moving the steel ball up and down by means of the magnet; this insured rapid equilibrium at the new conditions and reliable and reproducible values. The pressure was increased by very small increments until

the bubble disappeared. The pressure indicated by the Heise gage was taken as the bubble point.

C. Dew Point Observations

In the determination of the dew point at a fixed temperature the sample was expanded by reducing the pressure until total vaporization occurred; then the pressure was increased incrementally until the first trace of liquid appeared. Usually this first trace of liquid appeared as a small black spot between the steel ball and tube wall. However, in the critical region, the first appearance of liquid was sometimes observed as infinitesimal droplets throughout the sample and sometimes as liquid flowing down the side of the tube. After each pressure increase, the sample was stirred as explained previously.

D. Critical Point Observation

In the determination of the critical point both the pressure and temperature were varied alternately by small increments. The approach to the critical point was indicated by the appearance of a temporary light brown color of the sample (to transmitted light) when slight pressure changes were made. The temperature and pressure were then adjusted so that the meniscus appeared in the center of the sample, i.e., half the sample was liquid

and half was vapor. Small increases in temperature and pressure were made in such a manner as to maintain the meniscus in the midpoint position until it completely disappeared and one homogeneous phase was present. The critical point was characterized by a brown color when light was transmitted through the sample and a milky-white opaque appearance when light was reflected. Again, the sample was always stirred vigorously each time the temperature or pressure was changed in order to insure equilibrium.

PREPARATION OF GAS SAMPLES

A. Purity of Propane and n-Butane

The n-butane and propane were supplied for this investigation by the Phillips Petroleum Company and were stated to be of 99.80 per cent purity and were used without further purification. Samples of each gas were frozen under high vacuum and noncondensable gas was pumped off and measured amounts of the deaerated gas transferred to glass ampoules and sealed.

The physical properties of n-butane were determined by this author and are listed in the Appendix. Physical properties of propane used in this study were taken from reliable sources in the literature; these values are also presented in the Appendix.

B. Gas Loading Procedure Using Gas Microburette

The steps in the loading of the gas sample were as follows:

If a new sample was being loaded,

1. The metal plug (R) was removed from the back leg of the compressor block (Figure I-1).
2. The mercury level was raised in the back leg and the solid metal plug was screwed into the back leg.

3. The mercury pot was screwed onto the front leg and was filled with mercury (Figure II-2).
4. The mercury-filled experimental tube was inverted in the mercury pot.
5. A clean gas-collecting bulb was inverted in the mercury pot and filled with mercury by applying a vacuum to the bulb.
6. The gas-collecting bulb was filled with pure gas by displacement of mercury.
7. The gas microburette was purged three times with the pure gas.
8. The desired amount of pure gas was drawn into the graduated section of the gas microburette, and this sample was expelled into the experimental tube. (Several increments were sometimes necessary to complete the final sample.)
9. The microburette and gas-collecting bulb were removed.
10. The experimental tube was inserted into the front leg, and the mercury was removed from the mercury pot.
11. The mercury pot was removed from the front leg, and the experimental tube is secured in the leg.
12. The plug was removed from the back leg, and the pressure line was attached.
13. The vapor jacket was put in place around the experimental tube, and the apparatus was then ready for operation.

If pure gas was being added to an old sample, the above procedure was varied. In this case, the experimental tube was already in the compressor block. First, the old sample was liquefied by raising the pressure; then a dry ice bath was placed around the old sample. Next, the

metal plug was removed from the back leg, and the mercury level in it was raised. A solid metal plug was then screwed into the back leg. The screw collar and metal sleeve were removed from the front leg, and the mercury pot was attached to the front leg. After this, the same procedure as described above was used, starting with step 5.

When a new mixture was desired, the above procedure was repeated, and a new increment of gas was added to the old mixture. When the sample became too large for the sample tube, a smaller sample was loaded. Further details are given in the Appendix.

EXPERIMENTAL RESULTS

P-V-T-X data for the propane-n-butane system are presented in Appendix V; several graphs are derived from these data. Figure 3 shows plots of P-T curves, and Figure 4 represents temperature-density relations. Large scale plots of Figures 3 and 4 were used to obtain the summary of data presented in Table 1.

The data for critical cricondenbar and cricondentherm points are presented in Table 4; Figures 5 through 9 represent these data graphically as related to composition. These plots are used to define the limiting points on the T-X plots given in Figure 10. Figure 10 shows the relations between temperature and composition of the coexisting liquid and vapor phase at constant pressure; these relationships are also summarized in Table 2. Equilibrium K ratios were calculated from data obtained from Figure 10. Plots of $\ln(K)$ versus pressure (K at constant temperature) are presented in Figure 11; a summary of the K values is presented in Table 3.

Figures 12 through 14 represent plots suggested by Etter and Kay (5). They are plots of critical, cricondenbar, and cricondentherm pressure versus average molecular

weight. Also, critical locus curves for several binary n-paraffin hydrocarbon systems with propane as the common component are shown in P-T plots in Figure 15. The last figure (Figure 16) is a plot of critical temperature versus mole per cent propane for the several n-paraffin systems.

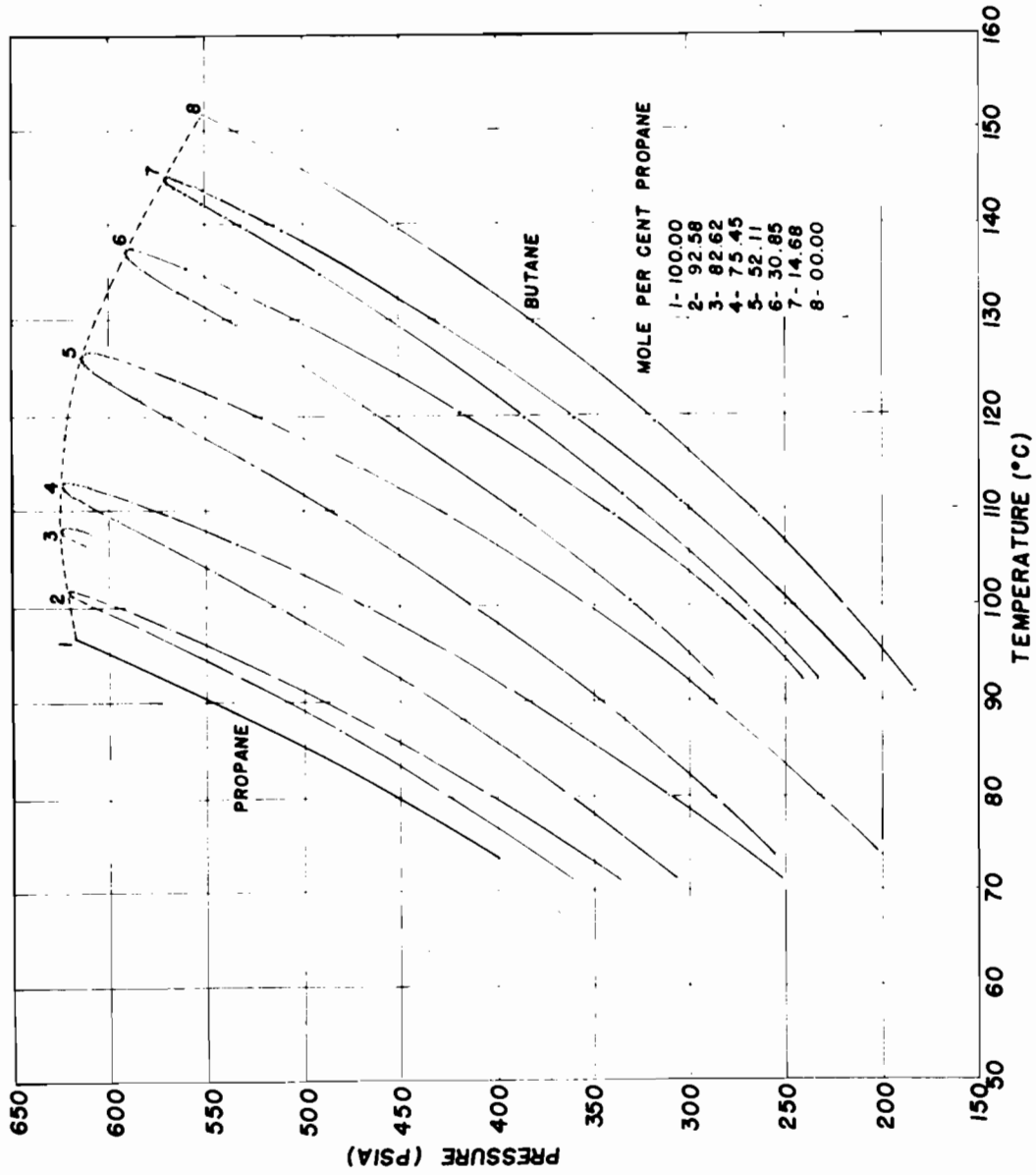


FIGURE 3--PRESSURE-TEMPERATURE DIAGRAM FOR THE
PROPANE-N-BUTANE SYSTEM

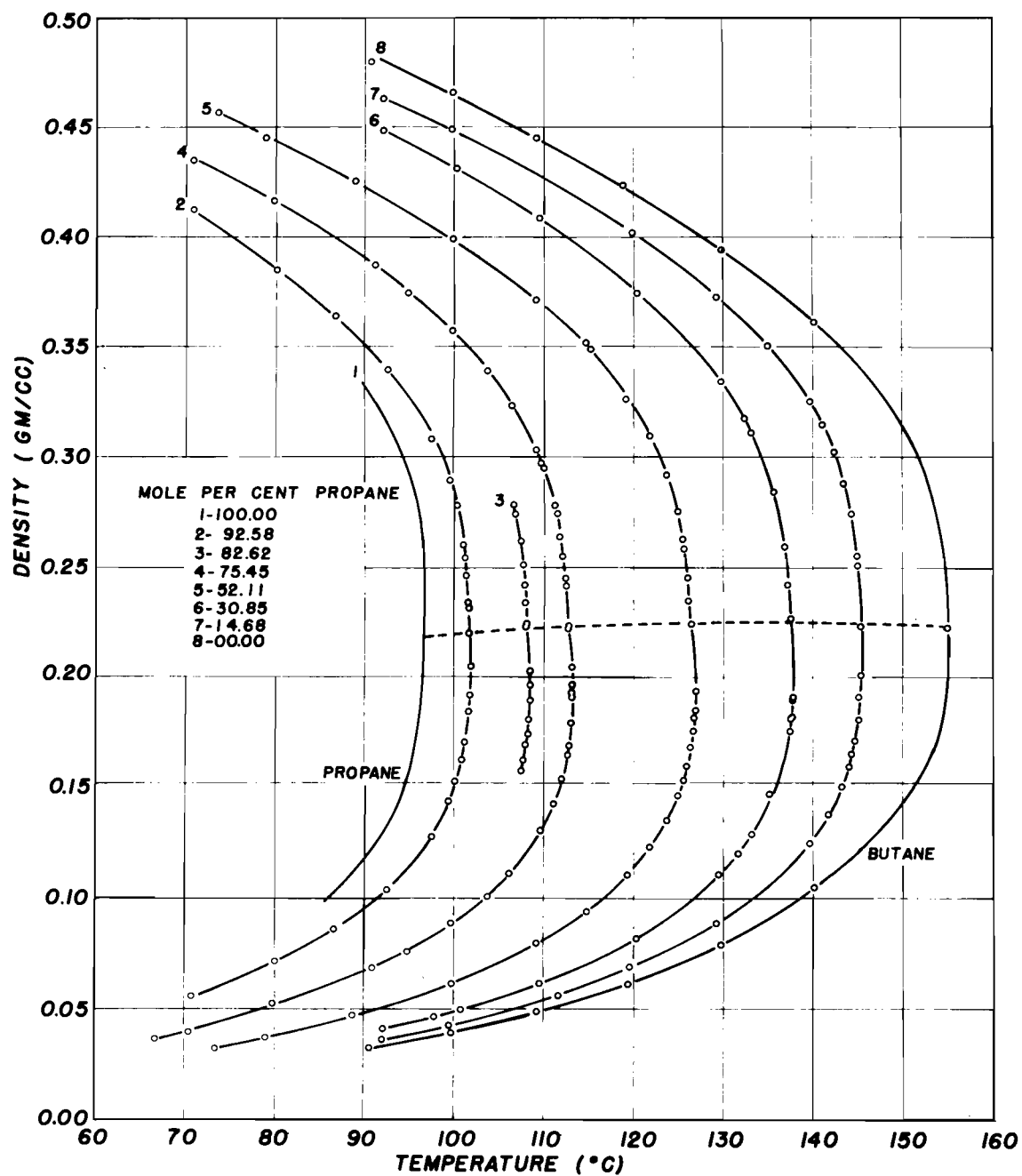


FIGURE 4-TEMPERATURE-DENSITY DIAGRAM FOR THE PROPANE-N-BUTANE SYSTEM

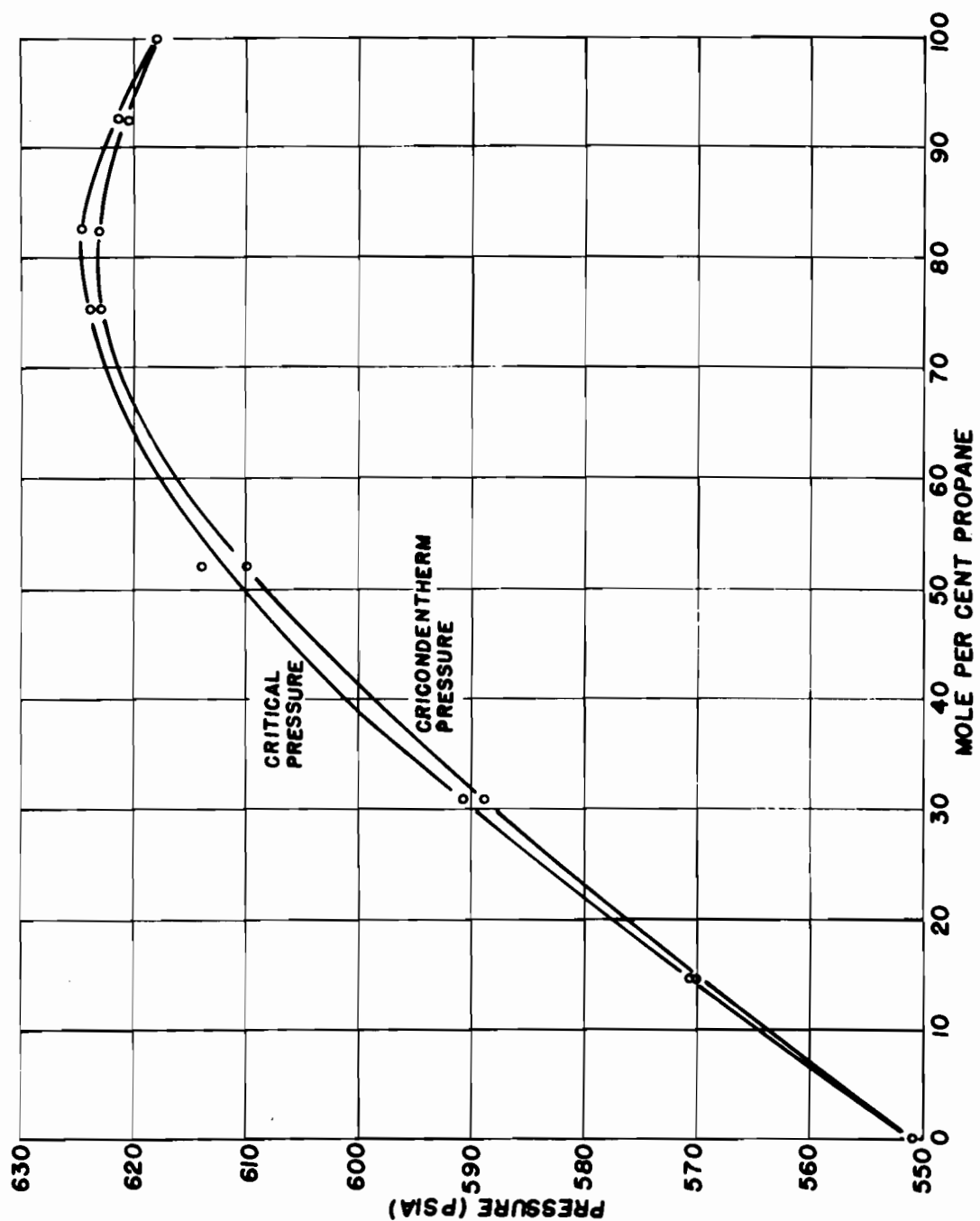


FIGURE 5-PRESSURE - COMPOSITION RELATIONSHIPS

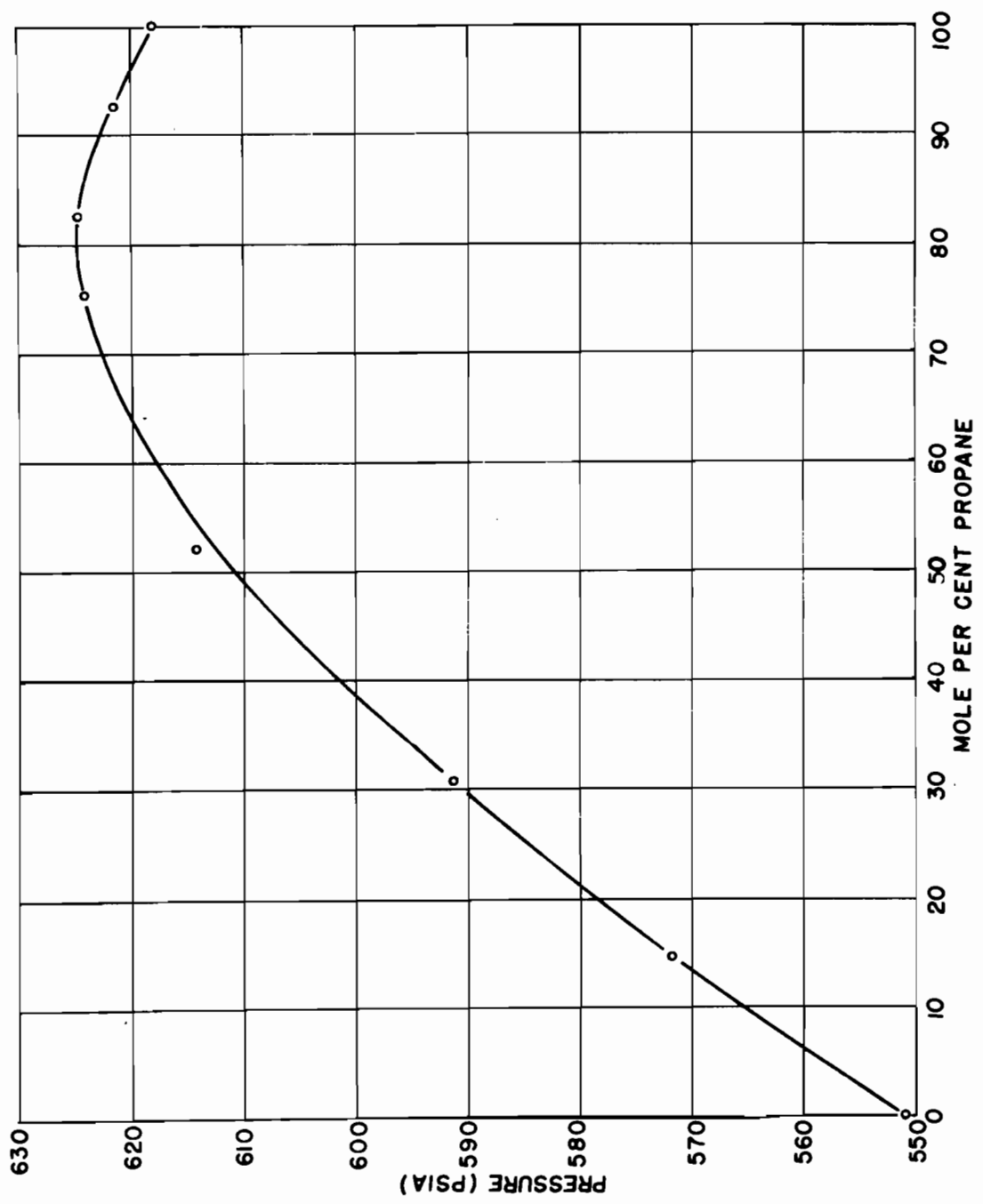


FIGURE 6-CRICONDENBAR PRESSURE-COMPOSITION RELATIONSHIP

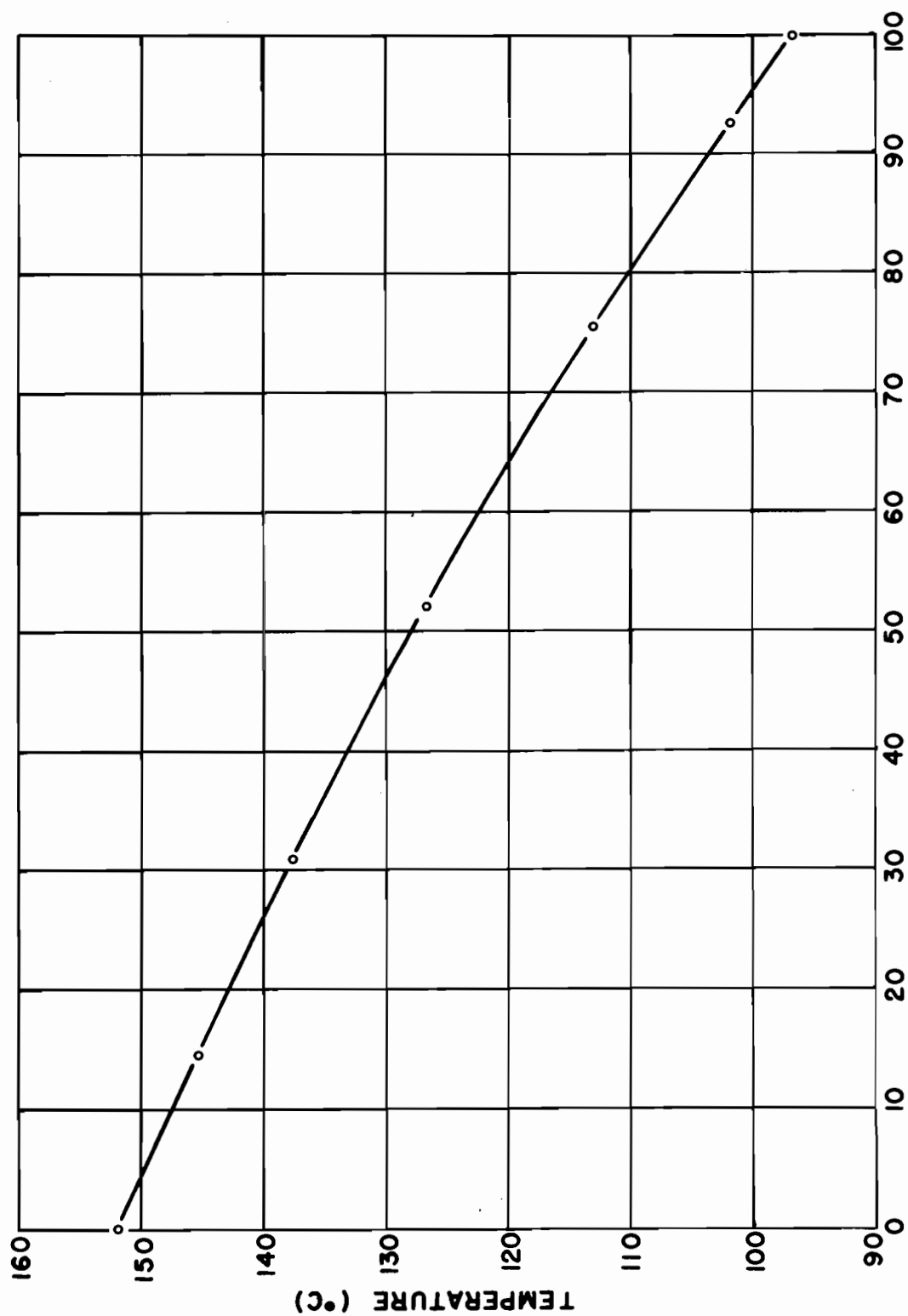


FIGURE 7-CRITICAL TEMPERATURE-COMPOSITION RELATIONSHIP

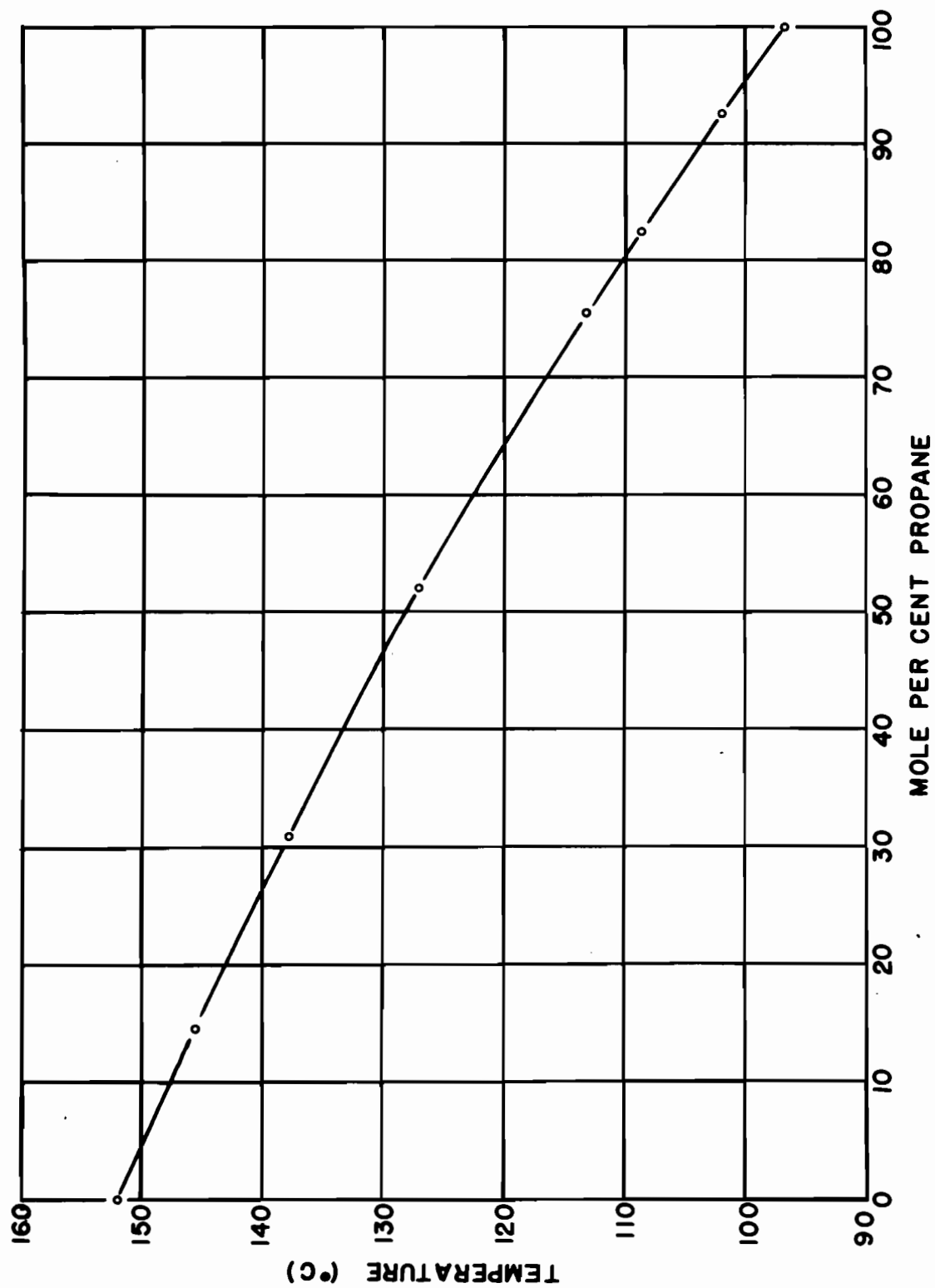


FIGURE 8-CRICONDENTHERM TEMPERATURE-COMPOSITION RELATIONSHIP

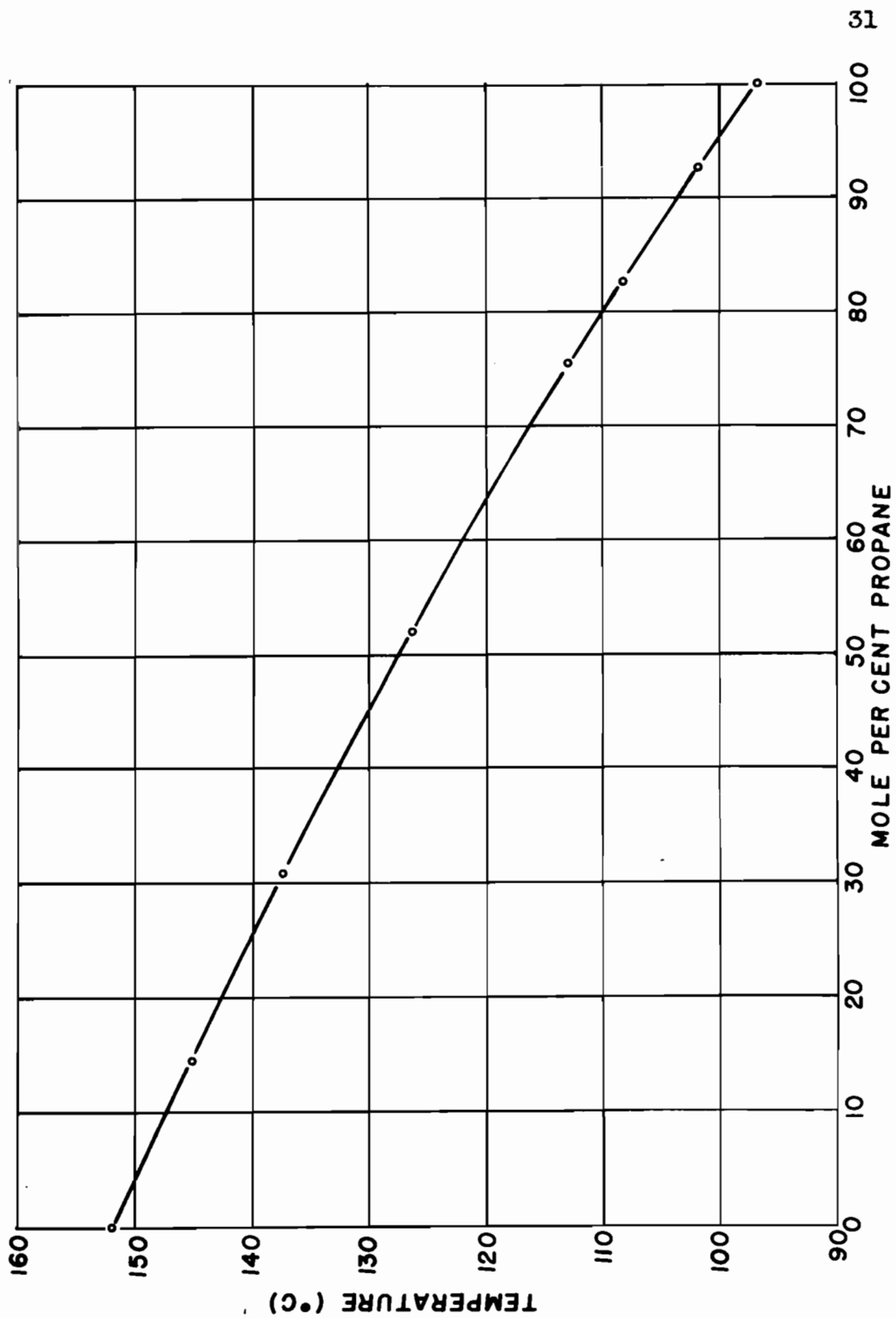


FIGURE 9 -CRICONDENBAR TEMPERATURE-COMPOSITION RELATIONSHIP

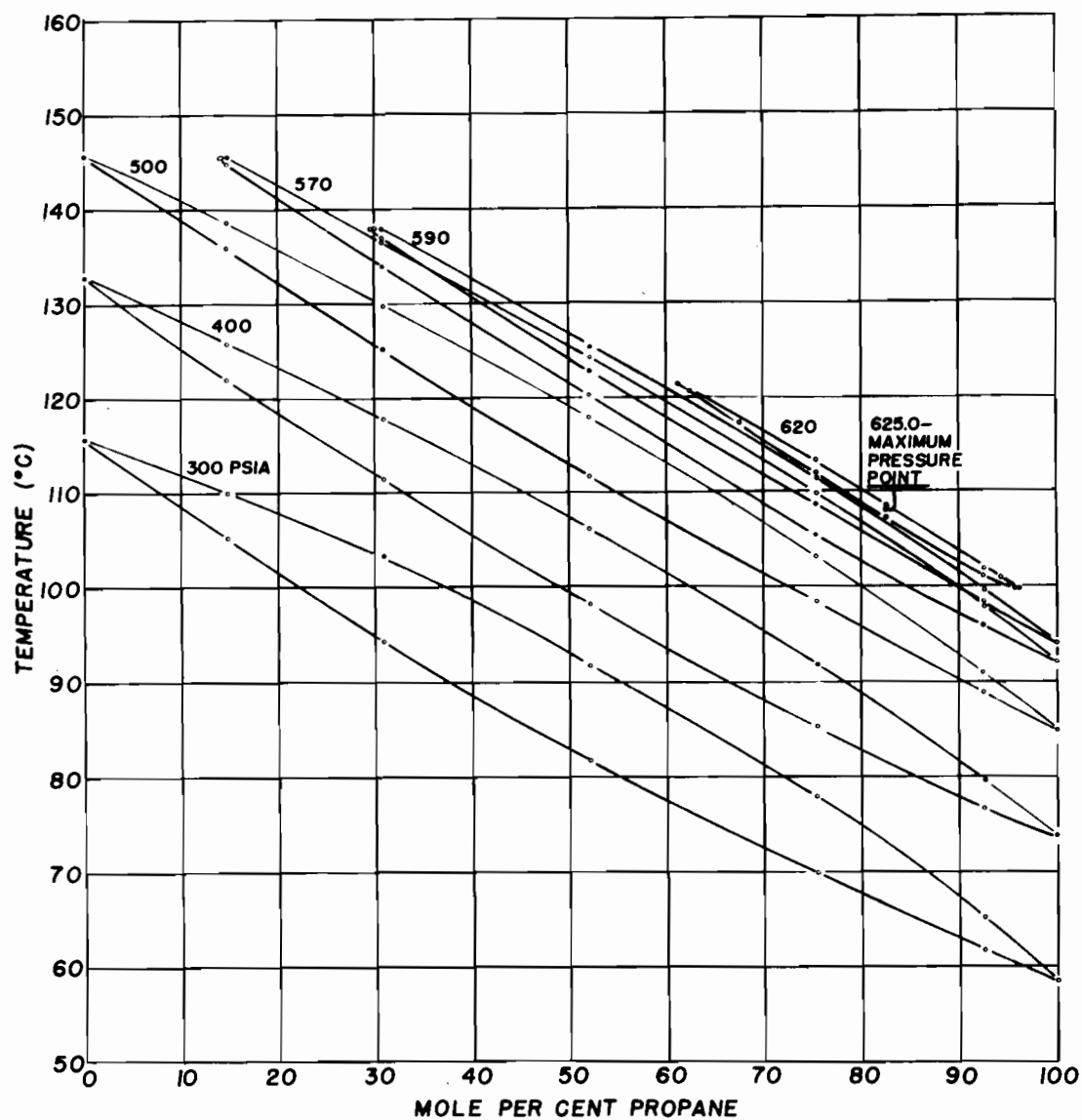


FIGURE 10-TEMPERATURE-COMPOSITION DIAGRAM FOR THE PROPANE-N-BUTANE SYSTEM

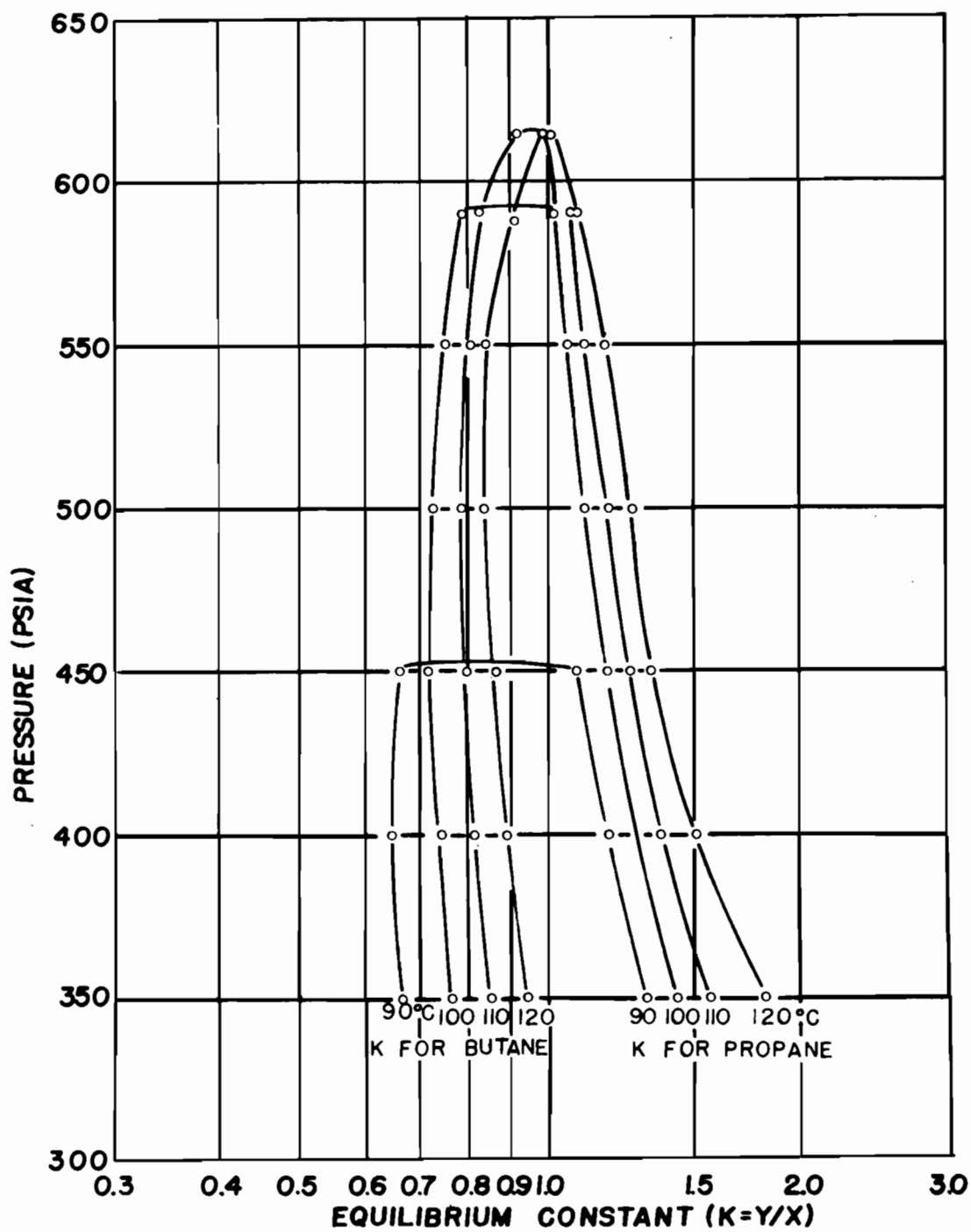


FIGURE 11-PRESSURE-EQUILIBRIUM RATIO
RELATIONSHIP

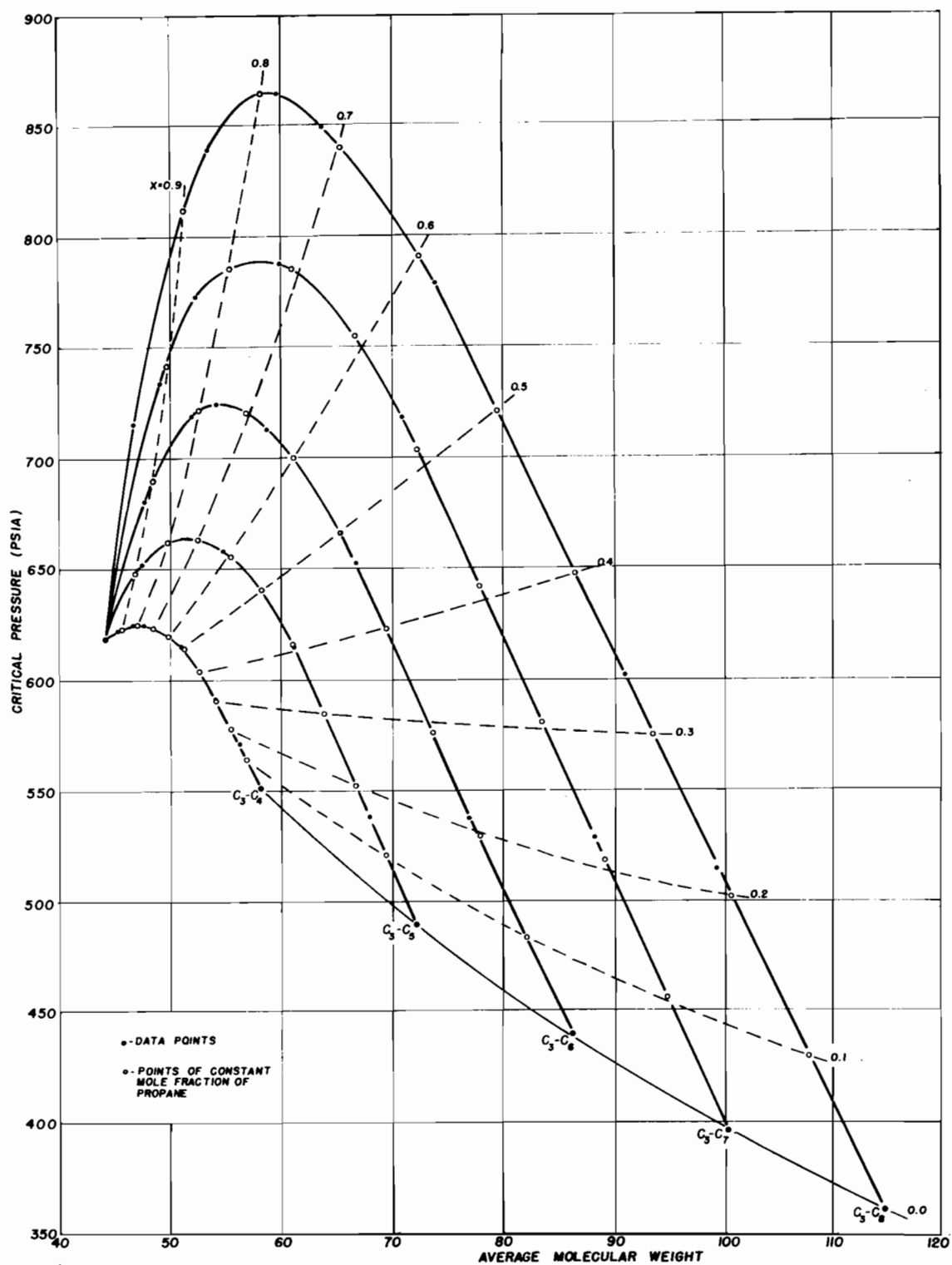


FIGURE 12-CRITICAL PRESSURE-AVERAGE MOLECULAR WEIGHT RELATIONSHIP

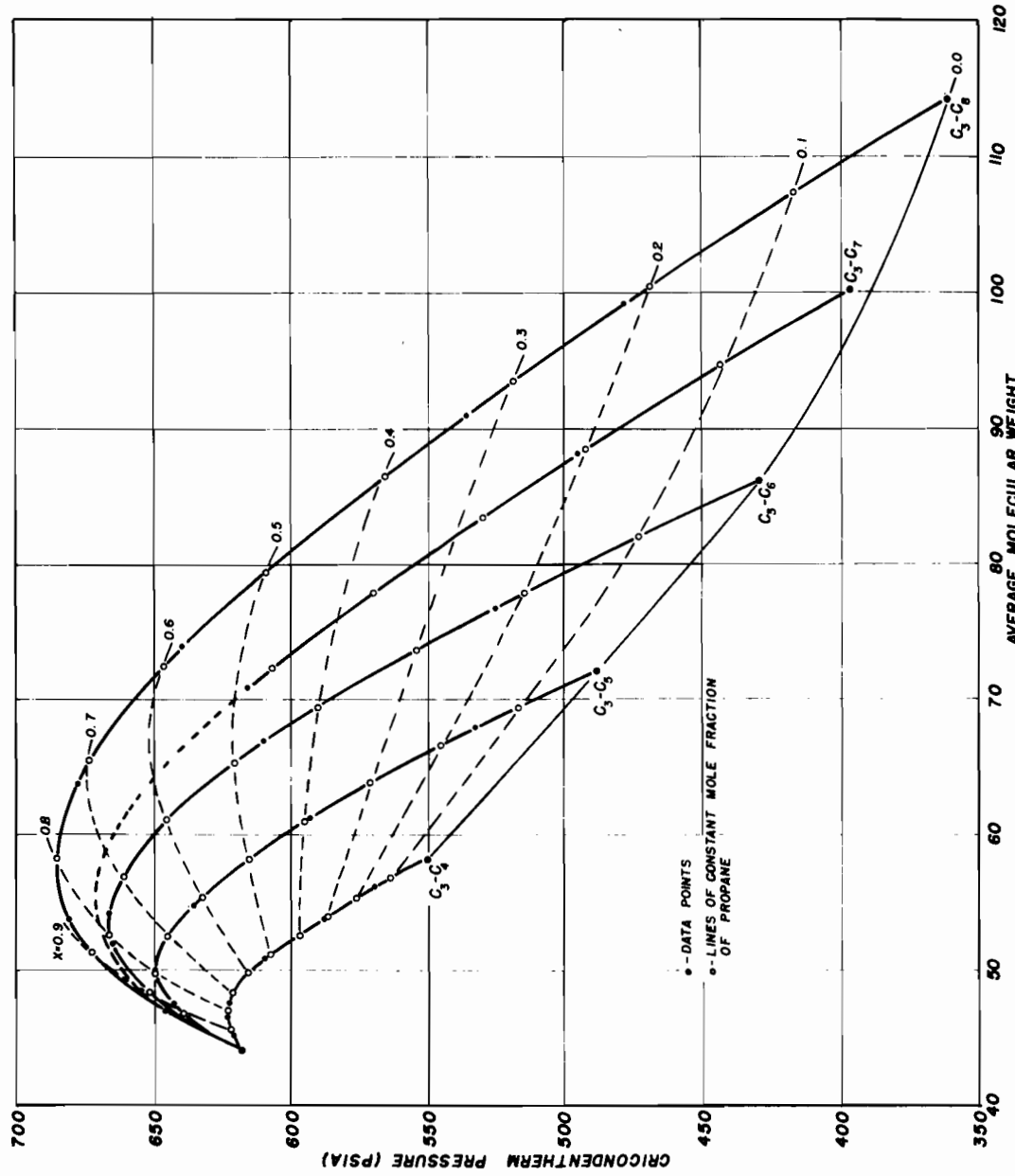


FIGURE 13-CRICONDETHERM PRESSURE-AVERAGE MOLECULAR WEIGHT RELATIONSHIP

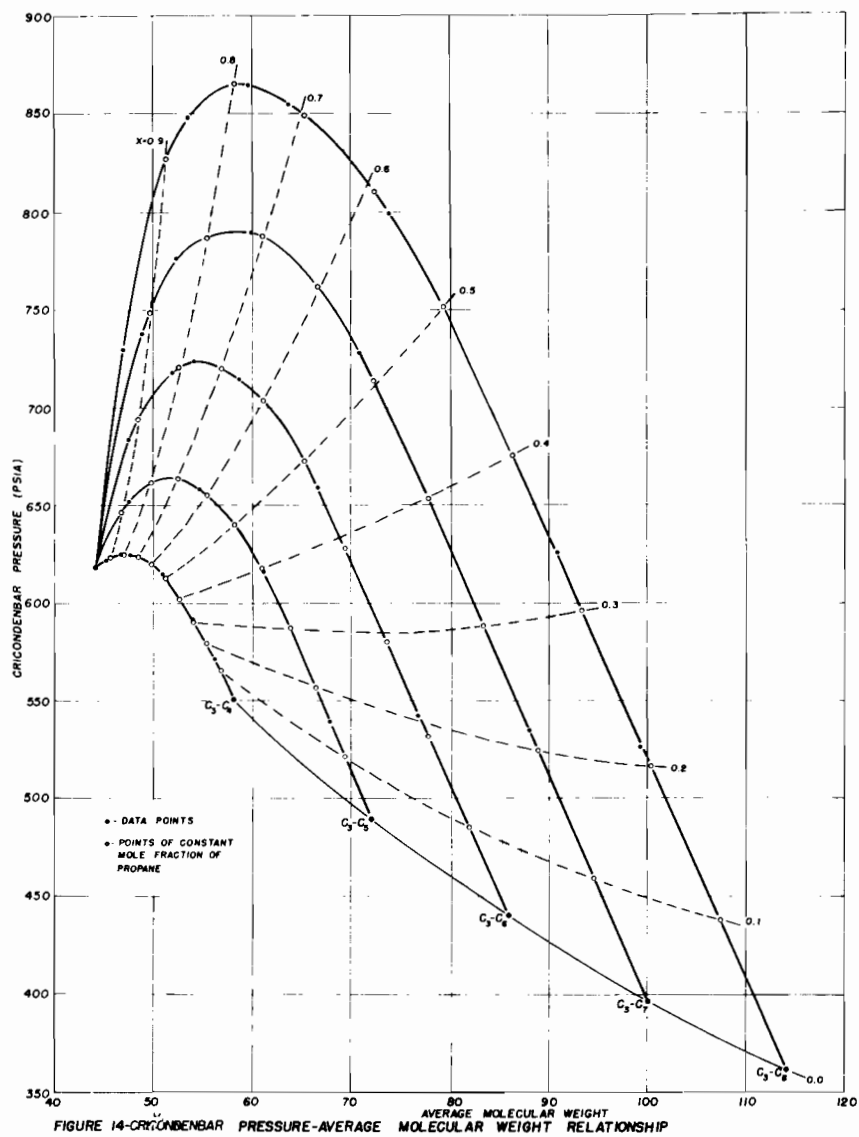


FIGURE 14-CRICODENBAR PRESSURE-AVERAGE MOLECULAR WEIGHT RELATIONSHIP

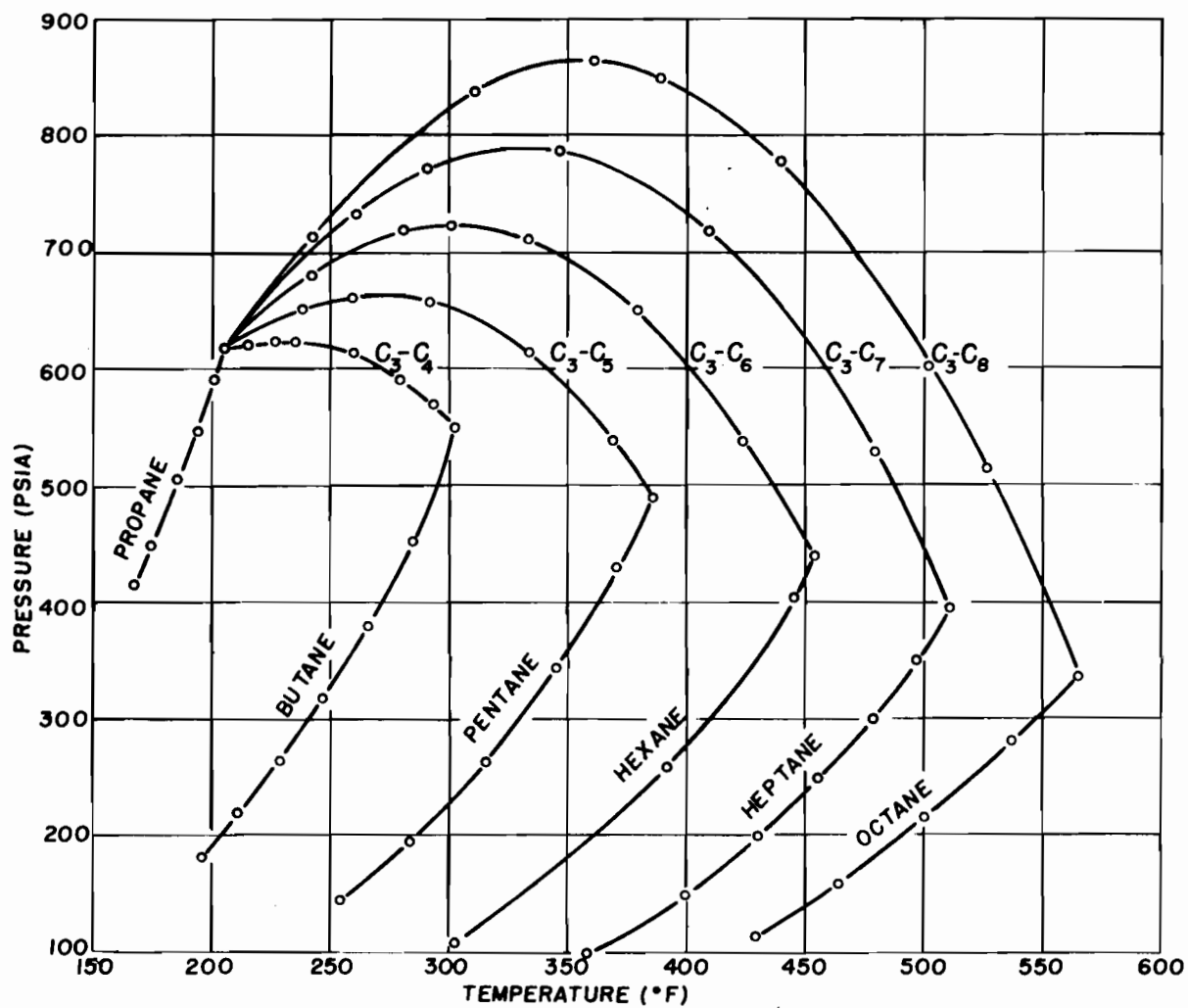


FIGURE 15-CRITICAL PRESSURE-TEMPERATURE RELATIONSHIP OF PROPANE BINARIES

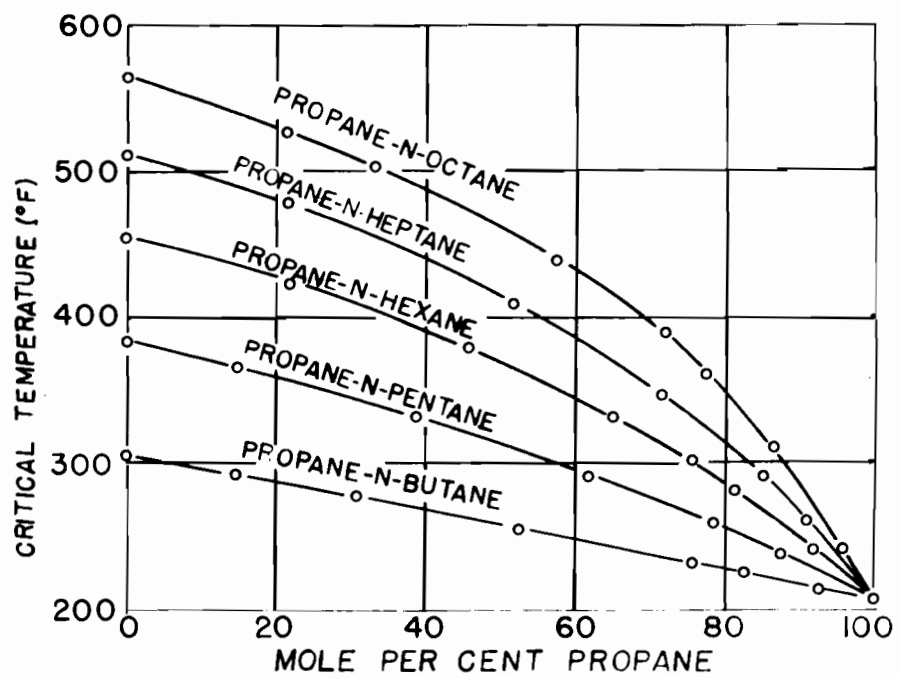


FIGURE 16-RELATIONSHIP BETWEEN CRITICAL TEMPERATURE AND COMPOSITION OF PROPANE BINARIES

SUMMARY OF TEMPERATURE, PRESSURE, AND DENSITY DATA
AT PHASE BOUNDARIES OF PROPANE-N-BUTANE SYSTEM

TABLE 1-A

Mole Per cent 14.68% Propane

Pressure (psia)	LIQUID		VAPOR	
	Temperature (°C)	Density (gm/cc)	Temperature (°C)	Density (gm/cc)
225.0	89.9	-----	95.8	.0382
250.0	95.6	.4556	101.1	.0436
300.0	105.3	.4372	110.0	.0539
350.0	114.1	.4170	118.3	.0660
400.0	122.1	.3950	125.8	.0796
450.0	129.5	.3719	132.5	.0968
500.0	136.0	.3450	138.6	.1191
525.0	139.2	.3279	141.4	.1337
540.0	141.1	.3140	143.9	.1554
550.0	142.4	.3029	144.7	.1687
560.0	143.6	.2890	145.2	.1804
565.0	144.2	.2783	145.4	.1866
567.5	144.5	.2720	145.6	-----
570.0	144.9	.2620	-----	-----

TABLE 1-B

Mole Per cent 30.85% Propane

Pressure (psia)	LIQUID		VAPOR	
	Temperature (°C)	Density (gm/cc)	Temperature (°C)	Density (gm/cc)
250.0	84.9*	-----	94.1	.0421
300.0	94.8	.4418	103.4	.0522
350.0	103.5	.4227	111.0	.0631
400.0	111.5	.4029	117.9	.0758
450.0	118.7	.3800	124.2	.0914
500.0	125.3	.3559	129.9	.1086
525.0	128.6	.3407	132.5	.1234
550.0	131.6	.3238	134.8	.1385
560.0	132.8	.3148	135.7	.1460
570.0	134.0	.3044	136.6	.1562
580.0	135.2	.2917	137.5	.1508
585.0	135.9	.2820	137.8	-----
590.0	136.8	.2646	137.9	-----

*Read from a plot of $\ln(P)$ versus $1/T$.

TABLE 1-C

Mole Per cent = 52.11% Propane

Pressure (psia)	LIQUID		VAPOR	
	Temperature (°C)	Density (gm/cc)	Temperature (°C)	Density (gm/cc)
250.0	72.1*	-----	82.8	.0402
300.0	81.8	.4397	91.7	.0499
350.0	90.4	.4213	99.4	.0603
400.0	98.1	.4030	106.2	.0524
450.0	105.1	.3844	112.3	.0863
500.0	111.7	.3664	117.8	.1034
525.0	114.9	.3504	120.3	.1142
550.0	117.9	.3361	122.7	.1266
570.0	120.3	.3221	124.4	.1380
590.0	122.7	.3034	126.0	.1562
600.0	124.0	.2899	126.6	.1670
605.0	124.6	.2820	126.9	.1786
610.0	125.3	.2705	127.1	-----
615.0	125.7	.2624	127.0	-----

*Read from a plot of $\ln(P)$ versus $1/T$.

TABLE 1-D

Mole Per cent = 75.45% Propane

Pressure (psia)	LIQUID		VAPOR	
	Temperature (°C)	Density (gm/cc)	Temperature (°C)	Density (gm/cc)
300.0	69.9*	-----	78.2	.0484
350.0	77.9	.4198	85.3	.0580
400.0	85.5	.4021	91.9	.0697
450.0	92.3	.3834	97.9	.0830
500.0	98.4	.3630	103.1	.0985
525.0	101.4	.3503	105.6	.1079
550.0	104.2	.3362	108.0	.1191
570.0	106.4	.3236	109.8	.1301
590.0	108.6	.3077	111.4	.1447
600.0	109.7	.2969	112.1	.1535
610.0	110.8	.2832	112.8	.1654
615.0	111.3	.2766	113.1	.1526
620.0	112.0	.2628	113.3	-----
622.5	112.4	.2516	113.4	-----

*Read from a plot of $\ln(P)$ versus $1/T$.

TABLE 1-E

Mole Per cent 92.58% Propane

Pressure (psia)	LIQUID		VAPOR	
	Temperature (°C)	Density (gm/cc)	Temperature (°C)	Density (gm/cc)
350.0	69.3*	-----	72.9	.0574
400.0	76.6	.3946	79.6	.0694
450.0	83.1	.3758	85.5	.0823
500.0	88.8	.3562	91.0	.0983
525.0	91.6	.3433	93.5	.1073
550.0	94.3	.3303	96.0	.1187
570.0	96.4	.3169	97.8	.1290
590.0	98.4	.3011	99.6	.1434
600.0	99.4	.2910	100.4	.1518
610.0	100.4	.2780	101.2	.1646
615.0	100.9	.2688	101.6	.1740
620.0	101.1	.2640	101.7	.1800

*Read from a plot of $\ln(P)$ versus $1/T$.

TEMPERATURE-COMPOSITION RELATIONS OF PROPANE-N-BUTANE
SYSTEM AT CONSTANT PRESSURE

TABLE 2-A

Pressure = 300 psia

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.000	116.2	116.2
0.100	108.6	112.0
0.200	101.6	108.1
0.300	94.9	103.7
0.400	88.8	98.6
0.500	83.1	93.1
0.600	77.8	87.3
0.700	72.7	81.2
0.800	67.7	75.3
0.900	62.9	67.3
1.000	58.5	58.5

TABLE 2-B

Pressure = 400 psia

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.000	132.8	132.8
0.100	125.8	128.3
0.200	118.6	123.4
0.300	112.1	118.2
0.400	105.7	113.1
0.500	99.6	107.4
0.600	93.6	101.3
0.700	88.2	95.2
0.800	82.9	88.8
0.900	77.9	81.6
1.000	73.8	73.8

TABLE 2-C

Pressure = 500 psia

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.000	145.7	145.7
0.100	139.0	141.1
0.200	132.3	135.8
0.300	125.7	130.4
0.400	119.1	124.8
0.500	112.9	119.2
0.600	107.2	113.1
0.700	101.5	106.7
0.800	95.8	100.1
0.900	90.2	92.7
1.000	84.8	84.8

TABLE 2-D

Pressure = 570 psia

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.140	145.5	145.5
0.200	141.2	142.6
0.300	134.4	136.9
0.400	128.0	131.3
0.500	121.7	125.6
0.600	115.3	119.7
0.700	108.8	113.4
0.800	102.6	106.8
0.900	97.2	99.8
1.000	92.1	92.1

TABLE 2-E

Pressure = 590 psia

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.296	137.9	137.9
0.400	130.6	132.7
0.500	124.2	126.7
0.600	118.1	120.8
0.700	111.8	114.8
0.800	105.8	108.6
0.900	99.8	101.5
1.000	94.1	94.1

TABLE 2-F

Pressure = 620 psia

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.612	121.4	121.4
0.700	115.6	116.6
0.800	109.1	110.2
0.900	102.6	103.6
0.962	99.7	99.7

TABLE 2-G

Pressure = 625.0*

Mole Per cent Propane	Liquid (°C)	Vapor (°C)
0.826	108.1	108.1

*Maximum pressure at which liquid and vapor properties are not identical.

TABLE 3
EQUILIBRIUM RATIOS FOR PROPANE AND N-BUTANE

Temperature (°C)	Pressure (psia)	K_{c_3}	K_{c_4}
90	350	1.30	0.66
	400	1.18	0.65
	450	1.09	0.66
	500	-----	-----
100	350	1.42	0.76
	400	1.28	0.75
	450	1.18	0.71
	500	1.10	0.73
	550	1.05	0.75
	590	1.03	0.78
	620	-----	-----
110	300	1.90	0.92
	350	1.58	0.85
	400	1.37	0.82
	450	1.26	0.79
	500	1.18	0.78
	550	1.10	0.81
	590	1.06	0.83
	620	1.02	0.92
120	350	1.83	0.94
	400	1.51	0.89
	450	1.33	0.87
	500	1.26	0.84
	550	1.17	0.84
	590	1.09	0.91
	620	1.01	0.98

TABLE 4

PROPANE-N-BUTANE

Mole Per cent Propane	Average Molecular Weight	T _c	Critical Point P _c	ρ _c	T	Maximum Pressure P _{max}	ρ	Maximum Temperature T _{max}	ρ	
		(°C)	(psia)	(gm/cc)	(°C)	(psia)	(gm/cc)	(°C)	(psia)	(gm/cc)
0.00	58.1	152.09	550.8	0.2217	----	----	----	----	----	----
14.68	56.2	145.40	570.8	0.2243	145.16	571.8	0.2509	145.52	570.0	0.2005
30.85	53.9	137.70	590.9	0.2260	137.45	591.9	0.2414	137.92	587.7	0.1900
52.11	50.9	126.65	614.1	0.2238	126.43	614.8	0.2347	127.09	609.8	0.1841
75.45	47.6	112.97	624.0	0.2223	112.97	624.0	0.2217	113.38	622.8	0.1924
92.58	45.2	101.76	621.5	0.2195	101.76	621.5	0.2195	101.92	620.4	0.2044
82.62*	46.6	108.29	624.7	0.2212	108.12	625.0	0.2334	108.62	623.6	0.1960
100.00	44.1	96.57	618.0	0.2262	----	----	----	----	----	----
		Mole Fraction Propane				Average Molecular Weight				
		.0				58.1				
		.1				56.8				
		.2				55.4				
		.3				54.0				
		.4				52.6				
		.5				51.2				
		.6				49.8				
		.7				48.4				
		.8				47.0				
		.9				45.6				
		1.0				44.1				

*Obtained through personal communication with S. W. Chun, candidate for Doctor's Degree at the Ohio State University

TABLE 5-A

SYSTEM: PROPANE-N-PENTANE (17)

Mole Per cent Propane	Average Molecular Weight	Critical Point		Maximum Pressure		Maximum Temperature	
		T _c	P _c	T	P _{max}	T _{max}	P
		(°F)	(psia)	(°F)	(psia)	(°F)	(psia)
0.00	72.12	385.0	489.4	-----	-----	-----	-----
14.70	67.89	368.6	538.1	357.5	539.1	369.3	533.7
38.73	61.15	332.2	614.0	329.7	616.3	335.3	595.0
61.62	54.74	292.4	657.7	291.7	658.0	297.1	636.0
78.62	49.98	259.0	662.0	259.7	662.0	263.5	650.0
87.78	47.42	237.7	651.8	239.0	652.0	240.2	643.0

Mole Fraction Propane	Average Molecular Weight
0.0	72.1
0.1	69.4
0.2	66.6
0.3	63.8
0.4	61.0
0.5	58.2
0.6	55.4
0.7	52.5
0.8	49.2
0.9	46.8
1.0	44.1

TABLE 5-B

SYSTEM: PROPANE-N-HEXANE (18)

Mole Per cent Propane	Average Molecular Weight	Critical Point		Maximum Pressure		Maximum Temperature	
		T _c	P _c	T	P _{max}	T _{max}	P
		(°F)	(psia)	(°F)	(psia)	(°F)	(psia)
0.0	86.00	454.4	440.0	-----	-----	-----	-----
21.98	76.77	423.6	537.5	425.6	526.1	419.3	542.3
45.98	66.69	379.5	652.1	387.6	610.4	374.3	659.0
64.87	58.75	332.5	712.2	344.8	648.7	326.5	714.4
81.29	51.86	280.9	718.2	294.4	665.6	285.5	719.8
75.99	54.09	300.2	723.8	314.3	666.6	300.2	723.8
91.76	47.46	242.3	680.2	249.8	662.0	245.4	683.3

Mole Fraction Propane	Average Molecular Weight
.0	86.17
.1	82.0
.2	77.8
.3	73.6
.4	69.4
.5	65.3
.6	61.1
.7	56.9
.8	52.6
.9	48.4
1.0	44.1

TABLE 5-C

SYSTEM: PROPANE-N-HEPTANE (15)

Mole Per cent Propane	Average Molecular Weight	Critical Point		Maximum Pressure		Maximum Temperature	
		T _c	P _c	T	P _{max}	T _{max}	P
<hr/>							
		(°F)	(psia)	(°F)	(psia)	(°F)	(psia)
<hr/>							
0.00	100.20	511.7	396.8	-----	-----	-----	-----
21.39	88.02	478.5	528.7	471.2	535.0	483.8	496.0
51.87	70.95	409.5	717.8	406.4	728.0	429.8	616.0
71.54	59.93	346.9	787.4	341.6	790.0	374.0	661.0
85.06	52.37	291.4	772.6	298.4	776.0	318.0	630.0
90.90	49.10	261.6	733.5	266.0	738.0	280.4	648.0

Mole Fraction Propane	Average Molecular Weight
.0	100.20
.1	94.6
.2	89.0
.3	83.4
.4	77.8
.5	72.3
.6	66.6
.7	61.0
.8	55.4
.9	49.7
1.0	44.1

TABLE 5-D

SYSTEM: PROPANE-N-OCTANE (7)

Mole Per cent Propane	Average Molecular Weight	Critical Point		Maximum Pressure		Maximum Temperature	
		T _c	P _c	T	P _{max}	T _{max}	P
		(°F)	(psia)	(°F)	(psia)	(°F)	(psia)
0.00	114.22	564.8	361.6	-----	-----	-----	-----
21.43	99.02	526.7	514.0	517.0	525.8	523.7	479.9
33.06	90.83	503.7	601.7	487.2	626.7	512.5	536.9
57.29	73.89	438.9	778.1	419.5	798.4	464.1	641.0
71.75	63.74	388.4	849.9	375.8	854.8	463.2	678.1
77.50	59.75	360.7	864.5	358.9	864.6	-----	-----
86.40	53.52	310.5	839.2	325.1	848.0	355.7	681.3
95.89	46.87	242.3	714.9	256.7	738.4	268.9	646.2

Mole Fraction Propane	Average Molecular Weight
.0	114.22
.1	107.4
.2	100.4
.3	93.4
.4	86.4
.5	79.4
.6	72.4
.7	65.4
.8	58.3
.9	51.3
1.0	44.1

DISCUSSION OF RESULTS

Figures 3 through 11 are standard plots representing P-V-T data and are similar to those presented for other binary, n-paraffin systems. Critical pressure versus average molecular weight for a series of binary systems containing propane as a common component is plotted in Figure 12. Lines of constant mole fraction are shown; these lines are practically straight for the lower molecular weight systems but are curved upward as the molecular weight increases in the series. All of these lines terminate at the molecular weight and critical pressure of propane. The locus of critical pressures of propane and the heavier normal paraffin hydrocarbons form the constant composition curve of zero.

Plots of the cricondenbar pressure and cricondentherm pressure versus average molecular weight for the same propane binary systems yield curves that are similar to the critical pressure plot; Figures 13 and 14 are these two plots. Etter and Kay (5) suggested that the lines of constant mole fraction would converge to the critical point of propane and would be straight; this correlation was based on limited data. Further study has shown this conclusion to be invalid. When heavier normal paraffins are employed as the second component in the binary, the lines of constant mole fraction

begin to curve upward. Etter and Kays' conclusions were valid over the limited data available when the correlation was made; however, they are not true for the whole spectrum on n-paraffin systems.

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APPENDIX I

APPARATUS

A. Compressor Block

The compressor block assembly shown in Figure I-1 was used to hold the experimental tube in a perpendicular position without strain. The two "legs" of the block consisted of two steel cylinders, threaded as shown. They were connected by a stainless steel tube; this tube contained a safety check valve (U). Nitrogen pressure was applied to the mercury in "leg" (S) through the threaded seal (R); this pressure was transmitted to the "leg" (L) and thus to the experimental tube (A) via the tubing and check valve (U). The check valve prevented the sudden surge of mercury if the experimental tube were broken. In normal operation steel ball (V) floated on the mercury in the valve; however, if the experimental tube broke, the sudden surge of mercury forced the ball into (W) and stopped the escape of the mercury.

The thickened collar (H) served as the primary point of suspension and retention for the experimental tube. The large rubber cylinder (E) served two purposes; it acted as a pressure seal, and it gave lateral support for the experimental tube.

"The primary support assembly (K) which normally rests on the shoulder in leg (L) is shown in the insert

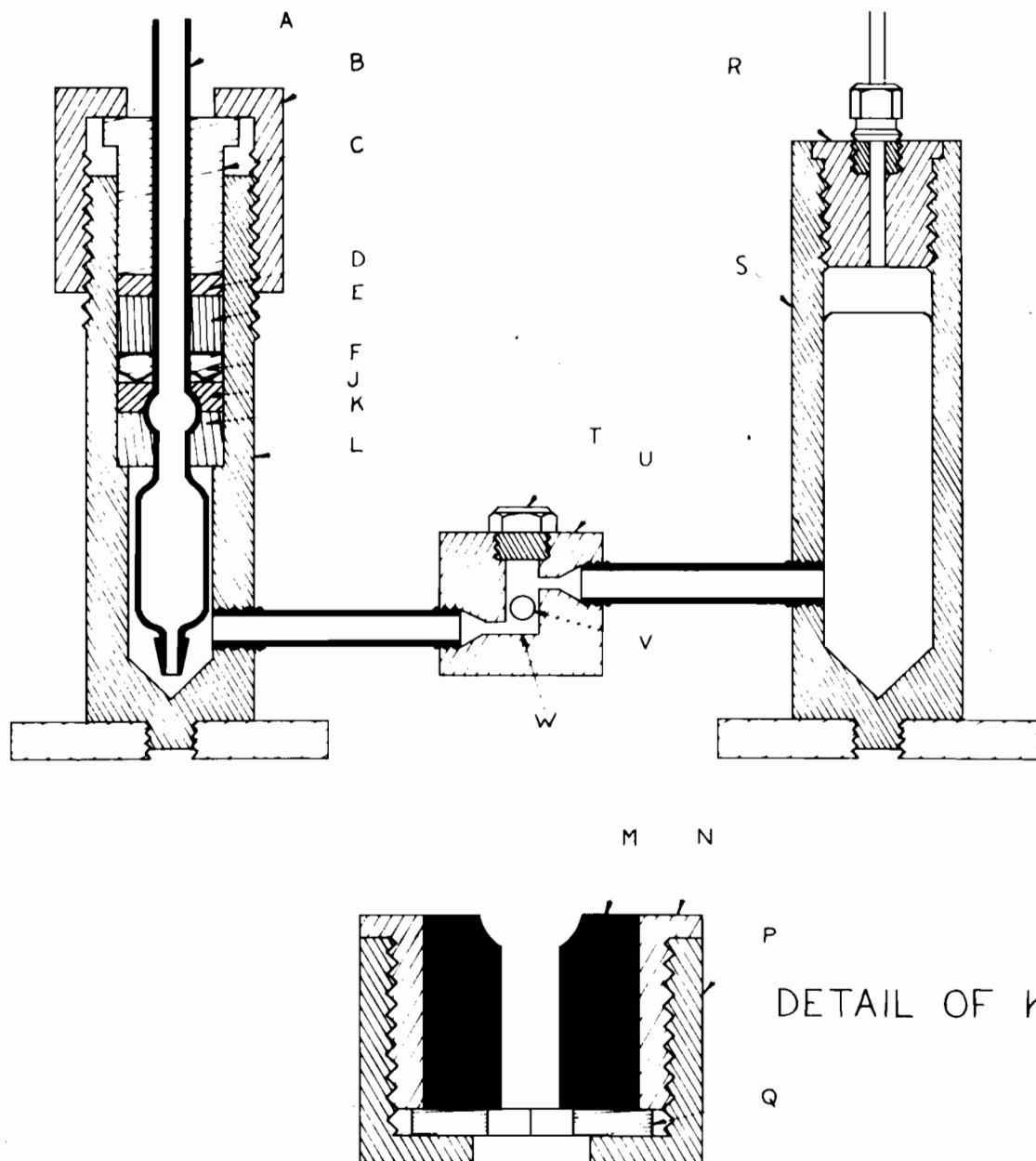


FIGURE I-1- COMPRESSOR BLOCK

in Figure I-1. This insert demonstrates the method of installing the cup onto the tube. A removable split ring (Q) was used to support the rubber cylinder (M). This was held against the inner member of the cup (W) by member (P). In order to prevent steel from coming in contact with the glass tube, the rubber washers (M) below and (J) above the tube collar (H) were used as the actual contacts. The indented center portion of the steel ring (F) prevented lateral movement of the tube, and, together with the upper washer (J), formed the upper support for vertical movement of the experimental tube." (7)

The steel washers (F) and (D) along with the steel sleeve (C) acted to compress the rubber sleeve (E) when the screw-collar (B) was hand tightened.

B. Experimental Tube

The thick-walled experimental tube is shown in cross-section in Figure I-2. The tube was fabricated from pyrex tubing. The upper capillary section was 2 mm (I.D.) precision bore tubing; the lower section was 3 mm (I.D.) precision bore tubing. The 2 mm section was carefully calibrated with respect to volume as a function of length, and all experimental measurements were made in this section. The thickened collar (13 mm O.D.) in the 3 mm section supported the tube as explained previously. The 18 mm (O.D.) bulb at the open end of the tube served as a gas reservoir

during sample loading. A male ground glass joint having a 10/30 standard taper was attached to the open end of the experimental tube and served as the vacuum train adaptor. The attachment was essential in the filling of the experimental tube with degassed mercury.

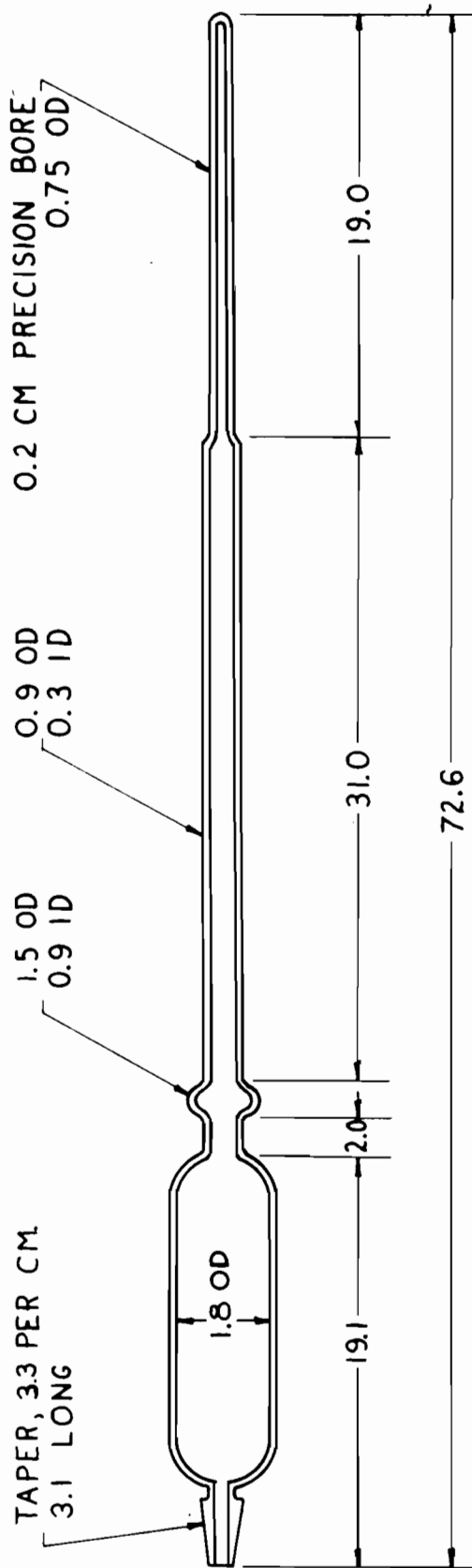


FIGURE 1-2 - EXPERIMENTAL TUBE

APPENDIX II

GAS LOADING PROCEDURE

A. Gas Loading Procedure Using Gas Microburette

Physical Description of Gas Microburette:

Samples of pure propane or n-butane were added to the experimental tube by means of a gas microburette. A schematic diagram of the microburette is given in Figure II-1. The essential parts of the apparatus were a stainless steel bellows (A) and a calibrated, precision-bore capillary tube (T). The calibrated section of the tube was 50 cm long (graduated in 0.1 cm increments) and 2.54 mm in diameter. The capillary tube had a volume of 0.05065 cc/cm. The extended section of the capillary tube (R^1 to R) was necessary in the loading procedure which will be explained later. The tip at (R) was drawn into a very small opening. The stainless steel bellows was filled with mercury. The bellows could be expanded or contracted by turning the knurled nut (N) which caused the threaded rod (NN) to move up and down.

The water reservoir (X) served the purpose of a constant temperature bath around the calibrated tube. The water in the reservoir was maintained at an equilibrium temperature by stirring with air bubbled through the jacket. The height of the calibrated tube could be adjusted by moving the microburette up or down the support rod (BB) by means of the knurled nut (CC).

Both propane and n-butane were loaded into the experimental tube using the following procedure. If the experimental tube already contained a mixture of gases, the pressure was raised on the sample until it completely liquefied. Next, the vacuum jacket (shown in Figure 1) was removed from around the experimental tube. Then a dry ice bath was placed around the sample so that it was cooled and its vapor pressure was reduced below atmospheric pressure. After this was accomplished, the pressure on the sample was reduced to zero psig.

Now, the metal female plug (R), as shown in Figure I-1 was removed and mercury was added to raise its level to just below the threads in the "back leg". A solid metal plug with an O-ring seal was then screwed into the "back leg"; the screw collar (B) and the steel sleeve (C) of Figure I-1 were removed from the "front leg", and the mercury pot shown in Figure II-2 was screwed into place. The mercury pot was filled with clean, distilled mercury, and then the experimental tube was slowly withdrawn from the compressor block to the level shown in Figure II-2 below the mercury surface.

If a new sample was being loaded, the tube would not already be in the compressor block. In this case, a clean experimental tube, filled with distilled mercury and

containing a steel ball, would be inverted in the mercury after the pot was filled.

The large end of a clean gas-collecting tube was submerged in the mercury pot. A vacuum was applied to the upper end of the collecting tube by using an aspirator, and the stopcock was opened, causing the mercury to rise above the stopcock, thus displacing the air in the collecting bulb. Then the stopcock was closed. The tip of a glass ampoule filled with high-purity gas was immersed in the mercury and inside the mercury-filled, gas-collecting bulb. The tip was then broken, and gas displaced the mercury in the bulb as is shown in Figure II-2.

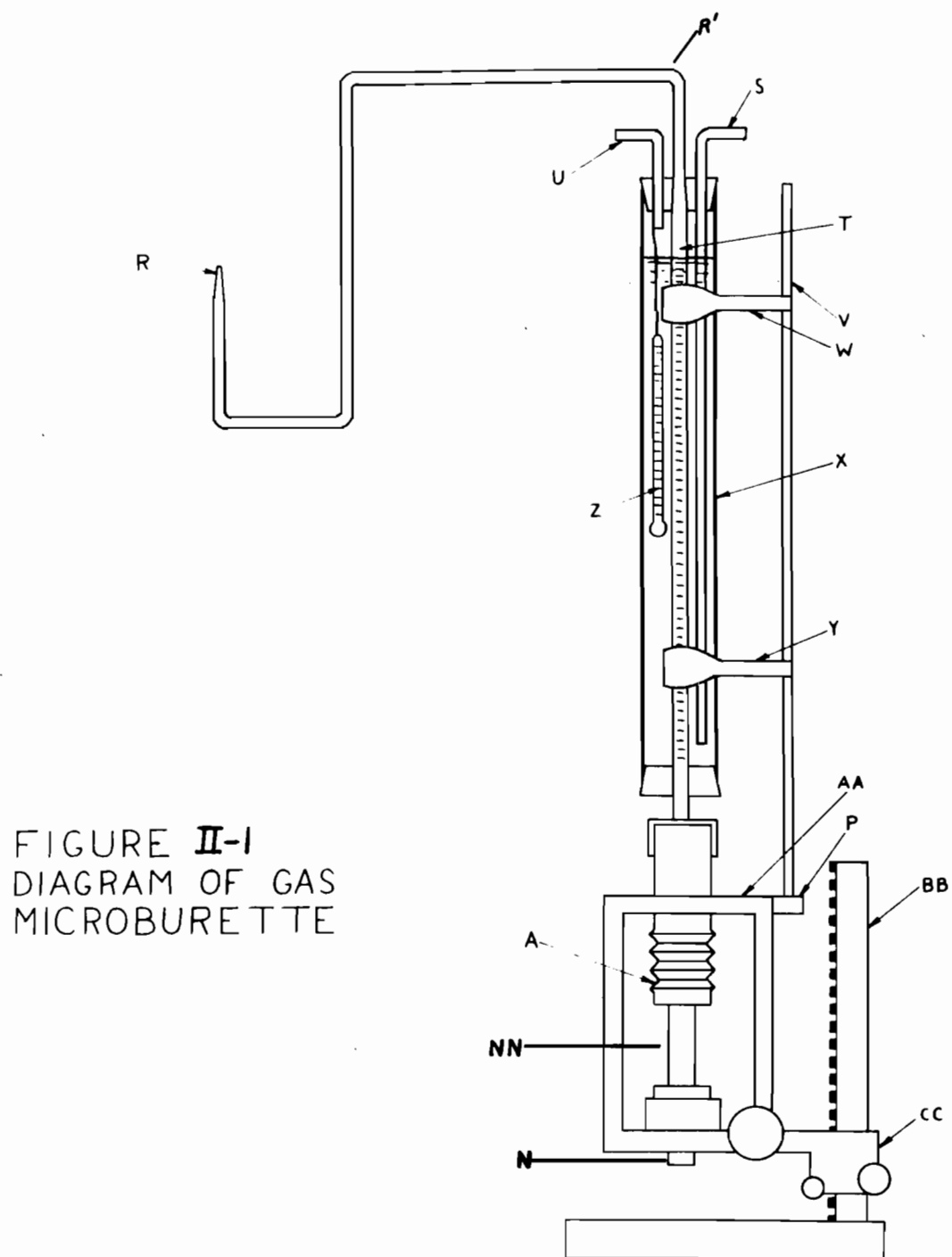
Next, the tip (R) of the microburette was immersed in the mercury and the bellows were contracted, filling the entire microburette tube with mercury. The tip (R) was then brought under the gas collecting bulb and into the pure gas. By expanding the bellows, a gas sample was drawn into the microburette tube; tip (R) was then lowered into the mercury, and mercury was drawn into the tube after the gas. The gas was used to flush the microburette tube. With the tip (R) below the mercury surface, the gas was expelled from the microburette capillary tube. The microburette was flushed in the above manner three times.

The desired amount of gas was drawn into the microburette tube as described above. Atmospheric pressure on the sample in the microburette was assured by adjusting the zero mark on the capillary tube to the same height as the mercury level in the mercury pot; this was accomplished by the use of a cathetometer.

Now, the top meniscus of the gas is brought to the zero mark on the microburette. The barometric pressure, water bath temperature, and length of gas sample were then recorded. Tip (R) was placed inside the experimental tube and the gas sample was expelled into its gas reservoir. See Figure II-2. The gas was brought to the top of the experimental tube by shaking it; when it reached the top, the gas was liquefied by the dry ice bath.

The gas microburette and the gas collecting tube were removed from the mercury pot. Simultaneously, mercury was removed from the pot and the experimental tube was lowered into the compressor block to keep its tip below the mercury level. When the mercury pot was empty, and the experimental tube was fitted in the compressor block, the mercury pot was removed from the front leg and the steel sleeve and screw collar (see Figure I-1) were replaced. The solid plug was removed from the back leg and the mercury level was lowered to 100 mm below the top of the back leg. The metal seal with the pressure line was connected to the

"back leg", and the pressure was then raised on the experimental tube. The dry ice bath was removed from the experimental tube and the sample was allowed to warm. Next, the vacuum jacket was put in place, and the apparatus was ready for operation.



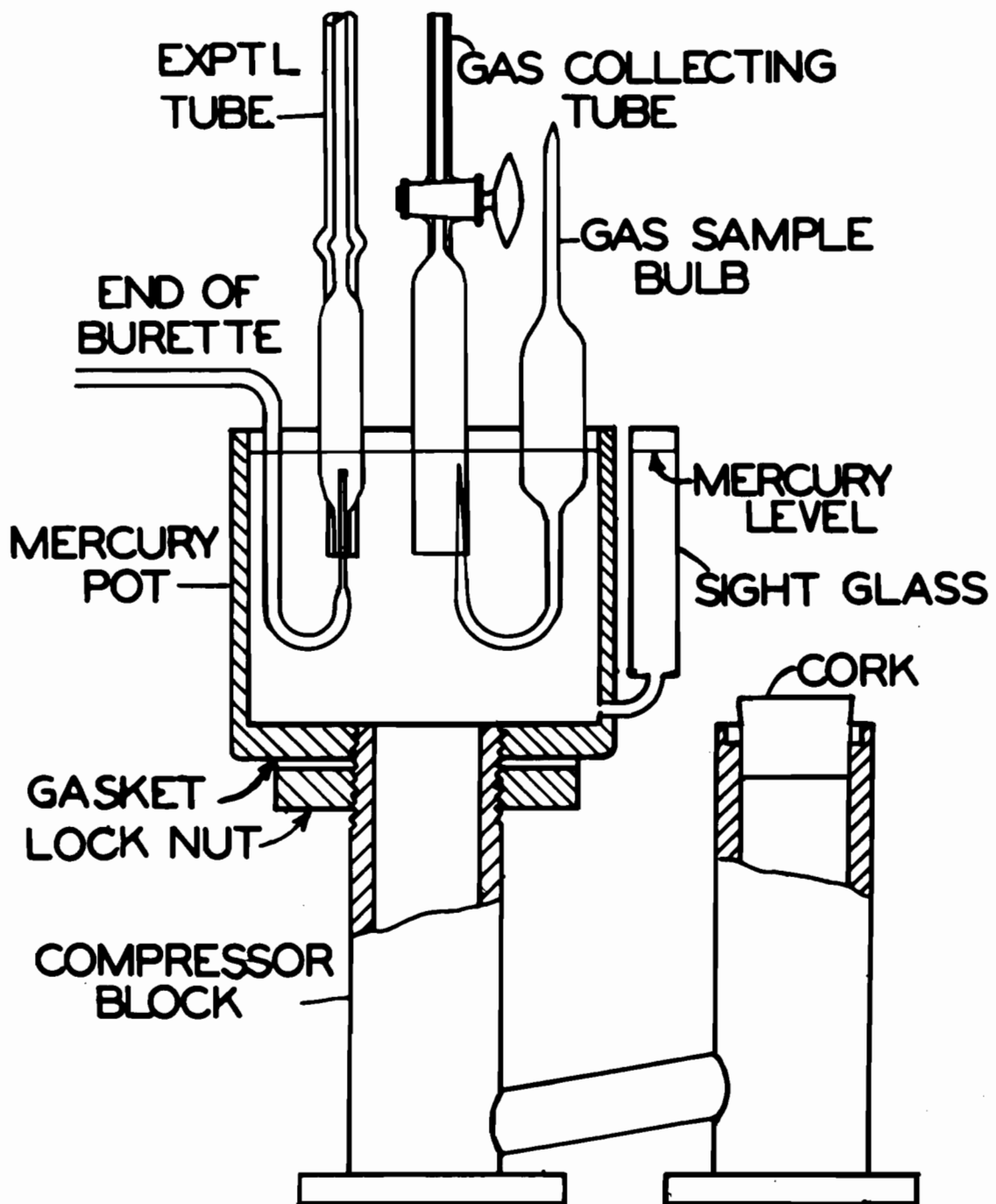


FIGURE II-2 - GAS LOADING

APPENDIX III

CALIBRATIONS

A. Thermocouple Calibration (11)

A copper-constantan thermocouple was used to measure the temperature inside the vapor jacket. It was calibrated by comparison with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards. The actual calibration of the thermocouple was done by Mr. James E. Williamson using a solid aluminum furnace block. The furnace consisted of a cylinder four inches in diameter by eleven inches long. The thermocouple probe and the resistance thermometer were inserted into holes drilled near the center of the cylinder and parallel to the axis. Heat was supplied by a resistance winding around the outside of the air bath. The temperature of the air bath was controlled by a Thermotrol, Model 1053 temperature controller, manufactured by Hallikaninan Instruments, Berkeley, California.

"Seven calibration points were obtained. At each temperature four to six comparisons of the thermocouple and thermohm were made. The readings of the thermohm were very steady. No random fluctuations were observed, and the temperature drifted less than 0.01°C for each set of readings. The results of the calibrations are given in

Table III-1. This calibration is estimated to be correct to within $.05^{\circ}\text{C}$ from 100° to 225°C ." (11)

The calibration data for the thermocouple was fitted to a curve by means of a regression analysis on the IBM 1620 computer. The constants for this curve are given in Table III-1.

TABLE III-1
THERMOCOUPLE CALIBRATION (11)

Temperature	EMF	EMF (calc.)	Δ
(°C)	(mv)	(mv)	
113.958	4.8876	4.8876	0.0
138.039	6.0461	6.0461	0.0
162.880	7.2794	7.2794	0.0
181.264	8.2162	8.2162	0.0
199.834	9.1830	9.1830	0.0
213.751	9.9199	9.9199	0.0
229.255	10.7535	10.7535	0.0

$$S_E^2 = 3.248 \times 10^{-9}$$

$$\begin{aligned} a &= -0.0594200 \\ b &= 0.03928239 \\ c &= 3.80426 \times 10^{-5} \\ d &= -1.5920 \times 10^{-8} \end{aligned}$$

B. Heise Bourdon Gage Calibration

A Heise Bourdon Gage was used to indicate the pressure. This gage was calibrated at pressures from 30 to 500 psig by comparison with a Type 6-201 Primary Pressure Standard manufactured by Consolidated Electrodynamics Corporation. At pressures from 500 to 1200 psig it was calibrated by comparison with a Starr dead weight gage.

In starting the calibration procedure, the manifold pressure was brought to exactly 30 psig by high pressure nitrogen. The 30 psig pressure was determined by means of an external mercury manometer (shown in previous drawings). The gage scale was then adjusted to exactly 30 psig. The calibration was conducted by raising the pressure incrementally, balancing the dead weight gage, and then reading the Heise gage. The results of the Heise gage calibration is given in Table III-2. It is estimated that the calibration is accurate to ± 0.5 psi from 30 to 500 psig and ± 1.5 psi from 500 to 1200 psig.

TABLE III-2
HEISE PRESSURE GAGE CALIBRATION

Primary Standard Pressure (psig)	Gage Reading (psig)	Correction to Heise Gage (psi)
30.0	30.0	0.0
40.0	40.0	0.0
50.0	49.8	-0.2
60.0	59.5	-0.5
70.0	69.6	-0.4
80.0	79.8	-0.2
90.0	89.8	-0.2
100.0	98.2	-1.8
120.0	119.2	-0.8
140.0	139.5	-0.5
160.0	159.8	-0.2
180.0	179.9	-0.1
200.0	199.8	-0.2
220.0	219.8	-0.2
240.0	239.9	-0.1
260.0	260.0	0.0
280.0	280.7	+0.7
300.0	300.3	+0.3
320.0	321.0	+1.0
340.0	341.2	+1.2
360.0	360.4	+0.4
380.0	380.4	+0.4

TABLE III-2 (Cont.)
HEISE PRESSURE GAGE CALIBRATION

Primary Standard Pressure (psig)	Gage Reading (psig)	Correction to Heise Gage (psi)
400.0	400.3	+0.3
420.0	420.0	0.0
440.0	440.0	0.0
460.0	460.0	0.0
480.0	480.0	0.0
500.0	500.0	0.0
519.0	518.4	-0.6
539.7	538.6	-1.1
562.4	561.3	-1.1
583.1	582.7	-0.4
601.3	601.2	-0.1
648.6	648.8	+0.2
699.7	699.9	+0.2
753.6	753.2	-0.4
803.3	803.0	-0.3
857.2	857.1	-0.1
905.0	905.2	+0.2
958.9	958.8	-0.1
1008.6	1008.2	-0.4
1062.5	1063.0	+0.5
1110.2	1110.0	-0.2
1148.7	1149.5	+0.8
1198.9	1199.7	+0.8

C. Sample Tube Calibration (11)

The sample tube was calibrated by determining the level volume, V_L , enclosed by the tube as a function of the distance, h , from the closed end of the tube. The level volume is defined as the volume enclosed by an imaginary plane cutting the tube normal to its axis. (11)

The precision-bore capillary tube was calibrated prior to being fused to the lower, larger section of the tube. It was cleaned before calibrating by washing with chromic acid solution, rinsing thoroughly with distilled water then acetone, and finally blowing dry with filtered air. The tube was then filled with distilled mercury. The length, h , of the mercury column and the height of the mercury meniscus, h_m , were measured to the nearest 0.0001 cm. with a precision cathetometer. The room temperature was measured with a mercury thermometer which had been calibrated by the National Bureau of Standards. The mercury was incrementally removed from the tube, and after each increment the height of the mercury and its meniscus was measured and recorded. Also, the weight of each increment was measured on an analytic balance. Care was taken to insure no loss of mercury during transfers. This procedure was repeated until the tube was emptied; then the tube was refilled and a second set of data was taken in the same manner.

Since the length and weight of each increment of mercury removed was known, the volume of the increment could be determined by dividing its weight by the density of mercury (11) at the measured temperature.

The level volume, V_L , at the calibration points was obtained by adding the volume complement of the mercury meniscus to the volume of mercury determined for that point. It was assumed that the meniscus was a segment of a sphere. (11) The volume complement was then given by the relation:

$$V_C = \pi r^2 h_m - \frac{\pi h_m}{6}(h_m^2 + 3r^2) \quad (1)$$

$$= \frac{\pi r^2 h_m}{2} - \frac{\pi h_m^3}{6} \quad (2)$$

If the tube bore is uniform, a linear calibration equation may be used:

$$V_L = a + bh$$

where "a" and "b" are constants to be determined by regression analysis from the calibration data. Also, "b" may be interpreted as the average cross-sectional area of the tube bore. "But $V_L = V_{hg} + V_C$; therefore,

$$V_{Hg} + \frac{\pi r^2 h_m}{2} - \frac{\pi h_m^3}{6} = a + bh = a + \pi r^2 h \quad (3)$$

collecting terms,

$$V_{\text{Hg}} - \frac{\pi h_m^3}{6} = a + b(h - \frac{h_m}{2}) \quad (4)$$

The calibration constants a and b are thus obtained as the intercept and slope of a least-squares line on a plot of the calibration data in the form $y(= V_{\text{Hg}} - \frac{\pi h_m^3}{6})$ versus $x(= h - \frac{h_m}{2})$." (11) The final calibration equation for the tube is

$$y = a + bx.$$

Table III-3 is a summary of the tube calibrations calculated on the IBM 1620 computer. The variance estimate of the calibration is s_E^2 . It is the best estimate of the precision of fit of the calibration data to the regression equation. The variance is calculated by dividing the sum of the squares of the deviations by the number of constants in the regression equation. Thus it approximates the mean square deviation of a given point from the regression line. The calibration constants followed by their 95% per cent confidence intervals are listed in Table III-3.

TABLE III-3
SAMPLE TUBE CALIBRATION

s_E^2	(cc ²)	1.75929×10^{-8}
a	(cc)	$-1.9241000 \times 10^{-3}$
(95%) a		5.15307×10^{-5}
b	(cm ²)	2.6127680×10^{-2}
(95%) b		3.9756154×10^{-6}

TABLE III-4
RESULTS OF LEAST-SQUARES ANALYSIS
CALIBRATION OF EXPERIMENTAL TUBE

h (cm.)	Y _{exp} (cc.)	Y _{calc} (cc.)	$\delta V \times 10^4$ (cc.)
21.84270	.568959	.568775	1.84
21.56490	.561754	.561517	2.37
20.19440	.525921	.525709	2.12
19.75270	.514219	.514168	.51
18.69430	.486576	.486515	.61
16.52370	.429630	.429802	-1.71
16.97225	.441438	.441521	-0.83
15.67130	.407429	.407531	-1.02
15.22455	.395693	.395858	-1.65
14.29950	.371561	.371689	-1.28
14.28820	.371272	.371393	-1.21
12.58070	.326646	.326780	-1.35
12.07160	.313269	.313479	-2.10
10.93350	.283630	.283743	-1.13
10.44310	.270843	.270930	-0.86
8.86935	.229863	.229811	.52
8.13855	.210803	.210717	.86
6.80255	.175979	.175811	1.68
6.08645	.157150	.157101	.50
5.13745	.132351	.132306	.46
4.18160	.107286	.107331	-0.46
3.43335	.087740	.087781	-0.42
2.67070	.067817	.067855	-0.38
2.11965	.053478	.053457	.21
1.66135	.041560	.041483	.76
.75670	.018044	.017847	1.97

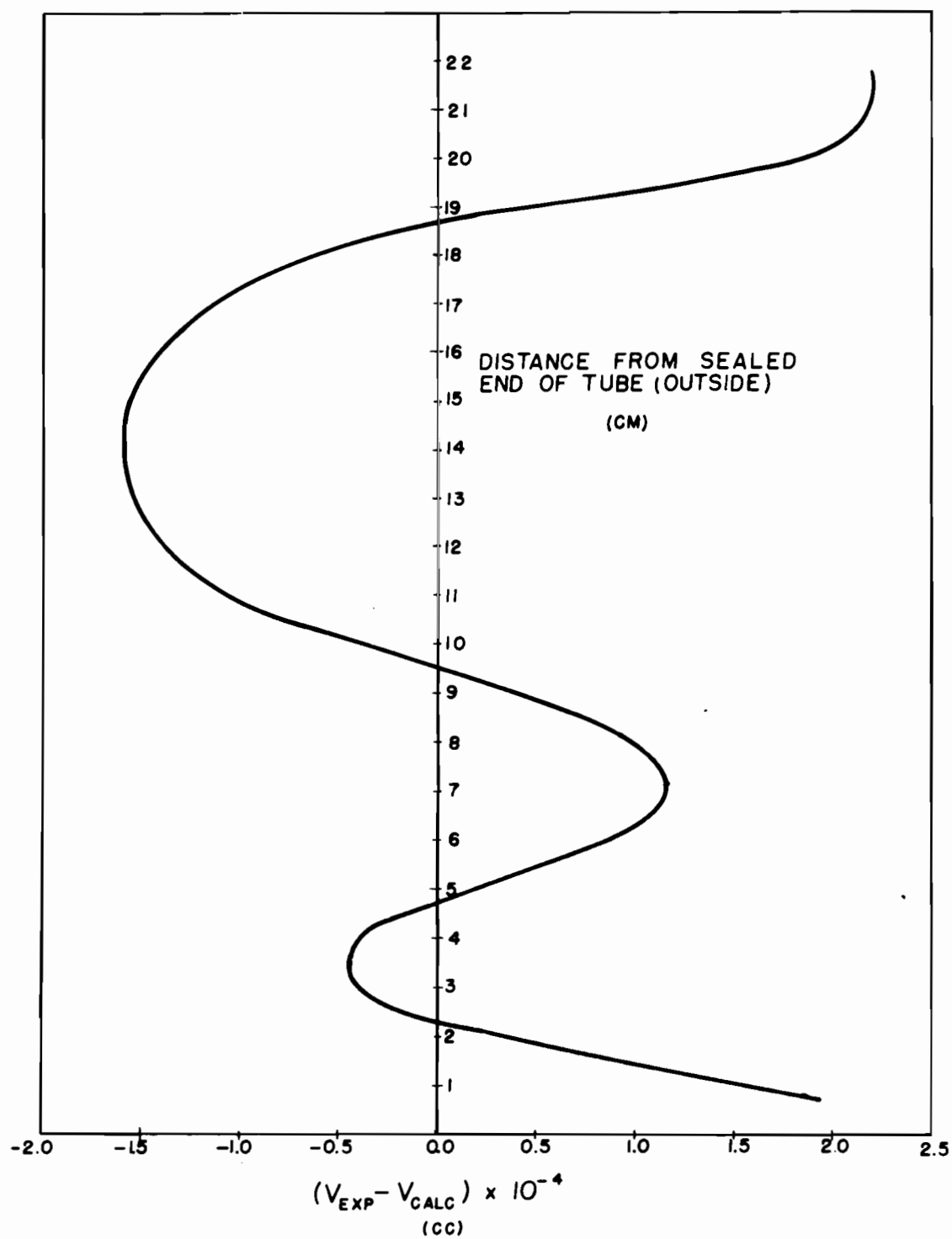


FIGURE III-1-EXPERIMENTAL TUBE VOLUME CORRECTION

Table III-4 presents the results of the least-squares analysis of the calibration data. The columns headed h and Y are the length of mercury column and volume of mercury as determined experimentally. The column Y_{calc} is the volume corresponding to h calculated from the regression equation. The quantity δV is the value, $Y - Y_{\text{calc}}$, or the difference between experimental and calculated volumes. The value δV can be added to the volume obtained from the regression equation to obtain a more accurate estimate of the volume. A plot of δV versus h was made and is presented in Figure III-1.

To calculate the volume of a gas sample using the regression equation, the volume complement of the mercury meniscus must be added to the level volume obtained from the regression equation. Now,

$$V_L = a + bn + \delta V \quad (5)$$

$$V_s = a + bh + b \frac{h_m}{2} - \frac{\pi h_m^3}{6} + \delta V \quad (6)$$

$$V_s = a + b \left(h + \frac{h_m}{2} \right) - \frac{\pi h_m^3}{6} + \delta V \quad (7)$$

APPENDIX IV

DATA REDUCTION AND SAMPLE CALCULATIONS

A. General Discussion

A sample data sheet is shown in Table IV-1. A Fortran program was written which would calculate sample temperature, pressure, and volume from these data. In Table IV-1 the left-hand column is a listing of the data necessary for completing calculations for the point; the right-hand column is the actual numerical data.

Lines 1 and 2 of the table identify the experimental point. Line 1 states the type of point and line 2 gives the identification number of the point. The particular point chosen for calculation is point 64, a dew point, in the 30.85 mole per cent propane mixture. Line 3 is the Heise gage reading. Line 4 is the correction for the gage reading at that pressure; it is obtained from a graph of the pressure corrections given in Table III-2. Line 5 is the sum of lines 3 and 4; it is the corrected gage pressure. Line 6 is the cathetometer reading at the top of the tube; line 7 is the reading at the top of the mercury meniscus (or the bottom of the steel ball); line 8 is the reading at the bottom of the meniscus. Line 9 is the cathetometer reading at the bottom of the hot zone, and

line 10 is the reading at the top of the back leg. See Figure IV-1. Line 11 is the distance of the mercury level below the top of the back leg; this distance was always adjusted to 100 mm by removal of mercury. Lines 13 and 14 are the cathetometer readings for the barometer top and bottom, respectively; line 15 is the difference of the two, which is the uncorrected barometric pressure.

Line 16 is the potentiometer readings, which is the thermocouple output emf. Line 17 (Z_H) is the length of the hot zone; it is obtained by subtracting line 9 from line 7. The length of the mercury column at room temperature (Z_C , line 18) is obtained by subtracting line 10 from line 9 and adding line 11. (See Figure IV-1.)

The length of the sample (H , line 19) is the difference between lines 6 and 7. Line 20 is the height of the mercury meniscus; it is obtained as the difference of lines 7 and 8. The item δV (line 21) is a correction term added to the calibration equation to obtain the sample volume; this value is obtained from Figure III-1.

The data reduction program used in this investigation was originally written and applied by A. E. Jones. (11) Thus, most of the detailed discussion of sample calculations will be direct quotes from the original work.

TABLE IV-1
SAMPLE DATA SHEET

		Dew Point
1. Type of Point		
2. NPT		64
3. Heise Gage	psi	528.0
4. Correction	psi	+0.8
5. Gage Pressure	psi	528.8
6. Reference	cm.	62.592
7. Top of Meniscus	cm.	56.119
8. Bottom of Meniscus	cm.	56.077
9. Bottom of Hot Zone	cm.	26.143
10. Top of Back Leg	cm.	17.956
11. Distance of Mercury from Top of Back Leg	cm.	10.000
12. Room Temperature	C°	24.0
13. Barometer Top	mm.	868.85
14. Barometer Bottom	mm.	112.40
15. Uncorrected Barometric Pressure		756.45
16. Potentiometer Emf	mv.	5.8170
17. Z_H	mm.	299.76
18. Z_C	mm.	181.87
19. H	cm.	6.473
20. H_m	cm.	0.042
21. δV	cc.	1.10×10^{-4}

B. Pressure Calculation

"The corrections to be applied to the indicated pressure are determined by means of a force balance around the compressor block. (See Figure IV-1) The pressure at the mercury-nitrogen interface of the back leg must be equal to the pressure in the mercury in the front leg at the same level. This pressure is the sum of the pressure exerted by the sample, P_{SMPL} , the pressure due to mercury vapor dissolved in the sample, P_{VAP} , the capillarity of the mercury meniscus, P_{CAP} , and the hydrostatic pressure of the mercury column from the meniscus to the level of mercury in the back leg. The calculation of this pressure is complicated by the fact that the mercury column extends into the vapor jacket. Thus, the upper part of the column is at the temperature of the sample while the lower part is at room temperature. A temperature gradient between these extremes must exist where the tube enters the vapor jacket. In practice, it was assumed that the mercury remains at room temperature up to the top of the rubber stopper which seals the bottom of the vapor jacket; it then immediately assumes the temperature of the sample. The mercury column then consists of a segment Z_H at the

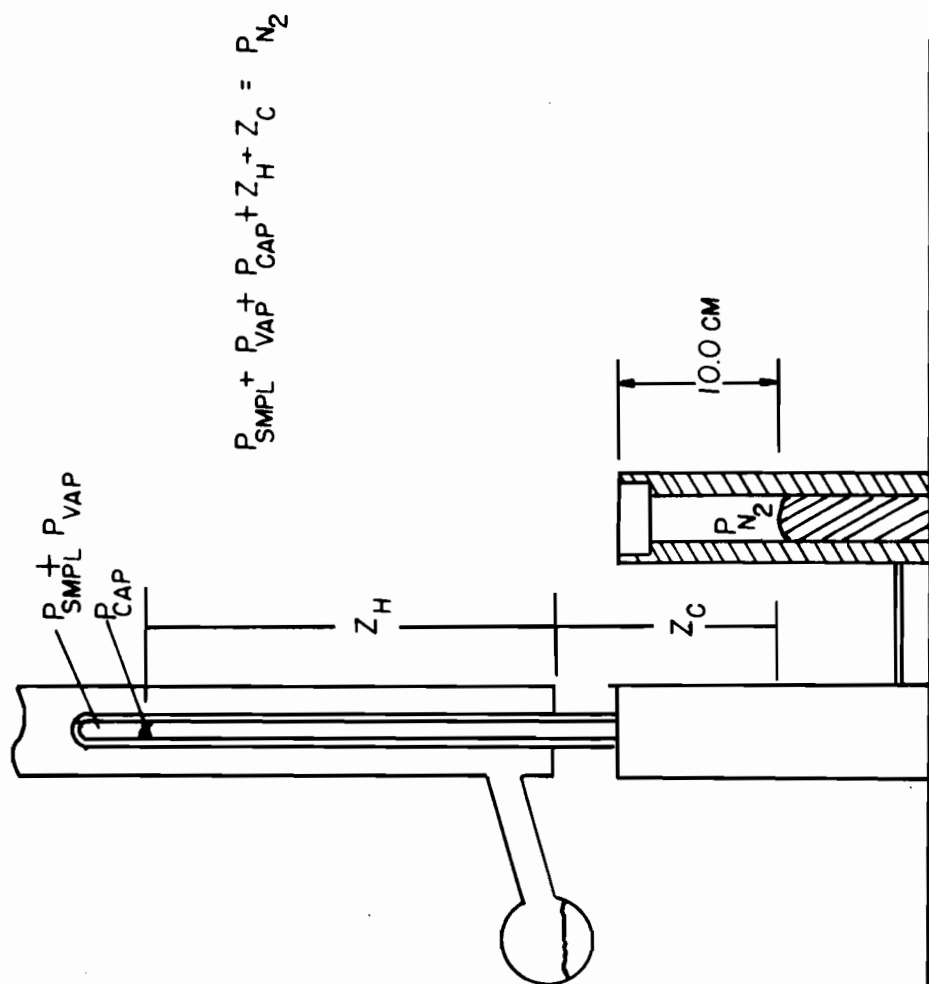


FIGURE IV-1—FORCE BALANCE AROUND COMPRESSOR BLOCK

sample temperature and a segment Z_C at room temperature."

(11) Thus, the force balance takes the form,

$$P_{IND} = P_{SMPL} + P_{VAP} + P_{CAP} + Z_H + Z_C \quad (1)$$

Here, P_{IND} is the indicated pressure of the Heise gage. Combining the above equations and adding the barometric pressure, P_{BAR} , the following equation for the sample pressure is obtained:

$$P_{SMPL} = P_{IND} + P_{BAR} - Z_H - Z_C - P_{VAP} - P_{CAP} \quad (2)$$

"The largest single correction to the indicated pressure is the addition of the atmospheric pressure. The atmospheric pressure was measured to the nearest 0.1 mm., at room temperature, and converted to an equivalent height of mercury at 0°C. using the following relation:

$$P_{BAR} = \frac{P_t}{1 + \alpha t} \quad (3)$$

where P_{BAR} is the equivalent barometric pressure at 0°C., P_t is the observed atmospheric pressure at $t^\circ\text{C}.$, and α is a function of temperature representing the difference of the coefficients of thermal expansion of mercury and of the brass scale of the barometer. The following form of α was used,

$$\alpha = 1.63392 \times 10^{-4} + 1.75 \times 10^{-10}t + 3.5116 \times 10^{-11}t^2, \quad (4)$$

where t is the room temperature in degrees Centigrade.

$$\alpha = 1.63392 \times 10^{-4} + 1.75 \times 10^{-10}(24.0) + 3.5116 \times 10^{-11}(24.0)^2 = 1.63392 \times 10^{-4}$$

$$P_{\text{BAR}} = \frac{756.45}{1 + 24.0 \times 1.63392 \times 10^{-4}} = 753.48 \text{ mm. Hg}$$

The next largest correction to the indicated pressure is the hydrostatic pressure of the mercury column. The pressure due to the segment Z_C is obtained by measuring Z_C and converting this measured pressure to an equivalent pressure at $0^\circ\text{C}.$, in the same manner as for the barometric pressure.

$$Z_C = \frac{Z_C}{1 + \alpha t} \quad (5)$$

$$Z_C = \frac{181.87}{1 + 24.0 \times 1.63392 \times 10^{-4}} = 181.16 \text{ mm. Hg}$$

The pressure due to the segment Z_H was obtained by measuring the distance between the mercury meniscus and the bottom of the hot zone directly with a cathetometer. This observed pressure was converted into an equivalent pressure at 0°C in the same manner as the barometric

pressure except that the sample temperature was used in the equations in place of the room temperature." (11)

$$Z_H = \frac{Z_H}{1 + \alpha t} \quad (6)$$

$$Z_H = \frac{299.76}{1 + 1.63392 \times 10^{-4} \times 133.33} = 293.34 \text{ mm. Hg}$$

A correction to the indicated pressure must be made due to the presence of capillary forces in the mercury column within the sample tube. It is known that there is a pressure differential across a curved surface separating two fluid phases. The pressure on the concave side of the mercury meniscus (within the mercury) must be greater than the pressure on the convex side; this pressure differential is necessary to maintain the curved meniscus against the force exerted by the interfacial tension. For an exact calculation of the pressure differential, the geometrical shape of the mercury meniscus and the value of the interfacial tension must be known. One source gave the value of the surface tension of mercury in contact with its own vapor as a function of temperature.

This equation is:

$$\gamma = 461.8 - 0.189t \quad (7)$$

where γ is the surface tension in dynes/cm. and t is the temperature in degrees Centigrade. The second source

gave a measured value for the surface tension of mercury in helium at 20°C. as 475 dynes/cm. Using this value at 20°C. and the temperature dependence of the above equation, the following relation for the interfacial tension of mercury as a function of temperature was derived:

$$\gamma = 478.8 - 0.189t \quad (8)$$

This equation was used for the interfacial tension of mercury with all mixtures studied. (11)

"Adamson (loc. cit.) derives the following expression for the pressure differential across a spherical interface:

$$P = \frac{2\gamma}{R} \quad (9)$$

γ is the interfacial tension and R is the radius of curvature of the spherical segment." (11) R can be calculated from the constant b from the regression analysis in the sample tube calibration. This constant is equal to the average cross sectional area of the tube bore. Thus,

$$R = \sqrt{\frac{b}{3.14159}} \quad (10)$$

Now,

$$P_{CAP} = 2\gamma / \sqrt{\frac{b}{3.14159}} \quad (11)$$

$$P_{CAP} = \frac{2(478.8 - 0.189t)}{\sqrt{\frac{0.026127680}{3.14159}} \times 1333.22}, \text{ where } t = 133.33^\circ\text{C}$$

$$P_{CAP} = 7.46 \text{ mm. Hg}$$

Since the sample is confined over a column of mercury, the correction for the vapor pressure of mercury (P_{VAP}) must also be made in obtaining the true sample pressure. The vapor pressure of mercury at the various sample temperature was obtained by a numerical interpolation of vapor pressure data for mercury. This numerical interpolation was included as a subroutine in the data reduction computer program. The vapor pressure data of mercury is given in Table IV-2.

"One additional pressure correction was applied to dew points only. Connolly has considered the difference in pressure across the curved surface of the tiny liquid speck between the steel stirring ball and the wall of the sample tube whose appearance marks the dew point. He shows that the pressure inside the speck will be higher than that in the vapor phase. The value of this pressure difference should then be added to the measured sample pressure to give the true dew point pressure. The approximate relation which Connolly gives to estimate this difference is

$$P = 8 \gamma \left(\rho_V / \rho_L \right) \frac{D_b}{D_s^2} \quad (12)$$

where γ is the surface tension of the speck; ρ_V and ρ_L are the vapor and liquid densities; D_b is the diameter of the ball; and D_s is the diameter of the speck.

TABLE IV-2

VAPOR PRESSURE OF MERCURY

Temperature (C°)	Vapor Pressure (mm Hg)
50	.01
75	.07
100	.28
125	.95
150	2.81
175	7.34
200	17.27
225	37.25
250	74.50
275	139.64
300	247.47
325	417.33
350	674.26

In applying this equation to the propane-n-butane system, γ , ρ_v , and ρ_L were taken to be the properties for pure n-butane. The surface tension of n-butane in equilibrium with its own vapor was measured by Katz and Saltman. They obtained a value of 15.4 dynes/cm. at 2.0°C. Stegemeier reported that the surface tension of n-butane could be correlated by an equation of the form

$$\gamma = \gamma_o(1 - T/T_c)^{11/9} \quad (13)$$

Using 15.4 dynes/cm. as γ at $T = 2.0^\circ\text{C}.$, γ_o was calculated to be 55.0 dynes/cm.

The orthobaric vapor and liquid densities for n-butane were obtained from the work of Kay. A plot of $\log_{10} (\rho_v / \rho_L)$ versus temperature was prepared. It was found that up to about 15 degrees below the critical temperature, the function could be represented by the linear relation

$$\log_{10} (\rho_v / \rho_L) = 0.01156 T - 5.384 \quad (14)$$

At temperatures where this relation was invalid, the surface tension was very small and the pressure correction was not sensitive to errors in ρ_v / ρ_L .

The steel ball used to stir the sample is 0.0517 cm. in diameter. The diameter of the speck was taken to be 0.004 cm., which is the value which Connolly (loc. cit.) assumed to be the smallest visible.

Substitution of these values in previous equations gives the following relation:

$$\Delta P = 20.614 \left(\rho_V / \rho_L \right) (1 - T/425.2)^{11/9} \quad (15)$$

The numerical constant includes a conversion factor to give ΔP in units of psi. T is the absolute temperature in °K. The magnitude of this pressure correction varies from 0.13 psi at 100°C. to zero at 152°C., the critical temperature of n-butane." (11)

"The sample pressure for dew points was calculated using the equation

$$P_{SMPL} = P_{IND} + P_{SPECK} + 0.019337(P_{BAR} - Z_H - Z_C - P_{VAP} - P_{CAP}) \quad (16)$$

Here P_{IND} is the corrected Heise gage pressure, P_{SPECK} is the pressure correction due to the curved surface of the speck, and the other symbols are the same.

The sample pressure for bubble points and critical points was calculated using the above equation with P_{SPECK} equal to zero." (11)

P_{IND} = Pressure indicated by Heise gage

P_{BAR} = Barometric pressure, corrected to 0°C

Z_H = Pressure of mercury column in hot zone,
corrected to 0°C

Z_C = Pressure of mercury column in cold zone,
corrected to 0°C

P_{VAP} = Vapor pressure of mercury at sample
temperature

P_{CAP} = Pressure drop across curved mercury meniscus

P_{IND} = 528.8 psig P_{BAR} = 753.48 mm. Hg

Z_H = 293.34 mm. Hg Z_C = 181.16 mm. Hg

P_{VAP} = 1.33 mm. Hg P_{CAP} = 7.46 mm. Hg

P_{SPECK} = 0.09 psi

P_{SMPL} = $528.8 + 0.09 + 0.019337(753.48 - 293.34$
 $-181.16 - 1.33 - 7.46) = 534.145$ psia

C. Volume Calculation

"The sample volume was calculated from the measured sample length, h , and the height of the meniscus, h_m , using the calibration equation for the sample tube. The tube calibration, however, was made at room temperature and atmospheric pressure; the measurements of the sample were made while the tube was at an elevated temperature and pressure. Therefore, corrections had to be made to the constants in the calibration equation to allow for the expansion of the tube with temperature.

The bulk temperature coefficient of expansion is 9.2×10^{-6} per degree centigrade from 0° to 300°C . If this value is denoted by α , then at temperature t all linear dimensions of the tube will have increased by the factor $1 + \alpha(t - 25.0)$ over the values measured when the tube was calibrated at 25°C . In the calibration equation

$$V = a_0 + b_0(h + h_m/2) - (\pi/6)n_m^3, \quad T = 25.0^\circ\text{C}. \quad (17)$$

the constant a_0 has the dimensions of volume, or $(\text{length})^3$. Therefore the value of a at $t^\circ\text{C}$. will be $a_0(1 + \alpha \Delta t)^3$, where $\Delta t = t - 25.0^\circ\text{C}$. Similarly, the constant b is the cross-sectional area of the tube and has the dimensions $(\text{length})^2$. Its value at $t^\circ\text{C}$. will be $b_0(1 + \alpha \Delta t)^2$. The calibration equation then becomes

$$V = a_0(1 + \alpha \Delta t)^3 + b_0(1 + \alpha \Delta t)^2(h + h_m/2) - (\pi/6)n_m^3, \quad T = t^\circ\text{C}." \quad (18)$$

The final equation used to calculate the sample volume for this tube is

$$V = a_0(1 + \alpha \Delta t)^3 + b_0(1 + \alpha \Delta t)^2(h + h_m/2) - (\pi/6)n_m^3 - 0.00208 + \delta V \quad (19)$$

The calibration constants for this tube are

$$a_0 = -1.9241000 \times 10^{-3} \quad T = 25^\circ\text{C}.$$

$$b_0 = 2.6127680 \times 10^{-2}$$

$$\Delta t = 133.33 - 25.0 = 108.33$$

$$1 + \alpha \Delta t = 1 + 9.2 \times 10^{-6} \times 108.33 = 1.000997$$

$$\delta V = 1.1 \times 10^{-4}$$

$$\begin{aligned} V = & -1.9241000 \times 10^{-3}(1.000997)^3 \\ & + 2.6127680 \times 10^{-2}(6.494)(1.000997)^2 \\ & - \frac{\pi}{6}(0.042)^3 - 0.00208 + 1.1 \times 10^{-4} \end{aligned}$$

$$V = 0.16585 \text{ cc.}$$

D. Temperature Calculation

The temperature of the thermocouple is obtained by substituting the measured emf in the calibration equation

$$\text{emf} = a + bt + ct^2 + dt^3 \quad (20)$$

and solving the equation for t by an iterative process.

Substituting the measured value, 5.8170 mv. for the emf in this equation, a value of 133.33°C is obtained for t .

E. Calculation of Mass of Sample Using Gas Burette

Table IV-3 presents a sample data and calculation sheet for a typical propane loading. The same calculation

procedure was used for both propane and n-butane. Items 1 through 8 of this table represent the data that were recorded during a gas loading.

Item 9 represents the uncorrected barometric pressure. A temperature correction (Item 10) was applied to the uncorrected barometric pressure to convert the pressure to centimeters of mercury at 0°C. The capillarity correction (Item 11) was estimated using the relation

$$\Delta P = 2 \gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (21)$$

r_1 is the radius of the bore of gas burette; r_2 is the radius of the sight glass attached to the mercury reservoir.

$$\Delta P = \frac{2 \times 425}{1333.2} \left(\frac{1}{0.127} - \frac{1}{0.60} \right) = 4.42 \text{ mm. Hg}$$

This correction must be subtracted from the measured pressure, since the mercury is at a higher pressure than the gas. Then the sample pressure (Item 12) is given by

$$P_s = 74.630 - .318 - .442 = 73.870 \text{ cm. Hg}$$

The sample volume (Item 15) is given by the product of the sample length and the calibration constant for the

gas burette plus the two mercury menisci complements
in the microburette tube.

$$V_s = 114.50 \times 0.055065 + .002814 = 5.802239$$

The sample temperature is 25.5°C. or 298.66°K. (Item 5)

The number of moles of sample is given by the
relation

$$n = \frac{P_s V_s}{ZRT_s} \quad (22)$$

where Z is the compressibility factor (Item 16) for the
gas.

Then,

$$n = \frac{738.70 \times 5.802239}{(.98408)(62361) 298.66} = 2.3385274 \times 10^{-4} \text{ g-moles}$$

TABLE IV-3
SAMPLE CALCULATION SHEET FOR
PROPANE LOADING

1. Data		3/19/64
2. Microburette Readings (Length of Sample)	cm.	37.25 39.05 <u>38.20</u>
3. Total of Burette Readings (Total Length of Sample)	cm.	114.50
4. Capacity of Burette Bore	cc./cm.	.05065
5. Microburette Temperature		25.5°C or 298.66°K
6. Room Temperature	C°	26.1
7. Top of Barometer	cm.	86.360
8. Bottom of Barometer	cm.	11.730
9. Uncorrected Barometer Pressure	cm. Hg	74.630
10. Temperature Correction	cm. Hg	-.318
11. Capillary Pressure	cm. Hg	-.442
12. Sample Pressure	cm. Hg	73.870
13. Volume of Sample Between Mercury Menisci	cc.	5.799425
14. Menisci Complement	cc.	.002814
15. Volume of Sample	cc.	5.802239
16. Compressibility Factor (Z)		.98408
17. Moles of Propane	moles	2.3385274×10^{-4}

APPENDIX V

EXPERIMENTAL DATA

TABLE V-1

Mole Per cent Propane = 00.00%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
1	DP	90.56	182.4	0.0318
2	DP	90.71	182.4	0.0316
3	BP	90.76	184.6	0.4785
4	DP	99.75	219.0	0.0389
5	BP	99.77	220.7	0.4651
6	DP	109.26	262.8	0.0483
7	BP	109.26	264.5	0.4446
8	DP	119.45	317.8	0.0609
9	BP	119.47	318.7	0.4231
10	DP	129.93	380.4	0.0784
11	BP	129.93	382.6	0.3933
12	DP	140.27	451.9	0.1043
13	BP	140.27	454.0	0.3619
14	BP (CP, CB, CT)	152.09	550.8	0.2217

CP = Critical Point

CT = Cricondentherm

CB = Cricondenbar

EXPERIMENTAL DATA

TABLE V-2

Mole Per cent Propane = 14.68%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
15	DP	110.79	304.0	0.0548
16	BP	110.88	330.5	0.4250
17	DP	119.84	359.7	0.0684
18	BP	119.84	385.2	0.4014
19	DP	129.43	426.4	0.0883
20	BP	129.47	450.6	0.3720
21	DP	139.76	510.6	0.1244
22	BP	139.76	529.5	0.3246
23	BP	145.40	570.8	0.2259
24	BP (CP)	145.40	570.8	0.2244
25	BP	145.08	570.5	0.2546
26	DP	145.39	567.6	0.1906
27	DP	145.11	563.6	0.1793
28	DP	144.75	560.2	0.1700
29	DP	144.46	556.2	0.1641
30	DP	144.06	551.7	0.1589
31	DP	143.28	543.8	0.1496
32	DP	141.94	530.0	0.1374
33	DP	141.91	530.0	0.1376
34	BP	144.46	567.3	0.2734
35	BP	143.62	560.8	0.2875
36	BP	142.58	551.2	0.3015
37	BP	141.07	539.6	0.3142
38	DP (CT)	145.52	570.0	0.2005
39	BP (CB)	145.16	571.8	0.2509
40	BP	135.05	491.2	0.3499
41	DP	99.54	242.7	0.0420
42	BP	99.54	269.4	0.4484
43	DP	92.02	209.3	0.0356
44	BP	92.04	233.8	0.4619

CP = Critical Point

CT = Cricondenterm

CB = Cricondenbar

EXPERIMENTAL DATA

TABLE V-3

Mole Per cent Propane = 30.85%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
45	DP	97.86	269.3	0.0455
46	BP	97.95	317.9	0.4352
47	DP	109.55	339.8	0.0606
48	BP	109.58	387.8	0.4081
49	DP	120.47	419.3	0.0818
50	DP	120.47	419.3	0.0818
51	BP	120.47	462.8	0.3736
52	DP	129.88	498.9	0.1107
53	BP	129.88	545.0	0.3340
54	BP (CP)	137.70	590.9	0.2261
55	DP	137.80	584.8	0.1819
56	DP	137.92	587.2	0.1888
57	DP (CT)	137.92	587.7	0.1900
58	BP	137.02	590.8	0.2588
59	BP (CB)	137.45	591.9	0.2414
60	DP	137.78	585.5	0.1810
61	DP	137.64	582.5	0.1746
62	DP	135.79	560.2	0.1467
63	BP	135.79	583.5	0.2835
64	DP	133.33	534.1	0.1287
65	BP	133.33	564.6	0.3108
66	DP	131.77	518.3	0.1199
67	BP	132.58	558.6	0.3169
68	DP	92.13	240.7	0.0402
69	BP	92.17	287.4	0.4475
70	BP	100.32	330.9	0.4305
71	DP	100.83	285.8	0.0488
72	DP	129.86	499.7	0.1112

CP = Critical Point

CT = Cricondentherm

CB = Cricondenbar

EXPERIMENTAL DATA

TABLE V-4

Mole Per cent Propane = 52.11%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
73	BP (CP)	126.65	614.1	0.2238
74	DP	126.65	600.0	0.1671
75	DP (CT)	127.09	609.8	0.1841
76	BP	125.70	612.1	0.2624
77	DP	125.70	586.7	0.1521
78	DP	126.17	592.6	0.1590
79	BP	125.14	608.6	0.2745
80	DP	125.14	579.4	0.1454
81	BP	123.91	599.5	0.2916
82	DP	123.91	564.5	0.1342
83	BP	121.98	583.9	0.3088
84	DP	121.98	541.5	0.1224
85	DP	119.79	519.5	0.1112
86	BP	119.79	565.5	0.3256
87	DP	109.31	424.8	0.0791
88	BP	109.32	480.4	0.3706
89	DP	99.91	353.3	0.0612
90	BP	99.93	412.2	0.3983
91	DP	88.99	283.7	0.0467
92	BP	89.00	341.3	0.4247
93	DP	79.16	230.0	0.0367
94	BP	79.18	286.2	0.4450
95	DP	73.60	201.9	0.0316
96	BP	73.65	256.4	0.4559
97	DP	114.86	472.1	0.0936
98	BP	114.86	524.4	0.3512
99	DP	126.80	603.7	0.1749
100	DP	127.04	611.2	0.1935
101	BP	125.85	613.3	0.2580
102	BP	115.38	528.4	0.3485
103	BP	126.21	614.6	0.2443
104	BP (CB)	126.43	614.8	0.2347
105	DP	126.94	607.3	0.1810

CP = Critical Point

CT = Cricondentherm

CB = Cricondenbar

EXPERIMENTAL DATA

TABLE V-5

Mole Per cent Propane = 75.45%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
106	BP (CB)	112.97	624.0	0.2217
107	BP (CP)	112.97	624.0	0.2223
108	DP	113.26	624.5	0.2044
109	DP	66.83	233.1	0.0360
110	DP	79.86	311.9	0.0503
111	BP	79.90	362.5	0.4154
112	DP	91.08	392.8	0.0681
113	BP	91.33	441.9	0.3861
114	DP	94.99	424.5	0.0760
115	BP	94.99	472.4	0.3740
116	DP	70.66	250.2	0.0389
117	BP	70.88	305.8	0.4346
118	DP	99.74	467.0	0.0881
119	BP	99.77	511.4	0.3571
120	DP	103.75	503.8	0.1006
121	BP	103.77	546.8	0.3382
122	DP	106.62	534.6	0.1130
123	BP	106.62	572.2	0.3226
124	DP	109.77	570.0	0.1300
125	BP	109.80	600.5	0.2962
126	DP	111.27	588.3	0.1426
127	BP	111.30	613.9	0.2774
128	BP	109.20	596.4	0.3021
129	BP	109.91	602.3	0.2949
130	BP	111.55	616.9	0.2735
131	BP	112.31	622.4	0.2549
132	BP	112.60	623.9	0.2441
133	DP	112.12	600.4	0.1537
134	DP	112.78	609.8	0.1639
135	DP	113.34	621.5	0.1903
136	DP (CT)	113.38	622.8	0.1924
137	DP	113.34	623.4	0.1960
138	BP	111.26	614.4	0.2770
139	BP	112.62	624.0	0.2416
140	BP	111.99	620.3	0.2632
141	DP	113.18	618.2	0.1788
142	DP	112.87	612.2	0.1681

CP = Critical Point

CT = Cricondentherm

CB = Cricondenbar

EXPERIMENTAL DATA

TABLE V-6

Mole Per cent Propane = 82.62%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
143	BP (CP)	108.29	624.7	0.2212
144	BP	108.24	624.7	0.2244
145	BP (CB)	108.12	625.0	0.2334
146	BP	107.80	623.7	0.2504
147	BP	107.98	624.6	0.2413
148	BP	107.60	621.9	0.2615
149	DP	107.61	605.8	0.1568
150	DP	107.82	609.4	0.1622
151	DP	108.49	619.4	0.1802
152	DP	108.60	622.3	0.1889
153	DP	108.59	624.5	0.2023
154	DP	108.37	616.9	0.1736
155	DP	108.22	614.4	0.1686
156	BP	106.68	614.0	0.2778
157	BP	106.93	616.3	0.2740
158	DP (CT)	108.62	623.6	0.1960

CP = Critical Point

CT = Cricondentherm

CT = Cricondenbar

EXPERIMENTAL DATA

TABLE V-7

Mole Per cent Propane = 92.58%

Point Number	Type Point	Temperature (°C)	Pressure (psia)	Density (gm/cc)
159	DP	70.81	335.1	0.0548
160	BP	70.93	358.7	0.4118
161	DP	86.75	461.2	0.0856
162	BP	86.80	481.6	0.3637
163	DP	80.21	405.6	0.0706
164	BP	80.25	427.8	0.3840
165	DP	92.60	516.4	0.1039
166	BP	92.61	534.2	0.3390
167	DP	97.64	568.0	0.1275
168	BP	97.66	582.8	0.3077
169	DP	99.55	589.6	0.1431
170	BP	99.55	602.0	0.2891
171	DP	101.15	608.8	0.1620
172	BP	101.15	617.0	0.2595
173	DP	101.76	618.3	0.1845
174	BP (CP, CB)	101.76	621.5	0.2196
175	BP	101.34	619.5	0.2539
176	DP	101.38	612.8	0.1699
177	DP	101.78	611.8	0.1844
178	DP (CT)	101.92	620.4	0.2045
179	BP	101.54	620.0	0.2456
180	BP	101.72	621.0	0.2308
181	DP	101.87	619.7	0.1915
182	BP	101.69	621.3	0.2330
183	DP	100.36	599.8	0.1528
184	BP	100.40	610.0	0.2780

CP = Critical Point

CT = Cricondentherm

CB = Cricondenbar