Phase Diagram of a Mixture of Natural Gas and Natural Gasoline Near the Critical Conditions

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A PHASE diagram showing boundary curve and quantity of liquid in the two-phase region was determined for a mixture of natural gas and natural gasoline in the region of its critical conditions. The temperatures and pressures of phase measurements were in the range of 85° to 212° F. and 1300 to 2600 lb. per sq. in., respectively, with the critical conditions at 169.5° F. and 2615 lb. per sq. in. abs. Color phenomena were observed in the region of the boundary curve from 102° to 192° F. Approximate densities of the single-phase and two-phase regions and analysis of the system are included.

Boundary curves between the single-phase and the two-phase regions have been determined for several binary mixtures containing hydrocarbons.^{2,3,4,6,7,10,11,12,14} These investigators did not report the relative amounts of liquid and vapor within the two-phase region. The equilibrium values obtained from the dew-point and bubble-point data can be used to compute the lines showing percentage of liquid on the pressuretemperature phase diagram⁸ but the positions of the lines near the critical temperature and pressure are uncertain. Relative amounts of vapor and liquid were obtained for a gasoline and a naphtha¹ within the two-phase area but not in the region of the critical temperature and pressure. The bubble-point and dew-point lines, as well as the percentage liquid lines within the two-phase region, were determined by visual observations in glass apparatus.

Apparatus

An arrangement of the apparatus is given in Fig. 1, showing the Jerguson gauge A with glass windows B. Pressure was supplied by the

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² References are at the end of the paper.

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mercury pump C and measured by a calibrated Bourdon gauge D. Agitation to insure equilibrium was obtained by rocking the entire gauge assembly around axis E-F. A constant-temperature air bath permitted control of the temperature of the gauge. The scale beside the glass



window was used to calibrate the volume of the gauge by mercury displacement. This scale was used to measure the position of the gas-liquid meniscus, if present, and to measure the hydrocarbonmercury meniscus.

VOLUME MEASUREMENTS

The entire system was filled with mercury, to remove air, then natural gasoline was drawn into the gauge through line K, by allowing the

 TABLE 1.—Liquid Percentage as a Function of Pressure and Temperature

 Pressure. Lb.
 Total
 Liquid
 Percent Pressure. Lb.
 Total
 Liquid
 Percent

Pressure, Lb.	Total	Liquid	Percent-	Pressure, Lb.	Total	Liquid	Percent-
per Sq. In. Abs.	Volume, C.C.	C.C.	age Liquid by Volume	per Sq. In. Abs.	Volume, C.C.	Volume, C.C.	age Liquid by Volume
Temperature 85° F.			Temperature 102° F.				
2,500	51.6	Single	phase	2,585	53.0ª	Single phase	
2,483	52.0	49.5	95.2	2,575	53.2	Single phase	
2,425	53.2	42.7	80.2	2,568	53.2	Single	phase
2,317	55.7	37.1	66.6	2,567	53.2	52.6ª	98.9
2,175	59.7	33.3	55.7	2,557	53.4	51.3	96.0
1,935	68.0	29.6	43.5	2,547	53.9	48.9	90.7
1,591	85.8	27.3	31.8	2,525	54.2	44.3	81.5
1,475	93.5	26.4	28.2	2,505	54.9	41.4	75.3
1,325	105.6	24 . 2	22.9	2,580	55.2	38.7	70.1
1,248	113.7	23.5	20.7	2,450	56.1	37.0	65.9
1,160	124.0	22.9	18.5	2,410	57.3	35.4	61.6
1,085	132.6	21.9	16.5	2,350	58.9	33.2	56.4
1,040	139.1	21.9	15.7				
Temperature 119° F.			Temperature 145° F.				
2,605	56.1	Single	phase	2,613	60.0	Single	phase
2,583	56.4	51.8	91.7	2,607	60.0	Single	phase
2,570	56.7	48.7	85.9	2,603	60.1	56.2	93.6
2.558	56.9	46.7	82.1	2,596	60.9	49.0	80.4
2,535	57.6	42.9	74.5	2,590	60.9	47.6	78.2
2,501	58.1	3 9.6	68.1	2,575	61.2	41.6	68.0
2,537	60.0	36.2	60.3	2,537	62.3	36.8	59.1
2,359	62.1	33.4	53.8	2,400	66.3	31.7	47.9
2,272	64.6	31.6	48.8				
2,16 0	68.6	30.1	43.9				
Temperature 151° F.			Temperature 166° F.				
2,609	60.9	Single	phase	2,615	64.0	Singl	e phase
2,605	60.9	Single	phase	2,610	64.2	35.5	55.2
2,600	61.0	56.7	93.0	2,600	64.3	32.8	51.0
2,597	61.2	51.3	83.8	2,585	64.7	31.8	49.1
2,583	61.8	42.9	69.4	2,515	67.9	30.8	45.4
2,560	62.1	37.6	60.5	2,183	78.2	26.0	33.2
2,495	64.2	33.6	52.3	2,000	86.6	25.0	28.9
2,390	67.5	31.0	45.9	1,875	93.1	24.0	25.8
				1,740	101.1	22.1	21.8
				1,595	111.6	21.3	19.1
				1,460	122.9	20.0	16.3
				1,345	134.6	19.2	14.3

^a Experimental volumes \times 0.86 since this run was taken with larger amount of material in system. After this run some of the uniform phase was vented off to give a workable volume for system.

mercury to gravitate to the pump with values H and I open. Natural gas was metered in another glass-windowed gauge at 645 lb. per sq. in. abs. and then injected into line K with the removal of the mercury level

Pressure, Lb. per Sq. In. Abs.	Total Volume, C.C.	Liquid Volume, C.C.	Percent- age Liquid by Volume	Pressure, Lb. per Sq. In. Abs.	Total Volume, C.C.	Liquid Volume, C.C.	Percent- age Liquid by Volume
Те	Temperature 169° F.		Temperature 171° F.				
2,615	64.2	Single	phase	2,615	65.6	Single phase	
2,614	64.3	32.0	49.8	2,605	65.6	Single	phase
2,606	64.5	31.3	48.5	2,603	65.7	Single	phase
2,599	65.1	31.0	47.6	2,595	65.8	26.9	40.9
2,585	65.2	30.5	46.7	2,582	66.1	27.9	42.2
2,560	65.9	29 . 6	44.9	2,570	66.3	28.1	42.4
2,510	67.3	28.9	42.9	2,548	66.9	28.1	42.0
2,167	80.0	25.9	32.4	2,503	68.4	27.9	40.8
1,960	89.7	24.5	227.3	2,235	78.0	26.0	33.4
1,760	100.8	22.0	21.8	2,093	84.2	25.1	29.8
1,390	132.2	20.3	15.4	1,942	91.7	24.4	26.6
				1,773	101.8	22.7	22.3
				1,680	108.0	21.7	20.1
				1,590	114.7	21.0	18.3
				1,495	122.9	20.4	16.6
				1,410	130.8	19.4	14.8
				1,328	140.3	19.4	13.8
Temperature 181° F.			Temperature 181° F. (Continued)				
2,615	67.2	Single	phase	2,530	69.8	26.5	38.0
2,610	67.2	Single	phase	2,285	78.4	25.3	32.3
2,605	67.3	Single	phase	2,163	83.6	25.0	29.9
2,600	67.7	14.5	21.4	2,020	90.3	24.1	26.7
2,592	67.7	22.1	32.6	1,825	101.1	22.0	21.8
2,583	68.0	24.0	35.3	1,688	110.6	21.2	19.2
2,569	68.3	25.3	37.0	1,565	119.6	19.9	16.7
2,559	68.8	25.8	37.5	1,363	139.5	18.5	13.3
Temperature 192° F.			Temperature 212° F.				
2,623	69.3	Single	phase	2,535	76.4	Single phase	
2,590	69.4	Single	phase	2,525	76.5	6.1	8.0
2,579	69.7	5.9	8.5	2,512	77.0	6.9	9.0
2,575	69.8	10.4	14.9	2,475	78.4	10.4	13.3
2,560	70.4	15.7	22.3	2,425	80.0	14.1	17.6
2,540	70.8	18.4	26.0	2,410	80.8	14.9	18.5
2,510	71.7	20.4	28.5	2,350	83.0	16.6	20.0
2,460	73.5	21.8	29.7	2,270	86.4	17.6	20.4
2,395	76.2	22.4	29.4	2,077	95.4	17.6	18.5
2,333	78.7	22.8	29.0	1,935	103.3	16.8	16.3
2,173	85.5	22.3	26.1	1,810	111.2	16.4	14.8
1,888	100.1	20.3	20.3	1,740	116.4	15.8	13.6
1,693	113.3	18.8	16.6	1,645	124.3	15.5	12.5
1,561	123.8	17.9	14.5	1,535	133.2	14.0	10.5

TABLE 1.—(Continued)

to the bottom of the gauge. Gas was added until a brown color appeared at the interface between the vapor and liquid regions, indicating that the critical conditions were likely to be within the temperature and pressure range of the apparatus. Valve J was then closed and all volume changes of the system were made by raising or lowering the mercury level in the gauge.

Previous experiments had shown that the best procedure to obtain the phase diagram was to drop the pressure isothermally from the singlephase region to within the two-phase area.

After each pressure change on the system, the apparatus was rocked to thoroughly agitate the system, insuring equilibrium before volume or pressure readings were taken. The first measurements at 85° F. were considerably below the critical temperature, and so pressure drops in the single-phase region obtainable by withdrawing small quantities of mercury showed the meniscus to appear near the top of the gauge and appear at lower positions with subsequent pressure drops. Following each pressure drop, the measurements of pressure and positions of menisci were recorded after agitation. These data and the calibration curve of the volume of the gauge gave the data for Table 1.

A series of experiments at constant temperatures from 85° to 212° F. was made. The data are tabulated in Table 1 and the percentage liquid values are plotted as a function of pressure for each isotherm in Fig. 2. The pressure drop required to change the system from a uniform phase to a definite percentage liquid became smaller as the temperature was raised above 85° F. (Fig. 2). At 169° F., a pressure drop estimated to be one pound caused the single phase to change to a 50.2 per cent vapor and 49.8 per cent liquid system. At temperatures above 169° F. the meniscus between vapor and liquid appeared near the bottom of the gauge for the first pressure drops, rose with pressure reduction for a small pressure drop, and then receded with larger pressure drops.

PHASE DIAGRAM

The data of Fig. 2 are cross-plotted on the usual coordinates of pressure and temperature with lines of constant liquid quantity as shown in Fig. 3. The phase diagram is qualitatively similar to what might be expected from known properties of hydrocarbon mixtures.^{5,9} The volumetric capacity of the apparatus was not sufficient to reach the lower dew-point curve and the temperatures attainable were below the maximum temperature at which two phases may exist.

The critical conditions of the system are shown to be close to 169° F. and 2615 lb. per sq. in. abs., the point of intersection of the percentage of liquid. The 169° F. points are not evident on Fig. 3 because they practically coincide with the boundary curve. A study of the behavior of the 166°, 169°, and 171° F. isotherms near the uniform phase region of





Fig. 2 indicates that the critical temperature is likely to be about 0.5° F. above the 169° F. Visual observations of the behavior indicate that a temperature can be found at which the meniscus will appear in the middle of the system with an infinitely small pressure drop. This point would then be the exact critical condition, as this condition is boundary to both that of the bubble-point phenomena, where small pressure drops cause the meniscus to appear at the top of the container, and the dew phenomena, where small pressure drops cause the meniscus to appear at



Percentages indicate liquid in system.

the bottom of the container. After agitation adjacent to the critical conditions the entire system was a reddish brown foam. Upon completion of agitation, simultaneous separation of the foam into a uniform but colored phase occurred at the bottom and at the top of the hydrocarbon system. The menisci between the clear phases and the foam traveled from the top and from the bottom toward the middle of the gauge. As the middle was reached, the foam disappeared and a faint meniscus appeared at midposition, showing the upper phase to be gas and the lower to be liquid.

The spacing of the 100, 90, 80, and 70 per cent liquid lines of Fig. 3 at temperatures as far as 60° F. from the critical temperature is at smaller pressure intervals than might have been expected, although computations using carefully predicted equilibrium constants had indicated this condition. The nature of the quality lines in the isothermal retrograde

condensation area above the critical temperatures are as expected. Fig. 3 shows that a dew-point vapor at 178° F. and 2605 lb. will yield 40 per cent by volume of liquid phase by retrograde condensation when dropping the pressure to 2540 lb. at 173° F. Pressure drops on the system in this region often showed condensation of portions of the vapor and boiling of the liquid to occur simultaneously. The composition of the phases could change with no net change in the volumetric proportion of the liquid phase.

It should be noted that no isobaric retrograde phenomena can occur with the mixture chosen.

Color Phenomena

The striking color phenomena¹³ accompanying the measurements near the critical temperature are worthy of note. At pressures considerably above the two-phase region the system was colorless. As the pressure was lowered toward the bubble point or dew point, the single phase took on a reddish color. At temperatures near the critical this color was a bright mahogany red but a faint color effect was perceived in the entire range from 102° to 192° F. The pressure range over which the color persisted on these isotherms was about 20 to 25 lb. The single phase grew in color over a range of about 5 to 10 lb. above the phase boundary and reached its greatest depth just prior to the formation of two phases. The color persisted in both phases in the two-phase region with pressure drops below the boundary as great as 15 lb., although a large reduction in depth of color occurred as this region was entered. A gradual increase in maximum intensity of color occurred as the isotherms approached the critical temperature. There was no evidence that the color described would disappear with added agitation or during the time intervals between experimental observations.

DENSITIES

The information given above was all that was initially expected from the measurements but it was considered worth while to plot the volumes of the system. Fig. 4 gives pressure-volume data for the two-phase system. As little attempt was made to measure the volume of the system in the single phase, the break between the two-phase region and the single-phase region is difficult to obtain unless the pressures were used at 100 per. cent liquid or vapor as given in Fig. 2. These two sources permit computation of the volumes of the system at the singlephase boundary.

A measured volume of the single phase was analyzed by fractional distillation, obtaining the composition given in Table 2. The summation of the weights of the hydrocarbons and the volume of the sample at 2500 lb. and 85° F. gave an approximate density of 0.35 grams per cubic centimeter. The fractionating-column operation was not entirely satis-

Compound	System Having Phase Diagram of Fig. 3, Mol Fraction	System Having $T_{\sigma} = 72^{\circ}$ F., $P_{\sigma} = 2520$ Lb. Mol Fraction
Methane	0.597	.732
Ethane	0.089	.081
Propane	0.050	.027
Butanes	0.049	.026
Pentanes	0.093	.060
Hexanes and heavier ^a	0.122	.074

TABLE 2.—Analyses of Systems

^a The distillation range not determined but may be estimated from the A.S.T.M. of the gasoline used, 80° A.P.I., as follows:

Deg. F.	Percentage Evaporated	Deg. F.
96 107 112 119 127 137	60 70 80 90 E. P Besidue, 1.8 per cent	152 168 189 224 309
	96 107 112 119 127 137	Deg. F. Percentage Evaporated 96 60 107 70 112 80 119 90 127 E. P 137 Residue, 1.8 per cent

factory, and so the analysis and density are not completely reliable. However, the weight of hydrocarbons in the system while the pressurevolume data were being taken was computed as 18.1 grams based on this density. Also, the densities of the system at the single-phase boundary were computed and are plotted as a function of saturation temperature in Fig. 5.

Two points are significant in these data. First, no unusual change is observed in the shape of the pressure-volume curves for the two-phase system as one passes from temperatures below the critical temperature to the region of retrograde condensation. Secondly, the plot of saturated density appears to be a smooth curve for the bubble-point liquid below the critical temperature and for the dew-point vapor above the critical temperature.

MISCELLANEOUS OBSERVATIONS

Preliminary to the above experiments, considerable work was done on asphalt solubility in volatile hydrocarbon solutions. Also, another system was taken to the critical temperature by changing its composition instead of the temperature. The analysis of this critical mixture is given in Table 2 for a mixture having a critical temperature of 72° F. and a critical pressure of 2520 lb. per sq. in. abs. The natural gasoline was the same for both systems reported, but the natural gases, from a Gulf Coast well, differed in the pressure and temperature at which they were separated from a liquid.

The experiments using the 24.4° A.P.I. crude oil,⁸ propane, and natural gas in the glass-windowed gauge showed two significant results.



Fig. 5.—Density of system at bubble points and dew points.

Upon adding a proper ratio of the constituents at room temperature and pressures of the order of 1500 lb., four phases appeared to form; an upper gas phase; a low-density, nearly colorless liquid; a reddish brown denser liquid, and a sludge or plastic solid on the bottom of the container.

The transformation from the single-phase region to the two-phase region was observed for the less dense liquid and the gas phase with the usual brownish red color and without any apparent effect caused by the presence of the second liquid phase. The sludge or solid phase could be blown from the gauge under 1500 lb. pressure. The asphaltic substance so removed was accompanied by some gas but was solid at atmospheric conditions. The asphalt had a molecular weight of 979 as compared to 345 for the original crude, both measurements using the lowering of the freezing point of benzene.

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DISCUSSION

(Charles Warner presiding)

E. A. STEPHENSON,* Lawrence, Kansas.—The phase diagram presented by Dr. Katz deals with an actual natural gas-natural gasoline system, such as is found in many of our distillate pools where no oil is known to be present, or where a gas gap occurs of such magnitude that its phase behavior resembles that of distillate pools.

In view of the current interest in this problem, it seems desirable to express the physiochemical relations in as many different ways as possible; hence the phase data that Dr. Katz has obtained are also presented as functions of the reduced pressure and reduced temperature. These are then plotted to the same scale on both ordinates, so as to eliminate the distortion that results through the use of scales based on pounds and Fahrenheit degrees.

With a critical pressure equal to 2615 lb. per sq. in., and the critical temperature equal to 169.5° F. (629.5 Rankine), it then appears that 0.1 of a unit of reduced pressure represents for graphical purposes 261 lb., and 0.1 of a unit of reduced pressure 63° Rankine. The distortions just mentioned are eliminated when reduced functions of pressure and temperature are used, as shown on Fig. 6.

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DISCUSSION

However, even the modified phase diagram does not reveal the complete story of the relative effects of pressure and temperature changes. If possible, supplementary data on the specific heat of the various gases and liquids should be obtained, and an entropy-enthalpy diagram prepared for the gaseous and liquid components. This is



Fig. 6.—Phase diagram of system composed of natural gas and natural gasoline using reduced pressures and temperatures. Percentages refer to liquid volume.

$P_c = 2615$ lb. per sq. in. abs.; $T_c = 169.5^{\circ}$ F.

by no means an easy task, since the composition of both gas and liquid change with each change in pressure and temperature.

Attention might be called to the greater importance of pressure changes in the general range of 0.9 to 0.96 reduced pressure and 0.9 to 1.0 reduced temperature. On

the other hand, where the temperatures are above $1.0P_r$, and the pressures below $0.9P_r$, the greater influence of temperature change becomes obvious.

Finally, Dr. Katz should be complimented for this excellent contribution to one of the difficult problems which petroleum engineers face today; i.e., the phase behavior of high-pressure wells. Gradually the technique is being developed for the correct solution of the problem.