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UNITED STATES
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BUREAU OF MINES
JOHN W. FINCH, DIRECTOR

REPORT OF INVESTIGATIONS

FLOW CHARACTERISTICS, COMPOSITION, AND SOME LIQUID-PHASE PROPERTIES OF HYDROCARBON FLUIDS FROM A "COMBINATION" WELL

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BY

C. K. EILERTS AND M. A. SCHELLHARDT

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By C. K. Eilerts2 and M. A. Schellhardt3

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INTRODUCTION

Knowledge of the phase relations of the fluids that exist in the porous spaces of rocks constituting natural petroleum reservoirs and of the behavior of these fluids under various field conditions of operation is essential to the conservation of petroleum and natural gas and to their efficient recovery. The problem of determining whether these fluids are in the liquid or gaseous state and of recognizing the transitions that may take place as the material in the reservoir is subjected to different conditions of pressure and temperature confronts many producers today, especially in certain fields. The subject has grown rapidly in importance since the discovery of and production from deeper reservoirs that have correspondingly higher pressures and temperatures as compared with shallower

producing zones. In the shallower fields exploited in earlier years, the phase relations of the hydrocarbons in the reservoirs and during their travel from the reservoir to the surface were less essential factors in operating technique than they are in the deeper fields now being developed.

The tests described and data presented in this report are the preliminary results of a study made by the Bureau of Mines of the phase relations of the fluids in a deep high-pressure and high-temperature reservoir from which gas and hydrocarbon liquid of light gravity were produced. A study of well performance and liquid recovery at several rates of fluid flow, together with analyses of samples taken under conditions of steady flow, gave the essential data for this investigation. The present study, although limited to one well in one field (designated well M throughout this report), is a part of a major investigation of the fluid-energy relationships and the producing characteristics of high-pressure reservoirs. This report has particular application to the solution of problems pertaining to the operation of "combination" wells of the type described.

Terminology suited to a discussion of phase relations in wells of this type has not yet been developed by the industry. Terms commonly used in referring to oil wells and gas wells of the usual type do not meet all the needs for discussion of wells where gas and a light, volatile hydrocarbon liquid are recovered together with a relatively high ratio of gas to liquid. The situation is complicated further because definitions that may have been enunciated in efforts to classify wells on a commercial or regulatory basis, under some conditions may fail to express the purely technical viewpoint.

The terms "distillate" and "condensate" are being used more or less generally by the industry in referring to the liquid produced from wells of the type under discussion, and such wells frequently are called "distillate" wells. However, well M is referred to as a "combination" well, and as this report treats the subject purely on the technical side, the term "hydrocarbon liquid" or, for brevity, "hc liquid" is used.

ACKNOWLEDGMENTS

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The authors gratefully acknowledge the cooperation of the officials of the Tide Water Associated Oil Co., the Seaboard Oil Co., and the Lone Star Gas Co.

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The field work was facilitated by the cooperation of the personnel of the Tide Water-Seaboard Oil Co. and the Lone Star Gas Co., and special acknowledgment is made to T. R. Wade, R. H. Coe, J. C. Dennis, D. M. LaRoe, and J. H. Murrell, Tide Water-Seaboard Oil Co., Cayuga, Tex.; and to L. T. Potter, Lone Star Gas Co., Dallas, Tex.; D. P. Long, Lone Star Gas Co., Palestine, Tex.; and Aubrey Boyd, Lone Star Gas Co., Cayuga, Tex.

The report was criticized and valuable suggestions for its presentation were offered by J. H. Dunn, Lone Star Gas Co., Dallas, Tex.; T. A. Hall and George L. Nye, both of the Tide Water Associated Oil Co., Houston, Tex.; E. L. Rawlins, United Gas Public Service Co., Houston, Tex., and by E. S. Burnett, Chas. B. Carpenter, R. A. Cattell, H. C. Fowler, H. B. Hill, and H. C. Miller, all of the Bureau of Mines. R. C. Wright, Bureau of Mines, Bartlesville, Okla., drew the illustrations.

DESCRIPTION OF WELL

Well M was completed in September 1936 in the Trinity formation of lower Cretaceous age (east Texas-north Louisiana region) at a total depth of 7,558 feet below the surface of the ground. Interpretations of data provided by an electrical log of the formation exposed in the 206 feet of open hole between the casing seat and the total depth of the well indicated that the porosity of the formation varied somewhat and that possibly the lower section of the zone was more productive than the upper section. The pressure in the wellbore at a depth of 7,500 feet was assumed to represent the mean pressure at the face of the productive zone open in the well.

The well was equipped with a string of 7-inch (o. d.) casing set at 7,352 feet, and 7,512 feet of 2 1/2-inch (i. d.) tubing. The wellhead was equipped with a retractable tubing head. Views of the well and separators and of the "Christmas tree" are shown in figures 1 and 2, respectively. A diagrammatic sketch of the essential well and separator connections is shown in figure 3.

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^{4/} All well depths in this report are referred to the level of the ground surface as datum.

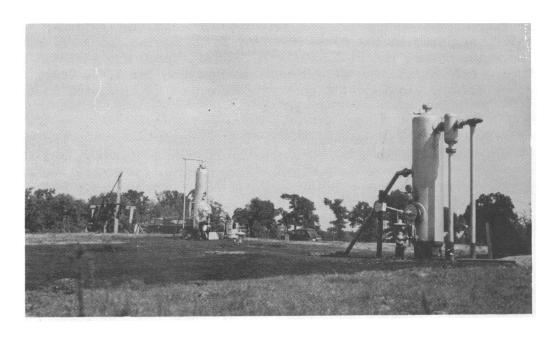


Figure 1.- Field view of wellhead and high- and low-pressure separators.

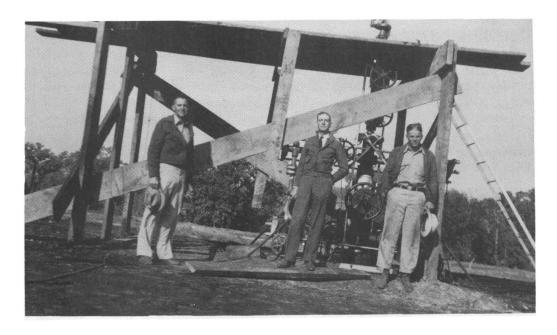


Figure 2.- Wellhead "Christmas tree."

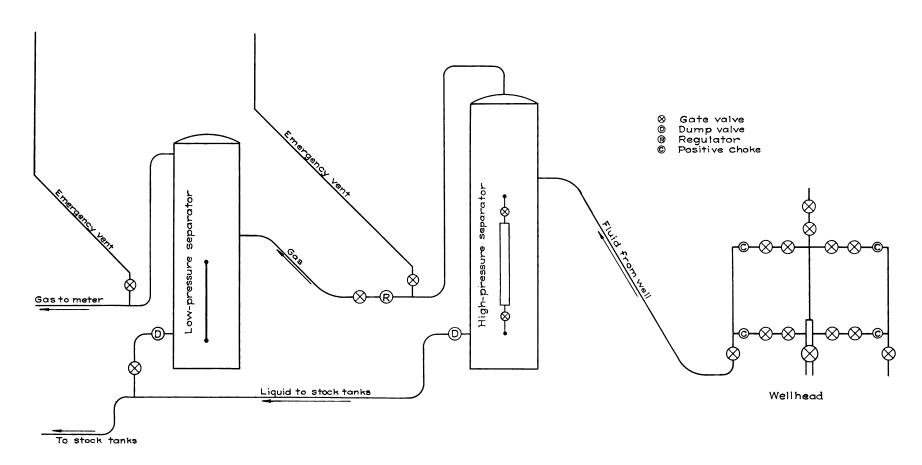


FIGURE 3. - FLOW DIAGRAM SHOWING ESSENTIAL WELL AND SEPARATOR CONNECTIONS

FIELD TESTS

The study of the producing characteristics of well M included two shut-in pressure tests and four flow tests. Ratios of gas to he liquid were determined under four rates of fluid recovery, ranging from a minimum of about 42 barrels of recovered he liquid and 1,650,000 cubic feet of gas (test 2) to a maximum of about 228.5 barrels of recovered he liquid and 9,105,000 cubic feet of gas per 24 hours (test 5). The imposed operating conditions involved changes in the pressure at the face of the productive zone in the well ranging from 3,177 pounds per square inch gage, while the well was shut in, to an operating pressure of 2,381 pounds per square inch gage, when it was flowing at the maximum delivery rate.

Samples of the fluid in the well and of the gas and liquid phases of the fluid in the high-pressure separator were taken during flow tests 2 and 3.

Shut-In Pressure Tests

The first shut-in pressure test (test 1) was made September 25, 1937, after the well had been closed-in for approximately 26 hours. Pressure and temperature gradients in the tubing were determined by lowering the pressure and temperature recording gages by stages from the lubricator on the wellhead to the lower end of the tubing. The second shut-in pressure test (test 6) was made on October 10 after a closed-in period of about 26 1/2 hours following the completion of the flow tests. Pressure and temperature data gaged during the shut-in tests are given in table 1 under tests 1 and 6, respectively. The pressure gradients established in the tubing by the shut-in pressure tests are shown graphically in figure 4.

Flow Tests and Sampling Conditions

Deliveries from the well were controlled by means of positive well-head chokes installed for the tests. The rate of fluid delivery and the well pressures were allowed to stabilize with no subsequent adjustment of the well-control devices except during test 2, when it was necessary to shut the well in for about 20 minutes to adjust the regulator between the high- and low-pressure separators.

The fluid produced from the well was discharged into a high-pressure separator. The liquid phase of the fluid was discharged from the high-pressure separator to the stock tanks, as indicated in figure 3. Gas discharged from the high-pressure separator was delivered into a low-pressure separator. Gas deliveries from the low-pressure separator were metered and discharged into a pipe line. Liquid that accumulated in the low-pressure separator was discharged into the stock tanks. The course of the fluid through the separators is shown by figure 3.

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Well Designation	Test	Date	Stab.	Flow	Тур	×	Wellhead	temp.2/	Wellhe	ad, Choke			s	ıb surfac	e press	urel s	and temp	eratur	2 at d	epths :	desig	na ted								Gas-	he	Gas,	Water	Gravit hc	ies Ges.	High pre	seure	Low-pre sa separat		Atmos-
	no.		period, hrs.	string,	of flo	υ; σε ε: Ω	p- tream rom	Down- stream from choke	Cas- Ting i		0 ft Pres	. 2/ ss. Tem	p. Pre	ft. 2/	200 Press	Oft. . Temp.	400 Press.	Oft. Temp.	5500 Press.	ft. Temp. I	6000 f	t.	6500 f	t. 7	000 ft.	73 ap. Press	500 ft.	7500 Press.	ft. Temp.	liquid ratio, cu.ft. per bbl.	l liqui bbis.	d cu.ft.	bbls.	13.0053	(Air					Press. 6/Temp.2
#Ne Elevation (ground) 301 ft. Top of pay, 7,352 ft.3/ Pembtration, 206 ft.	1	9-24-37 to 9-25-37	26.0	-	-	-	-	-	2	630 -	2585	5 7	7 258	9 103	2728	144	2876	174	-	-	3032	206	-	- 3	134 22	21 3156	5 225	3177	228	-	-	-	-	-	-	-	-			
Oasing, 7-inch set 7,352 ft.3/ Tubing, 2 1/2-inch at 7,512 ft.3/ Total depth, 7,558 ft.3/	2	9-28-37 to 10-3-37	73.0	7x2 1	/8 St	teady	110	33	2215 2	215 3/16	2229	7	4 220	5 114	2326	151	2464	178	2573	201	-	- :	2760	217 2	903 22	22 -	-	3105	229	39,300	42.0	1,650,000	0	61 .	635	250 43	3 :	253 46	:	14.6 93
	3	10-3-37 to 10-6-37	73.0	2 1/2	! St	tea dy	130	52	2500 2	475 1/4	2457	10	2 245	0 138	2604	166	2759	192	2862	210	-	- 2	2930	220 2	965 22	24 -	-	2996	226	34,035	88,6	3,016,000	2.6	60 .6	638	280 61	B 1	255 60	:	14.4 95
	4	10-6-37 to 10-8-37	26.5	7x2 1	/2 St	teady	140	71	23 2 0 2	370 5/16	2335	10	2 232	9 142	2457	170	2580	193	2663	210	-	- 2	2733	217 2	770 22	20 -	-	2809	223	34,800	154.3	5,371,000	1.9	61 .6	543	330 76	5 1	276 70	1	4,6 94
	5	10-8-37 to 10-9-37	25,0	7x2 1	:/2 St	t eady	155	110	1835 2	1/2	1981	. 7	196	2 153	2070	177	2174	194	2261	206	-	- 2	2313 2	210 2	347 21	.2 -	-	2581	21.9	39,800	228,5	9,105,000	2.0	60 .6	555	460 104	. 3	i25 96	1	4.5 68
	6	10-9-37 to 10-10-37		-		-	-	-	2600 2	590 -	2565	9	1 255	3 113	2685	152	2844	176	2950	193	-	- 3	5037	208 34	085 21	.7 -	-	5124	223	-	-	-	-	-	-					

Pressures expressed in pounds per square inch gage.

Temporatures expressed in degrees Pahrenheit.

Depth below surface of the ground.

Liquid recoveries based on volumes at etmospheric pressure and 60°F.

Gas recoveries based on volumes at 14.4 pounds per sq. in., absolute and 60°F.

Atmospheric pressure expressed in pounds per square inch absolute.

Disorepancies in pressures measured at these depths in comparison with pressures measured on tubing at surface are believed to be due to the lack of temperature equilibrium between the recording subsurface gage and the surrounding fluid at these depths.

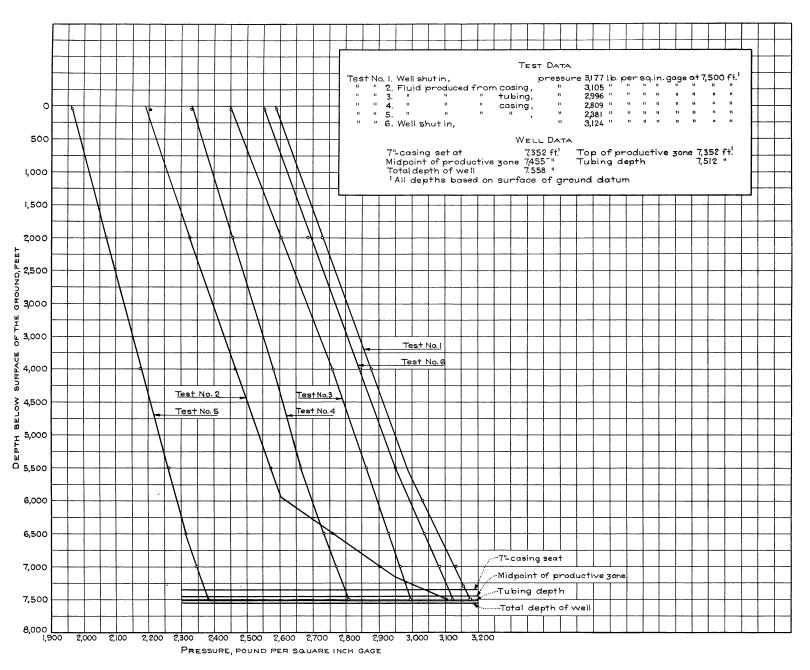
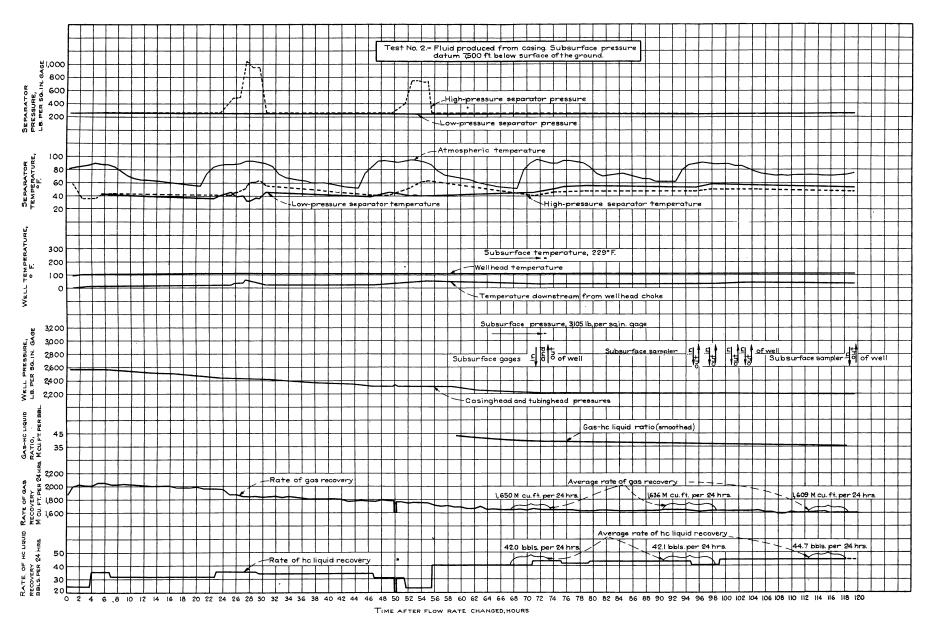
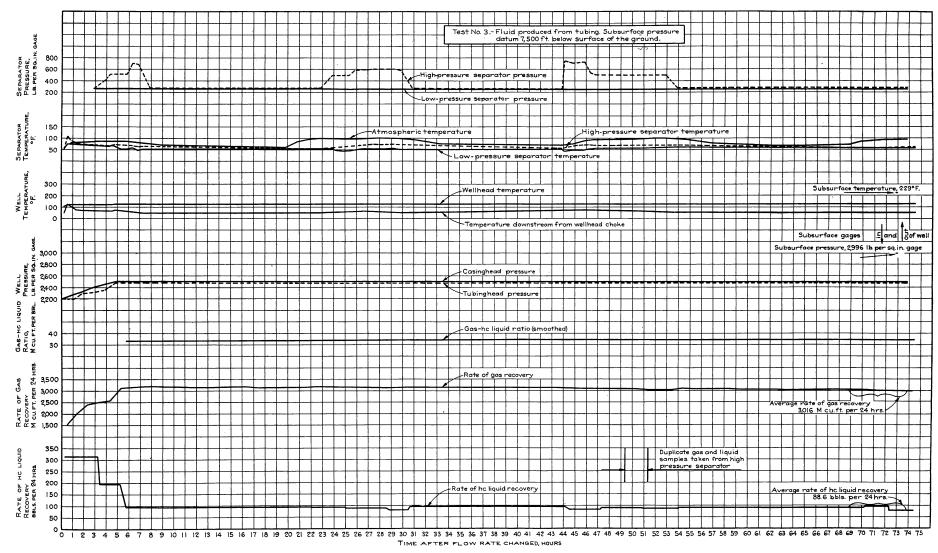


FIGURE 4- RELATIONSHIPS BETWEEN DEPTH AND PRESSURE IN TUBING FOR THE RESPECTIVE TESTS CONDUCTED ON WELL M





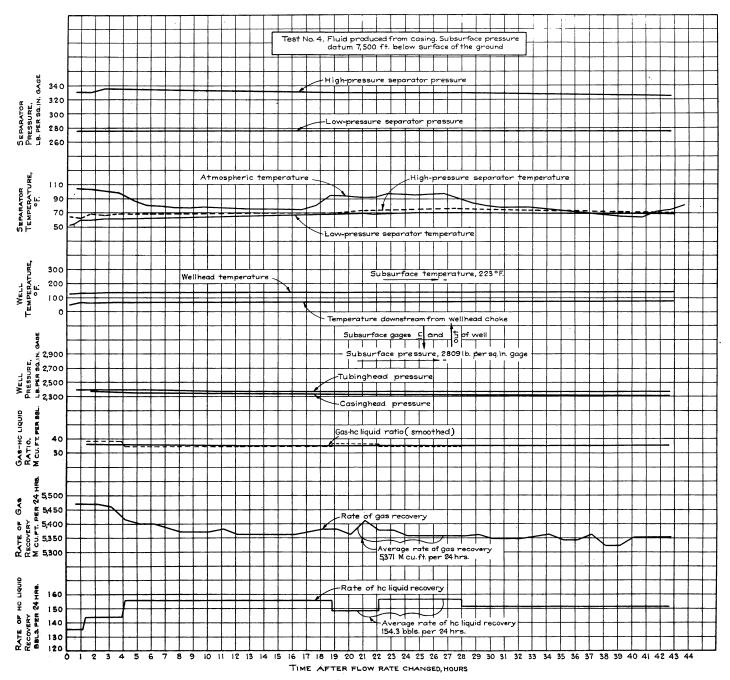


FIGURE 7- PRESSURE, TEMPERATURE AND RATE OF HC LIQUID AND GAS RECOVERY DATA; WELL M, TEST NO. 4

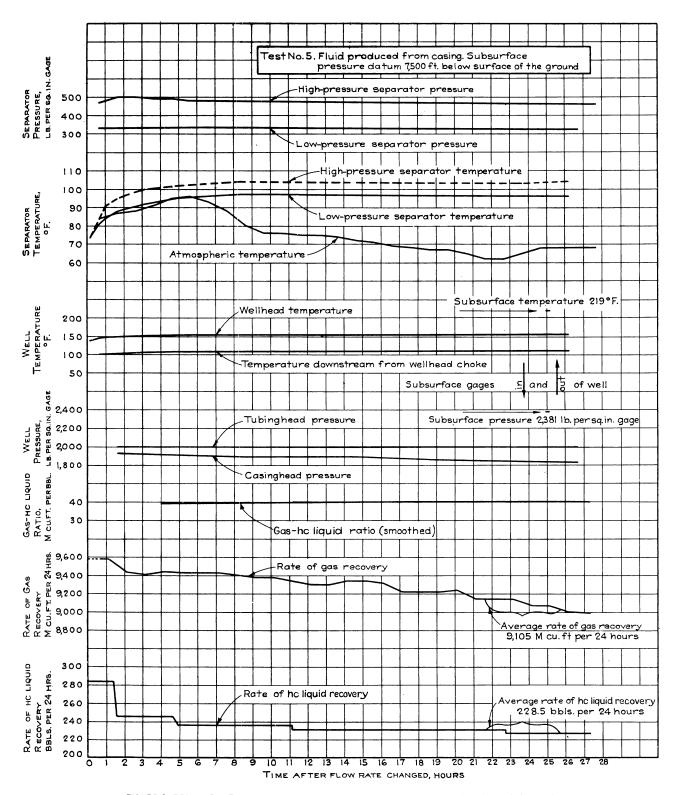


FIGURE 8- PRESSURE, TEMPERATURE, AND RATE OF HC LIQUID AND GAS RECOVERY DATA; WELL M, TEST NO. 5

Data observed and recorded throughout the flow tests included he liquid, water, and gas delivery; casinghead, tubinghead, high-pressure and low-pressure separator pressures, and the pressure on the meter used to measure gas deliveries from the well. Temperatures of the fluid up and down stream from the wellhead choke and in the high- and low-pressure separators were observed at intervals throughout the flow tests. The temperature of the gas phase of the fluid produced from the well was determined at a point downstream from the gas meter.

Gas recoveries from the well were measured by an orifice meter installed on the discharge line from the low-pressure separator. Gasdelivery rates were calculated from orifice-meter data in accordance with the method approved by the American Gas Association, 2/ and the values reported were corrected to base conditions of 14.4 pounds per square inch absolute and 600 F. The data for tests 2, 3, 4, and 5 were plotted against time in figures 5, 6, 7, and 8, respectively. Gas deliveries are shown as the average rate over periods of 1 hour, except for short periods when rapid changes made it desirable to indicate variations in the rate as they occurred. Rates of total liquid (hc liquid and water) and of hc-liquid recovery were calculated from data obtained by gaging the increase in level of the liquids in the stock tanks from time to time throughout the tests. Hydrocarbon liquid-recovery data represent the average rate of delivery during the intervals between the times when the tanks were gaged. Hydrocarbon-liquid and water-recovery data were corrected to a base temperature of 60° F. Casinghead, tubinghead, and separator pressure data are based on the average value of the respective pressures over 1-hour periods. Temperatures represent average values for 1-hour periods. Atmospheric-temperature data represent conditions recorded by an unshaded thermometer.

The respective flow tests are described briefly as follows:

Test 2

Test 2, the initial flow test, was begun on September 28. Fluid was produced from the casing and the delivery rate was controlled by a 3/16-inch positive choke. After a stabilization period of about 23 hours, pressures on the high- and low-pressure separators were about 260 and 250 pounds per square inch gage, respectively. The corresponding temperatures of the fluids in the high-pressure and low-pressure separators were about 41° E and 38° F., respectively. All the liquid was being recovered in the high-pressure separator, and no liquid was accumulating in the low-pressure separator, through which was passed the gaseous phase of the fluid discharged from the high-pressure separator. Since it was desired to obtain samples of the gas and liquid phases of the fluid from the high-pressure separator under relatively high pressure, an experiment was conducted to determine, approximately, the maximum pressure that

^{5/} Gas Measurement Committee Report No. 2, Natural Gas Department, American Gas Association, 420 Lexington Ave., New York, N. Y., May 6, 1935.

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might be maintained on the high-pressure separator with no resultant decrease in the liquid recovery therein and no formation of liquid in the low-pressure separator. First, the pressures were adjusted so that the pressures on the high- and low-pressure separators were 490 and 243 pounds per square inch gage, respectively. Corresponding temperatures were 50°F. on the high-pressure separator and 410F. on the low-pressure separator. Under these conditions, no liquid accumulated in the low-pressure separator. The pressure on the high-pressure separator then was increased and maintained at about 950 pounds per square inch gage. The pressure on the lowpressure separator remained about 243 pounds per square inch gage, and the corresponding temperatures on the high- and low-pressure separators were 62° and 36°F., respectively. Under these conditions, liquid accumulated in the low-pressure separator at the rate of about 3.5 barrels per 24 hours. On the following day (September 30) the pressure on the highpressure separator was increased from the normal operating pressure of about 260 pounds per square inch gage and maintained for about three hours at about 755 pounds per square inch gage.

A summary of the results of the experiment are shown in the following tabulation, which, in addition to the data obtained under the pressure conditions described, also includes the results obtained when a pressure of about 520 pounds per square inch gage was maintained on the high-pressure separator for about 1 1/2 hours during the second flow test (test 3).

Experiment Press., lb. per sq. in.gage Temperature, OF.					Hc liquid, re-
	High→	Low-	High-	Low	covery in low-
	pressure	pressure] 1.		pressure separ-
	separator	separator	separator	separator	ator, bbls.
					per 24 hours.
1 (test 2)	490	243	50	41	0.0
2 (do.)	95 0	243	62	36	3• 5
3 (do.)	755	242	62	40	1.6
4 (test 3)	52 0	255	70	54	0

Subsurface pressures and temperatures in the well were gaged on October 1 after a stabilization period of about 73 hours. The gaged pressure and temperature data and corresponding rates of hc liquid and gas recovery, as well as separator pressure and temperature data are given under test 2, table 1. The pressure gradient in the tubing is shown in figure 4, and pressures and temperatures in the tubing at a depth of 7,500 feet are shown in figure 5.

On the following day (October 2), after a stabilization period of about 98 hours, four attempts were made to obtain a sample of the liquid phase of the hydrocarbon fluid in the well. The sampling depth in the tubing was about 6,700 feet. Only one sample was obtained. On the

following day, as indicated on figure 5, another unsuccessful attempt was made to get a sample of the fluid. As shown by the casinghead and tubinghead pressure data plotted on figure 5, there was little change in these pressures between the time the subsurface pressure was gaged on October 1 and the time the subsurface sample was taken on October 2. It was assumed, therefore, that pressure conditions in the well when the subsurface sample was taken were approximately the same as those that obtained on the preceding day, when the pressure gradient in the tubing showed that the pressure in the tubing at a depth of 6,700 feet was approximately 2,823 pounds per square inch gage (see test 2, fig. 4).

There was no difference between the corresponding values of the casinghead and tubinghead pressures (see fig. 5), probably due to leakage of gas between the tubing and the annular space between the tubing and casing, resulting from the improper seating of the retractable section of the tubing. Thus, wellhead pressures on the tubing and casing tended to equalize under the conditions that prevailed during test 2.

Test 3

The second flow test (test 3) was begun on October 3. Fluid was produced from the tubing, and the delivery rate was controlled by a 1/4-inch positive choke. After a stabilization period of about 3 hours, the pressure on the high-pressure separator was increased from the normal operating pressure of about 280 pounds per square inch gage and maintained at about 520 pounds per square inch gage for about 1 1/2 hours. No liquid accumulated in the low-pressure separator under these operating conditions. Corresponding pressure data on the low-pressure separator and temperatures on the respective separators are described in the tabulated data (p. 8) given in the discussion of the experiment to determine the maximum pressure at which the high-pressure separator might be operated with no resultant formation of liquid in the low-pressure separator.

Duplicate samples of the liquid and gas phases were taken from the high-pressure separator on October 5 after a stabilization period of about 49 hours. Rates of recovery of the respective fluid phases, well pressures, and temperatures were relatively stable before and during the sampling period (see fig. 6).

Subsurface pressures and temperatures were gaged in the tubing on the following day (October 6) after a stabilization period of about 73 hours. The subsurface data are given under test 3 in table 1, and the pressure gradient in the tubing is shown graphically in figure 4. Pressures and temperatures in the tubing at a depth of 7,500 feet are shown on figure 6. Corresponding fluid-recovery rates and well-head pressures were changed only slightly from those that prevailed on the preceding day, when the samples of fluid were taken from the separator. Therefore, it is believed that subsurface pressures at the time the fluid samples were taken from the separator were approximately the same as those gaged on October 6.

Tests 4 and 5

Test 4, the third flow test, was begun on October 6 and was completed on October 8 after a stabilization period of about 43 hours. The fluid was produced from the casing, and the rate of delivery was controlled by a 5/16-inch choke. Subsurface pressures and temperatures in the tubing were gaged after a stabilization period of about 26 hours. Test 5, the fourth flow test, was begun on October 8 and completed on October 9 after a stabilization period of about 27 hours. Fluid was produced from the casing and the rate of delivery was controlled by a 1/2-inch choke. Subsurface pressures in the tubing were gaged after a stabilization period of about 25 hours.

Recovery data, wellhead and separator pressures and temperatures, and subsurface pressures gaged at a depth of 7,500 feet, that were recorded during tests 4 and 5, are shown in figures 7 and 8. Subsurface pressure and temperature data and corresponding fluid recovery and surface-pressure and temperature data are given in table 1. The pressure gradients in the tubing during the respective tests are shown graphically in figure 4.

Results of Flow Tests

Rates of recovery of the gas and liquid phases of the fluid produced from the well, and pressure and temperature conditions in the well and surface recovery system were more nearly stabilized during test 3 than they were during tests 2, 4, and 5.

Graphs are plotted in figures 5, 6, 7, and 8 to show "smoothed" ratios of gas to hc liquid for tests 2, 3, 4, and 5, respectively. There was little change in the trends of the curves showing these ratios during the latter parts of tests 3, 4, and 5, although rates of total fluid recovery were not constant throughout tests 3 and 4 and changed considerably during test 5.

The graphs showing the behavior of the relationship of the gas and liquid phases of the fluid recovered throughout the flow tests shown in figures 5, 6, 7, and 8 were plotted by smoothing plotted data based on the average of the rates of gas and hc liquid recovery for corresponding time periods, as illustrated in figure 7.

Values of cumulative hc liquid and gas recoveriew throughout test 3 were plotted against time, as shown by figure 9. Data on ratios of gas to hydrocarbon liquid based on rates of liquid and gas recovery calculated from these graphs also are plotted against time on figure 9. Comparison of the graphs representing ratios of gas to hc liquid in figures 9 and 6 shows that there was little discrepancy between the results obtained by the respective methods used for "smoothing out" these data.

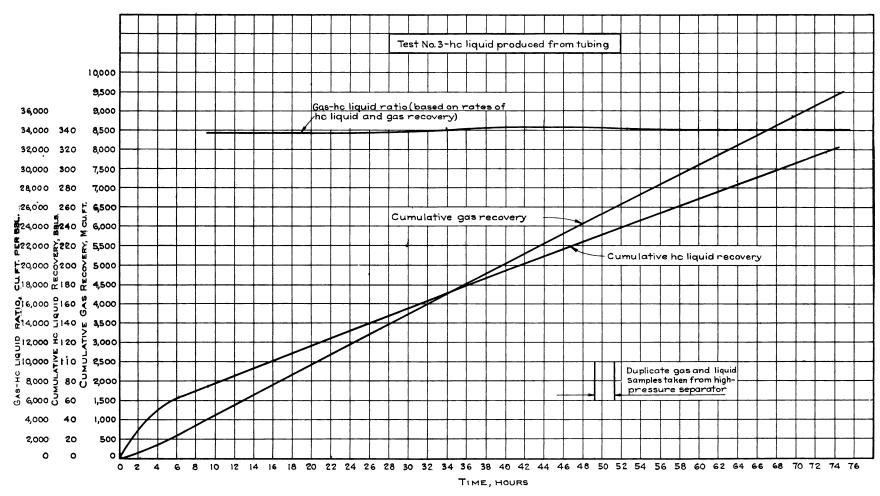


FIGURE 9-CUMULATIVE HC LIQUID AND GAS RECOVERY DATA; WELL M, TEST NO. 3

The results of the flow tests (see table 1) showed that the values of the ratios of the rates of gas recovery to the rates of hc liquid recovery, under the conditions that obtained when the subsurface pressures were gaged during the respective tests, ranged from 34,035 to 39,800 cubic feet of gas per barrel of hc liquid. The range of pressures at the face of the sand was from 3,105 to 2,381 pounds per square inch gage, and rates of recovery ranged from 42 barrels of hc liquid and 1,650,000 cubic feet of gas per 24 hours to 228.5 barrels of hc liquid and 9,105,000 cubic feet of gas per 24 hours. It will be noted that the data plotted on figure 5 show that the ratio of the gas to the hc liquid recovered during test 2 decreased from the value of 39,300 cubic feet of gas per barrel of hc liquid, under the conditions that prevailed during a 6-hour period that preceded the gaging of subsurface pressures, to a value of about 35,900 cubic feet of gas per barrel of hc liquid during a period just preceding the completion of the test. Thus, under the conditions that prevailed during the latter part of the tests, the ratios of gas to hydrocarbon liquid corresponding to tests 2, 3, 4, and 5 were 35,900, 34,035, 35,400, and 39,800 cubic feet of gas per barrel of hc liquid, respectively. Although the ratio of gas to he liquid for test 5 was somewhat greater than the average of the values of the ratios corresponding to tests 2, 3, and 4 that prevailed during periods just before the tests were completed, no attempt has been made to draw any conclusions from this difference, because flow conditions were less stabilized during test 5 than during the preceding tests 2, 3, and 4.

Comparison of the ratios of gas to hydrocarbon liquid that prevailed during the more stabilized periods of the respective flow tests showed, in general, that there was little evidence of change in the relationship between the rates of gas and hc liquid recovery that sometimes characterizes wells completed in reservoirs in which fluid exists in both gaseous and liquid states. Interpretations based on conditions observed during tests 1, 2, and 6, however, suggested either that liquid was formed in the well bore during test 2 or that possibly fluid from the reservoir entered the well in both the gaseous and liquid states. The data obtained in making shut-in pressure tests 1 and 6 showed that probably there was no liquid in the tubing at a depth of 7,500 feet (approximately 58 feet above the bottom of the well) under the conditions existing when the tests were made. It is reasonable to assume, also, that during that period when the well was shut in no liquid was present in the annular space above that level. Leakage that permitted the pressures on the tubing and annular space to equalize at the wellhead (a condition to which previous reference has been made) would have permitted a column of liquid. if present in the well bore, to be present at the same level in the tubing.

Wellhead pressures throughout a period of about 72 hours after test 2 was begun indicated that liquid was accumulating in the well bore (see fig. 5), and subsurface pressures gaged about 72 hours after the start of the test (see fig. 4) showed that the level of the liquid in the tubing was about 1,830 feet above the bottom of the well and that the column

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probably was composed of about 400 feet of water and about 1,230 feet of hydrocarbon liquid. Subsurface data showed that the pressure due to the liquid in the well was equivalent to about 28.6 pounds per square inch per 100 feet of liquid at a pressure of 2,831 pounds per square inch gage and a temperature of 220° F., respectively. The calculated value of the specific gravity of the liquid under these pressure and temperature conditions was 0.660.

The rate of liquid recovery had a generally increasing trend throughout the test. Separator pressures were relatively constant, except for short periods when the pressure on the high-pressure separator was increased for experimental purposes. Temperatures of the flowing fluid at the wellhead were relatively constant throughout the test. The averages of the separator pressures were somewhat higher during the latter period of the test than they were during the early period. Conditions during the latter period apparently were no more favorable for increased liquid recovery in the surface-recovery system than they were during the early period. However, the rate of liquid recovery was materially greater when well pressures indicated that liquid no longer was accumulating in the well than when the pressures indicated that liquid was collecting in the well bore. The indicated accumulation of liquid in the well bore suggests either that some hydrocarbon liquid entered the well with the gas or that the liquid present in the well. was formed in the well under the existing pressures and temperatures, which ranged from about 2,903 pounds per square inch gage and 222° F. at the productive zone to about 2,215 pounds per square inch gage and 110° F. at the wellhead.

PHYSICOCHEMICAL INVESTIGATION OF FLUID-PHASE RELATIONS

Objectives

The primary purpose of the physicochemical investigation was to determine the phase relations of the fluid in the reservoir. The analytical and physical identification of a liquid phase, if one existed, and the evaluation on a component basis of the vapor phase in equilibrium with it determined the emphasis in procedure. Measurement of physical properties of the reservoir vapor phase and, to a degree, the yield of liquid at the surface will be possible by additional laboratory study.

Theory of surface sampling for evaluation of reservoir fluid properties

If samples of liquid and gas could be taken from the separator at a well flowing steadily from an "ideal" reservoir, remixed in the proportions of the measured ratio of gas to hydrocarbon liquid, and brought to solution equilibrium at formation temperature and pressure, the resultant phases would be identical in composition and properties with the corresponding phases in the reservoir at formation pressure and temperature. A well is considered to be flowing steadily when the mass-time rate of production of each component has reached a constant value; and, for the

purposes of the hypothesis, a reservoir is considered ideal when it is of such extent or nature that formation pressure and temperature do not change in the time required for the rate of fluid flow to reach the steady state after mechanical adjustments at the well are made.

The continuous change in composition and properties of the phases along the path of flow from the remote sections of the reservoir, where static formation pressure obtains, to the sand face and up the flow string to the separator does not restrict the hypothesis. It is sufficient that at every point along this path of steady flow the pressure and temperature have fixed values and there is no accumulation or diminution in the mass of a component present. In the over—all view, with steady flow and an ideal reservoir, all material entering the separator must be withdrawn without fractionation from the homogenous reservoir phases which are in equilibrium at the static formation pressure and temperature.

In practice, steady flow, as previously defined, usually is not attainable and a reservoir can not fully satisfy the ideal requirements. The hypothesis applies at a limit, however, which usually may be so closely approached that samples obtained will be dependable for use in interpretation of reservoir phase relations.

Stabilization of the flowing well prior to surface sampling

A flow rate was chosen such that with the high-pressure separator operating at approximately 500 pounds per square inch, the temperature of phase separation would be lower than atmospheric temperature. Under these conditions, previous separator-pressure tests showed that a gas sample would not form a condensate in the storage cylinders.

The field data taken in connection with the stabilization of the selected flow rate have been reviewed in the previous discussion of test 3. Figure 6 illustrates the data that served in the field as criteria of flow stability. Production data for the separator-vapor phase and stock-tank liquidon a cumulative basis (see fig. 9) later were fitted with empirical equations by the method of least squares to facilitate accurate differentiation in the evaluation of the ratio of gas to hydrocarbon liquid. Although the ratio passed through a maximum in the forty-fifth hour of the test, the ratio (34,205 cubic feet per barrel of hc liquid) at the time the sample was taken was varying by less than 0.09 percent per hour 5 hours later and was within 170 cubic feet per barrel of hc liquid of the value attained on the following day. It is believed that indicated uncertainties as to flow stabilization will not be significant in laboratory evaluation of reservoir phase properties.

Sampling procedure

The arrangement of the separator gas-sampling equipment is shown schematically in figure 10. A general idea of the actual size, shape, and position with reference to the separator of the several pieces of equipment may be gained from figure 11. Standard cylinders of approximately 50 liters capacity each were arranged in a position that prevented condensate from collecting in them without being discovered on purging. During the sampling period, gas was admitted to the cylinders simultaneously at intervals until they were at full separator pressure.

The separator liquid-sampling equipment also is shown in figure 10. As the separator was operating below atmospheric temperature, solid carbon dioxide was used to refrigerate the connections from the separator shell to the hand pump. A purging value, placed upstream from the pump and kept open slightly during the sampling period, gave further assurance against warming the liquid and loss of the dissolved gas. The sample was obtained by displacing mercury from the 2-liter liquid sample receiver with separator fluid in the liquid phase under not less than 1,500 pounds per square inch maintained by the hydraulic pump. When I liter of liquid had been transferred in this manner, the upper valve on the receiver was closed and the pressure was relieved on the container by withdrawing the remaining mercury.

Samples of stock-tank liquid were taken during the sampling period in 1-gallon tinned cans.

The subsurface sample of the liquid-phase material was taken prior to the time of surface sampling while the well was flowing through the casing at the rate of 42.1 barrels of liquid per day. The sample, taken at a depth of 6,700 feet and approximately 700 feet below the liquid level in the tubing, was free of water and had a saturation pressure exceeding the tubing pressure at that point.

Procedure in the Laboratory

Preparation of samples for analysis

The specific volume of all liquid samples at reservoir temperature and pressure was measured in the laboratory. Apparatus for measuring specific volumes, as shown in figure 12, included a pycnometer for weighing the sample and an expansion cell for determining the saturation pressure. The stainless-steel pycnometer, weighing approximately 500 grams and having a capacity of 50 cubic centimeters, was used for pressures up to 4,500 pounds per square inch. Diaphragm valves at each end of the pycnometer, similar to the ones used by Sage and Lacey, facilitated complete drainage of mercury and assured positive closure.

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^{6/} Sage, B. H., and Lacey, W. N., Phase Equilibrium in Hydrocarbon Systems. Specific Heats of n-Butane and Propane: Ind. Engr. Chem., vol. 27, Dec. 1935, p. 1486.

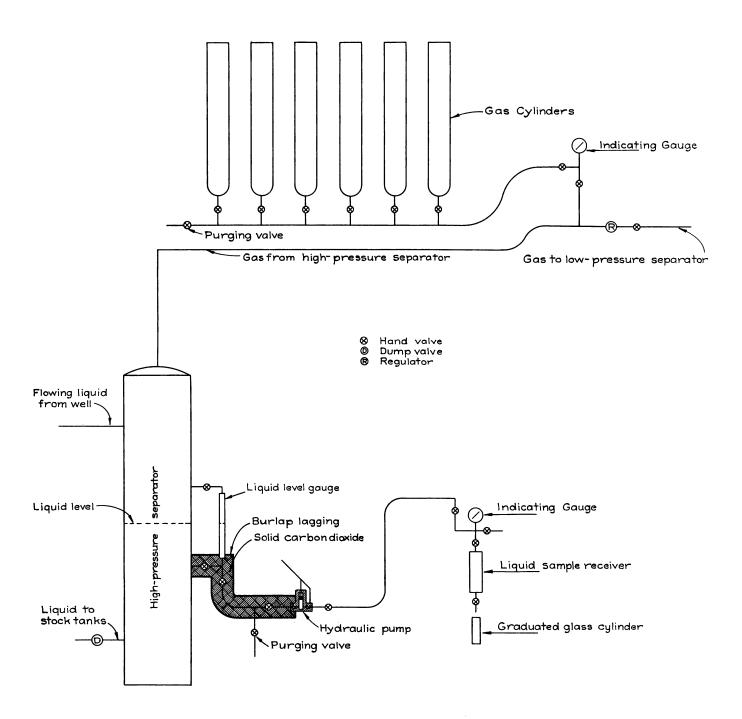


FIGURE 10-SCHEMATIC ARRANGEMENT OF APPARATUS USED IN TAKING VAPOR AND LIQUID-PHASE SAMPLES FROM THE HIGH-PRESSURE SEPARATOR

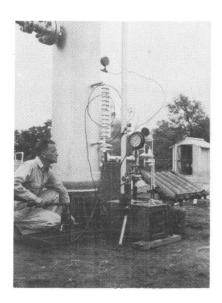


Figure 11.- High-pressure surface liquid sampling apparatus.

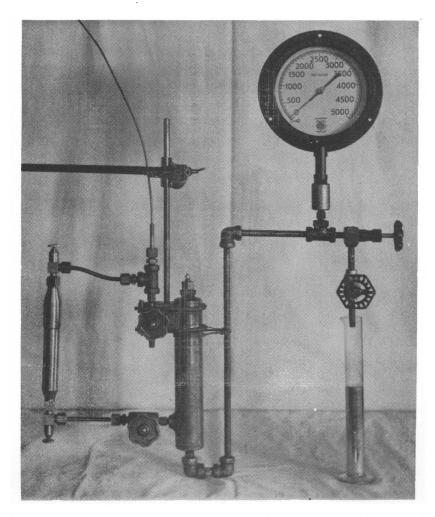


Figure 12.- High-pressure pycnometer and expansion cell assembly.

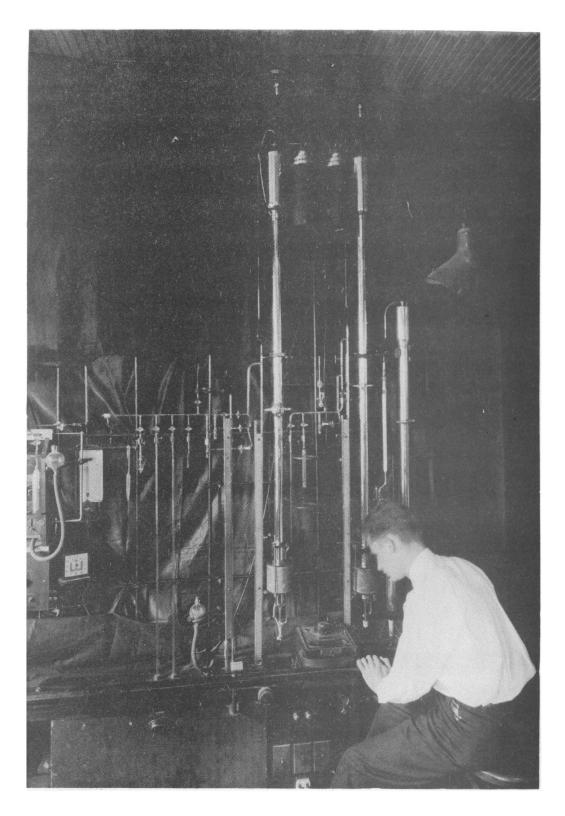


Figure 13.- Fractionating-column assembly.

Transfer of a homogeneous sample of the liquid phase from the assembly was accomplished by displacement of mercury until the pycnometer was full and an excess of approximately 40 cc of liquid was contained in the expansion cell. The apparatus, detached from the sample-storage cylinder, then was placed in an oil bath maintained at reservoir temperature, and additional mercury was removed from the apparatus to lower the pressure to that existing in the reservoir at the time the sample was taken. With the contents of the apparatus at constant temperature and pressure, the pycnometer was closed, removed from the bath, and weighed. Saturation pressure then was determined on the liquid in the cell by isothermal expansion into the two-phase region on removal of additional mercury.

Before any gas was withdrawn for analysis from the storage cylinders, one of them was inverted and the valve opened slightly to be sure no liquid-phase material had been condensed after sampling.

Analysis of Samples

The apparatus for the fractionation of both liquid and gas samples is shown in figure 13. The columns are of single-piece construction of the type described by Podbielniak []. Kettle design, length of reflux section, and condenser proportions were modified [] to facilitate the precise fractionation of hydrocarbon liquid mixtures. The principle of refractionation was applied to each component in succession through two groups of hexanes identified by their range of distillation pressures at the ice point. The maximum fractionation rate, controlled by a fixed orifice, was 500 cc (0.022 gm mol) per hour, with the column operating at a pressure of 300 mm or less of mercury. Nitrogen was determined from the vapor density of a first portion of the methane fraction and its density was measured by means of a glass weighing balloon.

The amount of carbon dioxide in the liquid samples was estimated from the composition of the separator gas and estimated values of equilibrium data.

The liquid that remained after hexanes were removed from the sample is referred to as "C7+ residue." The molecular weights of the residues were determined under the direction of Harry T. Rall, of the Bureau of Mines, using a cryoscopic procedure?

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⁷ Podbielniak, Walter T., Apparatus and Methods for Precise Fractional Distillation Analysis: Anal. ed., Ind. Engr. Chem., vol. 3, April 15, 1931, p. 177.

^{8/} A more detailed description of the columns and the analytical procedure is contemplated for future publication.

^{9/} Rall, Harry T. and Smith, Harold M., Physical and Chemical Properties of Petroleum Fractions. I. Behavior in Dilute Benzene Solution: Analed., Ind. Engr. Chem., vol. 8, Sept. 15, 1936, p. 324.

The results of a complete distillation of the stock-tank liquid by the Bureau of Mines Hempel method are reported in table 8.

The treatment of the gas samples was similar to that for the liquid samples, with the exception that refractionation was not used and distillation pressures were lower on butanes and heavier hydrocarbons. Carbon dioxide was determined by absorption in a potassium-hydroxide solution.

Differential liberation of the subsurface sample at reservoir temperature

A modification of the differential gas-liberation procedure described by Lindsly10 was used on the subsurface sample at the reservoir temperature (2280F.) The results of a checked liberation test are reported in table 2 and illustrated in figure 14. In the fifth and sixth columns of the table, the experimental data have been expressed on a relative basis with the liquid volume as unity at the reservoir temperature and saturation pressure. The curve plotted from these data (fig. 14) has been differentiated graphically to obtain the change in liquid volume that occurred on liberation of a unit volume of gas. Values of the differential are uncorrected for decompression of the liquid phase and changing composition of the liberated gas and are plotted in figure 14 as a function of the cumulative volume of gas liberated with the designation "partial" solute volume. The unit "cubic feet of liquid per cubic feet of gas" applies to liquid at 2280F. and gas at 14.4 pounds per square inch absolute and 600F.

Although the results obtained by differential liberation ordinarily may be considered only approximate measures of the volume changes that take place in the actual production of a subsurface liquid, this interpretation is not justified where a condensate is formed on expansion of the reservoir-vapor phase. The subsurface liquid may be subject to relatively large losses on production by liberation of dissolved gas, as indicated by the liberation data, but the volume of the remaining material is augmented by condensate so that experimental liberation data do not apply in their usual sense.

^{10/} Lindsly, Ben E., A Bureau of Mines Study of a "Bottom-Hole" Sample from the Crescent Pool, Okla.: The Petroleum Engineer, vol. 7, Feb. 1936, pp. 34-40.

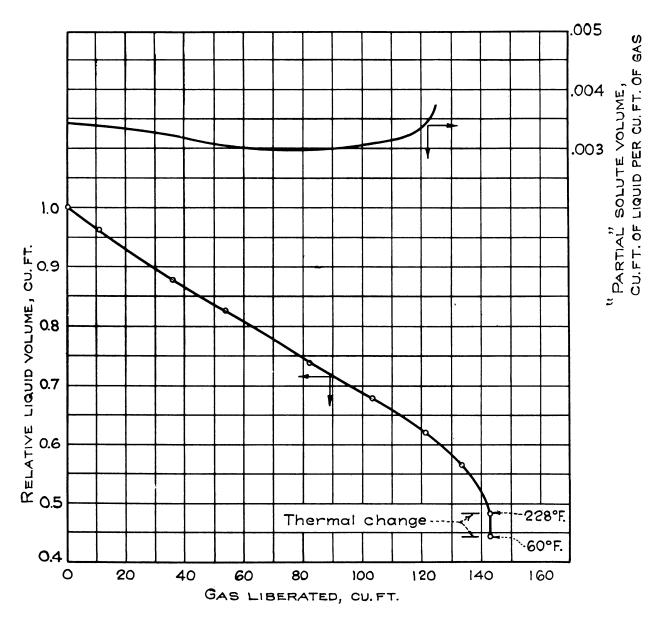


FIGURE 14. RELATIVE LIQUID VOLUME OF THE SUBSURFACE SAMPLE BY DIFFERENTIAL GAS LIBERATION AND PARTIAL SOLUTE VOLUME OF THE LIBERATED GAS AT 228° F.

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TABLE 2. - Differential gas liberation of subsurface liquid sample at reservoir temperature 1/2

	Experimenta	l data		Relative	data	
Pressure, pounds per square inch absolute	Temperature, OF.	Liquid volume,	Liberated gas, cc at 14.4", 60°	Liquid volume, cubic feet	Liberated gas, cubic feet at 14.4, 60°	"Partial" solute volume, cubic feet per cubic foot of gas
3,025	228	117.6	0	1.000	0.0	0.003,43
2,886	228	113.1	1,253	•963	10.7	•003•39
2,516	228	103.2	4,170	•878 ·	35•5	.003,22
2,176	228	97.1	6,271	. 826	53•3	.003,06
1,531	228	86.9	9,633	•739	81.9	.002,98
921	228	79•7	12,120	. 678	103.0	.003,06
345	228	72.8	14,236	.619	121.0	.003,38
69	228	66.5	15,655	•565	133.1	
14.3	228	56.9	16,816	• 484	143.0	dia va
14.3	60	52.3	16,816	•445	143.0	

Note. - Specific volume of the remaining liquid phase at 14.3 lb./in. 2 absolute and 60°F. = 1.288,7 cm⁵/gm.

^{1/} Table, courtesy of Peter Grandone, associate petroleum engineer, and Alton Cook, junior petroleum engineer, Bureau of Mines, Bartlesville, Okla.

Saturation Pressure-Temperature Data on the Subsurface Sample

It was of particular interest to determine whether the sample of liquid taken in the well was that of an accumulation of vapor-phase condensate in the well bore or liquid in the process of production which had been present in the reservoir sands in the liquid phase. Eventually the procedure in determining the original phases in the reservoir will. be to subject separator gas and liquid (mixed in the proportions of the measured ratio of gas to hydrocarbon liquid) to a pressure and temperature identical with that in the reservoir. If a liquid phase results, the physical properties of the liquid and its composition would not be altered if a co-existing vapor phase were removed without changing the temperature or pressure. Then, if the remaining liquid is subjected to a higher pressure and expanded isothermally at reservoir temperature. it should exhibit a saturation pressure equal to the formation pressure, and the gas first appearing as a vapor phase during the expansion would be identical in composition with that which had been removed previously. This identity of phase properties strictly would obtain only at the saturation pressure at formation temperature; at saturation pressures corresponding to other temperatures, the isolated liquid-phase properties would approximate those that would obtain in the presence of the original vapor phase. Within definite limits it should be possible. therefore, to obtain approximate data on the behavior of a two-phase system by experimenting with its isolated liquid phase.

In accordance with this theory, the saturation pressures of the subsurface sample were determined at 200°, 228°, and 260°, using the expansion cell illustrated in figure 12 and a piston gage for precise measurement of pressures. The laboratory work consisted of expanding the liquid phase until a plotted isotherm indicated the presence of a co-existing vapor phase. At the conclusion of the tests, enough separator gas was measured into a known quantity of the subsurface liquid to make its saturation pressure at formation temperature (2280F.) slightly greater than the static formation pressure (3,192 pounds per square inch absolute). The resultant change in composition of the subsurface liquid is shown in table 11. The procedure of determining saturation pressures was repeated at temperatures of 200°, 228°. 260°, and 290°F. With increasing temperature, the change in direction of the isotherm indicating saturation pressure became less and less abrupt. but at 290°F. was indicated positively, and although the critical temperature for the system possibly could be less than this value, the cricondenthermll was definitely greater than 290°F.

^{11/} The cricondentherm is the maximum temperature at which a system of mixed components can be maintained partly in the liquid phase by the application of pressure.

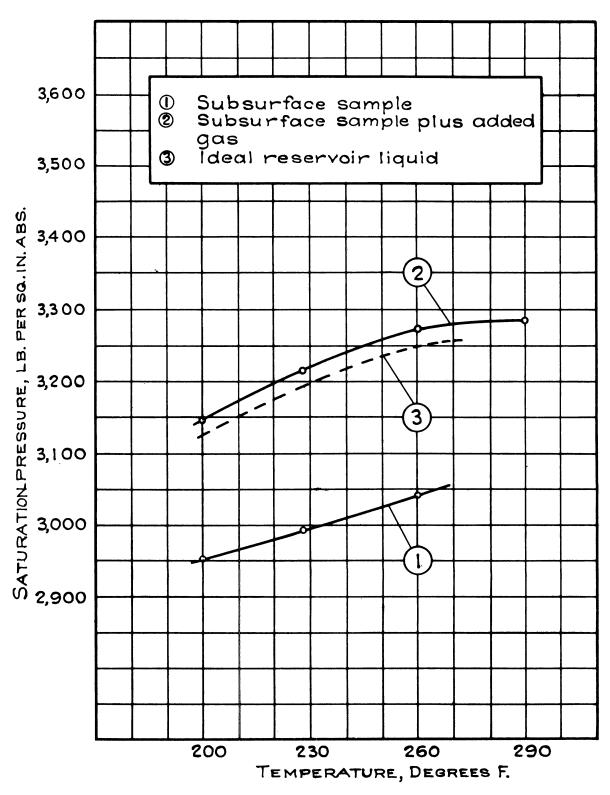


FIGURE 15. - SATURATION PRESSURE ON THE SUBSURFACE SAMPLE AS A FUNCTION OF THE TEMPERATURE BEFORE AND AFTER REPLACEMENT OF LIB - - ERATED GAS

The saturation pressure at formation temperature (228°F.) was always redetermined after saturating pressures at other temperatures had been measured. The results reported in table 3 and illustrated in figure 15 are, with but two exceptions, the mean of two or more determinations and are believed to be accurate to within 5.0 pounds per square inch.

TABLE 3. - Saturation pressures of the subsurface sample before and after replacement of liberated gas

Sample	Saturation pressures at indicated temperature, pounds per square inch absòlute				
	200°F.	2280F.	26 0°F •	290°F•	
Subsurface sample Subsurface sample	2,953	2,994	3,042	•• ·	
plus added gas Ideal reservoir	3,146	3 , 215	3 , 273	3,285	
liquid	3,126	3,192	3,2 ¹ 49		

The positive slope of the saturation-pressure curve shown in figure 15 for the subsurface sample is typical of the liquid to liquid-vapor phase-state boundary. The curve for subsurface liquid plus added gas has a positive slope but is concave downward and more nearly resembles the phase-state configuration of a system near the critical temperature. The "ideal reservoir-liquid" curve is based on values interpolated from the experimentally determined curves and represents the saturation pressures that would obtain on the subsurface sample with enough separator gas restored to it to increase its saturation pressure at formation temperature to 3,192 pounds per square inch absolute.

A more exact procedure (if it had been possible) would have been to have increased the saturation pressure of the subsurface sample by the addition of subsurface gas containing a larger percentage of the heavy components than the gas from the separator. The composition of the resultant liquid, however, would not have been altered appreciably, but the restored subsurface liquid sample would have been more likely to have remained a liquid at formation pressure and temperature.

A consideration of the laboratory results seems to indicate that at least part of the hc liquid produced by the well was liquid phase in the reservoir, and that the remainder of the liquid was formed by condensation of heavy components from vapors existing in the reservoir.

Interpretation of Analytical Results

Definition of Terms Used in Reporting Data

The gram mol is a measure of material quantity and when applied to an ideal gas is equivalent to 0.853,8 cubic feet at a temperature of 60°F. and a pressure of 14.4 pounds per square inch absolute. The gram mol times 453.6 is equivalent to the pound mol.

The term "gm mols/gmC7+" is a statement of composition and expresses the gram mols of a component in a sample containing 1 gram of "C7+" — the residue by fractionation consisting of heptanes and heavier. The "C7+" residues from the stock tank and separator-liquid phases were substantially identical, as indicated by the molecular-weight determinations, and therefore are assumed to be identical for the purpose of tracing the evolution of the liquid phase from the reservoir to the stock tank. The C7+ residue from either the separator or stock-tank sample is designated R. R has the molecular weight 139.9, and 212.6 pounds of R are contained in one barrel of hydrocarbon liquid in the stock tank at 60°F.

The mol fraction is the ratio of the molal quantity of a component in a given system to the sum, expressed in mols, of all components in the system. When the system is solely a vapor phase, the symbol y is used to denote the mol fraction; and for an all liquid system, x is used. The distribution of a component between co-existing vapor and liquid phases at equilibrium is expressed by the ratio y/x.

The reference mass is the mass of a liquid phase containing one gram of a specified heptane plus residue. The unit is grams per gram $C_{7+\bullet}$

The reference volume is the volume at a specified pressure and temperature of a liquid phase containing 1 gram of a specified heptane plus residue. The unit is cm^3 per gram c_{7+} .

The saturation pressure is the minimum pressure required to maintain a fluid in the liquid phase at a given temperature.

Results of the Analysis

The compositions of all samples, as determined by distillation analyses, are reported in tables 4 to 8. Where the reported values are the mean of more than one analysis, a probable error is given for each component based on the observed variation in the experimental results. The probable error is omitted where one result was given more weight than another in evaluating the mean.

Difficulties involved in separating the isomers account for the relatively large probable errors applying to the heavy components. For example, if the analysis of the separator liquid had been expressed without attempting to distinguish the isomers it would appear:

	Gm mol gm C ₇₄	.s x 10 ³
	Mean	Probable error
Butanes Pentanes	1,580,3	0.008,0 .005,4
Hexanes	2 . 17 0, 6	•005, 9

As an average for both the liquid and gas samples, the probable error in separation of components differing in molecular weight was $\pm 0.000,18$ gram mols, or ± 4.0 cc of gas.

The last columns of tables 5, 6, and 7 are submitted for the convenience of those who prefer the quantity unit "cubic feet per barrel. This unit also involves a conception of the quantities of gas that were dissolved in the liquid phases that, in production, became one barrel of hydrocarbon liquid in the stock tank.

The factors required for the computation of the last columns of tables 5, 6, and 7 were developed as follows:

Liquid from the stock tank, having the specific volume 1.3^{14} 7 cm3/gm at 60° F., weighs 260.2 pounds per barrel. From table 5, the reference mass indicates that a pound of heptane plus residue (R) is contained in 1.22^{14} , 11 pounds of hydrocarbon liquid, and one barrel contains 260.2, or 212.6 pounds of residue. The data in column 1 1.22^{14} , 11

of tables 5 and 6 may be read pound mols per pound R, and as the pound mol of gas occupies 387.2 cubic feet at 14.4 pounds per inch² and 60°F., the factor,

$$\frac{\text{cu. ft.}}{\text{1b. mol}}$$
 x 212.6 $\frac{\text{lb. (R)}}{\text{bbl.}}$ = 82,320 $\frac{\text{cu. ft. x lb. (R)}}{\text{lb. mol x bbl.}}$

has been used on the first column to obtain the last column, which bears the unit cubic feet per barrel of stock-tank liquid. The units employed in the last column are those commonly used and accepted, and it is recognized that the heavier components in the pure state would not exist as vapor at the standard pressure and temperature base.

The above factor alone was not sufficient for the computation of the last column of table 7 for the reason that the heptane plus residue from the subsurface sample was not identical with the corresponding residues (R) at the separator and stock tank. The molecular weight of the subsurface residue was 163.7, as against 139.9 for the residue (R), and it is apparent that condensates of heptanes, octanes, and perhaps appreciable quantities of heavier components from the coexisting vapor

phase were added to the subsurface residue in the process of production. To facilitate useful interpretations of the analytical data without engendering unacceptable errors pertaining thereto, an assumption was made as to the quality of the condensate, which would account for the change in molecular weight of the subsurface sample residue.

From the Hempel distillation data presented in table 8 and the relative vapor pressures of heptane and octane at reservoir temperature it is estimated that the heptane and heavier condensate had an average molecular weight of 104.1. Accordingly, every gram of the residue (R) contains X grams of this condensate, as determined by the relation:

$$\frac{1}{139 \cdot 9} - \frac{X}{104 \cdot 1} = \frac{1 - X}{163 \cdot 7},$$

from which X = 0.2972 gms and 1 - X = 0.7028 gms. This equation implies that the component quantities that were in the subsurface liquid with 0.7028 grams of its C₇₊ residue ultimately became (through loss of ethane and lighter and accumulation of propane and heavier condensate) the amount of separator liquid that contained 1.000,0 grams of the residue (R). Accordingly, the quantities, gas in solution, and reservoir-liquid volume relating the subsurface sample to the separator and stocktank samples, involve the use of the factor 0.7028. This factor was used in compiling the last column of table 7.

TABLE 4. - Analysis by fractionation of separator gas-(separator operating at 525.3 lb./in.²
absolute and 71.40F.)

	Perc	Percent by volume				
Component	Mean	Probable				
		error				
Carbon dioxide	1.155	0.045				
Nitrogen	2.128	•023				
Methane	88.266	.062				
Ethane	4 . 8 0 5	•059				
Propane	1.962	•066				
Iso butane	•492	.021				
Normal butane	.420	-				
Iso pentane	•250	-				
Normal pentane	.100	₩				
135-56 hexane	•110					
56-35 hexane	.072	_				
Heptane plus	240					
	100.000					

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TABLE 5. - Analysis by fractionation of sample at stock tank liquid

(Average temperature, 81° F.; barometric pressure, 14.5 lbs./in.2)

Component	$\frac{\text{Gm mols}}{\text{gm C}_{7+}} + 10^3$	X mol fraction	Gms gm C ₇₊	Cu. ft. bbl. stock-tank liquid
Carbon dioxide	.000,0	.000,00	.000,00	•00
Nitrogen	.000,0	.000,00	.000,00	•00
Methane	.003,5	.000,35	.000,06	•29
Ethane	.014,1	.001,40	.000,42	1,16
Propane	•053,8	.005,36	.002,37	4.43
Iso butane	.111,5	.011,10	.006,47	9.18
Normal butane	.239,6	.023,86	.013,91	19.72
Iso pentane	• 14714 , 14	.047,25	.034,20	39.05
Normal pentane	•369,5	.036,80	.026,64	30.42
135-36 hexane	.800,8	.079,76	.068,96	65•92
56-35 hexane	.825,4	.082,21	.071,08	67.95
Sum	2,892,6	.288,09	.224,11	238.12
C7+ residue	7.1480	.711,91	1,000,00	
Total	10.0406	1.000,00	1.224,11	

Note. - Specific volume of sample at 3,192 lb./in.² abs., 228° F = 1.427,9 ± .001,3 cm.³/gm. Specific volume of sample at 14.4 lb./in.² abs., 60° F = 1.347 ± .000,5 cm.³/gm. Specific volume of residue at 14.4 lb./in.² abs., 60° F = 1.310,8 - cm.³/gm.

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TABLE 6. - Analysis by fractionation of sample of separator liquid (Separator operating at 525.3 lb./in.² absolute and 71.40 F.)

Component	Gm : gm	nols + 10 ³	X, mol	Gms gm C ₇₊	Cu. ft. bbl. stock-tank liquid
	Mean	Possible error	fraction	D 1±	SUUL SUUL DAIR TIQUIU
Carbon dioxide	0.012,8	-	0.000,75	0.000,56	1.05
Nitrogen	.023,5	0.002,8	.001,39	.000,66	1.93
Methane	2.573,7	.007,4	.151,75	.041,26	211.87
Ethane	.782,6	.009,6	.046,14	.023,51	64.43
Propane	.955,6	.008,3	.056,34	.042,11	78.67
Iso butane	.607,0	.012,9	.035,79	.035,25	49.97
Normal butane	•973,3	.004,8	•057,39	.056,53	80.12
Iso pentane	1.089,3	.020,2	.064,23	.078,54	89.67
Normal pentane	.624,6	.025,6	.036,83	.045,03	51.42
135-56 hexane	1.176,1	.052,7	.069,34	.101,28	96.82
56-35 hexane	•9945	.058,6	.058,63	.085,64	81.87
Sum	9.813,0	.030,8	•578,57	.510,37	807.82
C7+ residue	7.1480		.421,43	1.000,00	
Total	16.961,0		1.000,00	1.510,37	

Note. - Specific volume of sample at 3,192 lb./in.² abs., 228° F. = 1.578,7 \pm .001,5 cm.³/gm. Specific volume of residue at 14.4 lb./in.² abs., 60° F. = 1.315,0 \pm .000,1 cm.³/gm.

TABLE 7. - Analysis by fractionation of sample of subsurface liquid (formation pressure, 3,192 lb./in.² absolute; formation temperature, 228°F.

Component	Gm mols gm C7+	$\frac{\text{Gm mols}}{\text{cm}} \times 10^3$		Cms gm C ₇₊	Cu. ft. bbl. stock-tank liquid
oomponent	Mean	P. E.	mol fraction	8 / +	Soll Stook talk liquid
Carbon dioxide	0.078,2	-	0.003,28	0.003,44	4.52
Nitrogen	•144,1	0.011,1	.006,04	•00,4 •0,4	8.34
Methane	11.320,8	.009,8	•474,26	•181,49	654.97
Ethane	1.897,9	.019,7	.079,51	•057,03	109.80
Propane	1.200,3	.008,2	.050,28	.0 52 , 89	69.45
Iso butane	•533,5	.009,0	.022,35	•030,99	30.87
Normal butane	.708,9	.007,1	.029,70	.041,17	41.01
Iso pentane	.570,3	.009,1	.0 23 , 89	.041,12	33.00
Normal pentane	•331,2	.005,4	.013,87	.023,88	19.16
135-56 hexane	•535,3	.009,3	.022,43	•046,09	30.97
56-35 hexane	•441,1	.021,3	.018,48	.037,99	25,52
Sum	17.761,6	.010,5	.744,09	•520,13	1,027.61
C7+ residue	6.1087	_	•255,91	1.000,00	
Total	23.8703		1.000,00	1.52013	

Note. - Specific volume of sample at 3,192 lb./in.² abs., $228^{\circ}F$. = 1.849,9 \pm .002,0 cm³/gm. Specific volume of residue at 14.4 lb./in.² abs., $60^{\circ}F$. = 1.274,9 \pm .000,1 cm³/gm.

TABLE 8. - Analysis of liquid from stock tank of well M by the Bureau of Mines Hempel method 1/

GENERAL CHARACTERISTICS

Specific gravity 0.738

A.P.I. gravity 60.2°

Percent sulphur less than 0.1

Color lighter than N.P.A. no.1

Saybolt Universal viscosity at 77°F. less than 32 seconds

Saybolt Universal viscosity at 100°F. less than 32 seconds

DISTILLATION

Dry distillation

Barometer 742 mm

First drop: 31°C. (88°F.)

Temperature, oc.	Per- cent cut	Sum, per- cent	Sp. gr. of cut	oA.P.I. of cut	Viscosity at 100°F.	Cloud test, OF.	Temperature,
Up to 50 50 - 75 75 - 100 100 - 125 125 - 150 150 - 175 175 - 200 200 - 225 225 - 250 250 - 275	3.7 9.7 16.1 18.2 10.1 12.3 8.8 6.7 5.0 4.4	3.7 13.4 29.5 47.7 57.8 70.1 78.9 85.6 90.6 95.0	0.639 .667 .703 .731 .746 .760 .771 .784 .797	89.9 80.6 69.8 62.1 58.2 54.7 52.0 49.0 46.0 43.2			Up to 122 122 - 167 167 - 212 212 - 257 257 - 302 302 - 347 347 - 392 392 - 437 437 - 482 482 - 527

Carbon residue of residuum less than 0.1%. Carbon residue of crude, nil.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	OA.P.I.	Viscosity
Light gasoline	29.5	0.683	75•7	_
Total gasoline and naphtha	78.9	0.724	63.9	
Kerosene distillate	16.1	-795	46.5	
Gas oil	-	-		
Nonviscous lubricating distillate	-	-	-	50 → 100
Medium lubricating distillate				100 - 200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	3.7	. 836	37.8	
Distillation loss	1.3	-		

¹ Analyzed by E. L. Garton under the direction of E. C. Lane, Nov. 4, 1937.

Physical Properties of the Liquid-Phase Samples

The specific volume of the liquid-phase sample at formation pressure and temperature and the saturation pressure at formation temperature were determined on all liquid samples prior to analysis. Expression of the analytical results on a mass basis provided the "reference mass" previously defined. The product of the specific volume and the reference mass gave the reference volume as follows:

$$\frac{\text{cm}^3 \text{ of liquid}}{\text{gm of liquid}} \times \frac{\text{gm of liquid}}{\text{g } \mathbf{C}_{7+}^2 \text{ contained}} = \frac{\text{cm}^3 \text{ of liquid}}{\text{gm } \mathbf{C}_{7+}}.$$

These data are reported in table 9.

Where the C7+ residues of samples from different points in the producing system are identical, the reference volume serves as a reliable quantitative indication of the change that occurred in the volume of the liquid phase as it was produced. In the last column of table 9 the separator and stock-tank liquids that had identical residues are compared on a relative basis. Because the C_{7+} residue from the subsurface liquid sample was much heavier than the residues from the separator and stock-tank samples, the factor 0.7028, the origin of which already has been given, was used to adjust the reference volume of the C7+ residue of the subsurface liquid sample so that it would be referred to the residue R of the surface samples. The relative liquid volumes evaluated in this manner indicate that the volume of subsurface liquid phase, which ultimately was included in one barrel of stock tank liquid, was increased by condensate from the co-existing vapor phase in expanding to separator pressure, and that between the separator and the stock tank was a decrease in volume of liquid because of liberation of dissolved gas.

TABLE 9. - Physical properties of the liquid-phase samples

	Saturation	Specific	Reference	Reference	l .
Sample	pressure,	volume,	mass,	volume,	liquid,
	1b./in.2	cm ³ /gm	gms	cm ²	volume
	absolute		gm C7+	gm C7+	
Subsurface sample				·	
at 3,192 lb./in.2 abs.	2,994	1.849,9	1.520,13	2.812,1	1/1,198,6
and $228^{\circ}F_{\bullet}$		+.002,0		·	
Separator liquid		_			
at 3,192 $1b./in.^2$ abs.	819	1.578,7	1.510,37	2.384,4	1,446,1
and 228°F.		+.001,5		- ,	·
Stock-tank sample		_			
at 3,192 lb./in.2 abs.	100	1.427,9	1.224,11	1.747.9	1.060,1
and 228°F.		+.001,3			
Stock-tank sample				1	
at 14.4 lb./in.2 abs.	_	1.347,0	1.224,11	1.648.9	1.000,0
and 60°F.		+.000.5	, , , , ,		, .
	<u> </u>	1	1	1	<u> </u>

^{1/} Referred to the residue (R) by estimate. 6526 - 27 -

Composition of the Flowing Fluid and of the Reservoir Phases

The ratio of gas to hydrocarbon liquid at the time the separator samples were taken was 34,205 cubic feet of separator gas per barrel of hydrocarbon liquid produced in the stock tank. As separator liquid rather than stock-tank liquid is mixed with gas in a laboratory preparation of the flowing fluid system, the proportions required will be evaluated from the following factors, each of which has been discussed previously:

34,205 cu. ft. gas bbl. stock-tank liquid
$$\left(387.2 \text{ cu. ft. gas} \times 212.6 \text{ lb. R} \right) = 0.415.5 \frac{\text{lb. mol gas}}{\text{lb. R}}$$
 or 0.415,5 gm mol gas gm R

The resulting datum may be expressed as the gram mols of separator gas required for mixing with an amount of separator liquid that contains one gram of the residue (R) to obtain a system having the composition of the flowing fluid. The second column of table 10 shows the amount of gas required on a component basis, the third column is taken from table 6, and the values given in the fourth column are the sums of the values given in the second and third columns. The composition of the fluid is expressed on a mol-fraction basis in the last column of the table. It is this mixture of separator liquid and gas that will be used later in a more exact evaluation of reservoir-fluid properties.

The composition of the reservoir-liquid phase has been estimated from the compositions of the subsurface sample and the separator gas that was added to it to increase its saturation pressure. By interpolation of the experimental data secured during the saturation pressure tests, it is estimated that for each reference mass of subsurface liquid used, 0.001,255 gm mols of separator gas are required to increase the saturation pressure to 3,192 pounds per square inch absolute. In the second column of table 11 the computed amount of each component added to the subsurface liquid as gas is given. The totals for each component of the estimated reservoir liquid phase appearing in the fourth column have been expressed on a mol-fraction basis in the fifth column.

Although the separator gas was not of the proper composition for restoring the saturation pressure of the subsurface liquid to exact formation conditions, the possible effect of this discrepancy may be estimated by comparing the magnitudes of the results expressed in the second and fourth columns of table 11. The gas that was lost by the subsurface sample probably had a composition approaching that given in the last column of table 12.

It has been shown previously that for every reference mass of liquid produced in the stock tank, one reference mass of liquid at the separator and 0.7028 reference mass of subsurface liquid were involved. On the further assumption that the factor 0.7028 will apply approximately to the ideal

reservoir liquid phase as given in table 11, the estimated composition of the reservoir vapor phase is as given in table 12. In the second column of table 12 the quantity of ideal reservoir liquid involved in flow is referred to the residue (R), and in the fourth column the reservoir liquid has been subtracted from the total flowing fluid. The remainder is necessarily ideal reservoir vapor phase and its composition on a mol-fraction basis is given in the last column.

The method of estimating reservoir vapor-phase composition does not imply that of the total fluid in the reservoir, 0.017,66 / 0.432,46 mol fraction is liquid and 0.414,80 / 0.432,46 mol fraction is gas. On the contrary, the method is based upon the theory that at the particular stabilized flow rate that furnished the surface samples, hydrocarbons were withdrawn from the reservoir liquid and vapor phases in these respective molal proportions.

Equilibrium Data

One of the more successful methods of predicting the distribution of a component between the co-existing vapor and liquid phases of a natural hydrocarbon system at equilibrium involves the so-called equilibrium "constant" (mol fraction in the vapor phase divided by mol fraction in the liquid phase). Values of $\frac{y}{x}$, however, for a given component at a given pressure and temperature vary somewhat from one system to another, depending upon the composition of the system. Until the extent of this variance is predictable it is significant to identify a system by its equilibrium constants.

The compositions of the co-existing phases in the high-pressure separator were determined, and the composition of the reservoir phases were estimated so that equilibrium data are indirectly available on the fluid from well M. These data are given in the first and third columns of table 13 in as many significant figures as are considered reliable. The data of Katz and Hachmuth 12 at corresponding pressures and temperatures, obtained on a crude oil from the Wilcox sand in the Oklahoma City field with apparatus specifically designed to insure equilibrium, are shown in the second and fourth columns of table 13 for comparison.

At the lower pressure, the principal variation between the two samples is in the values for methane. At the higher pressure and temperature there is the same order of variation for methane and an increased difference in the values for the heavy components. Although the greatest differences are to be expected at the higher pressures, a conclusion concerning them probably is not justified without further experimentation.

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^{12/} Katz, D. L., and Hachmuth, K. H., Vaporization Equilibrium Constants in a Crude Oil-Natural Gas System: Ind. Engr. Chem., vol. 29, September 1937, p. 1072.

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TABLE 10. - Composition of the flowing fluid on the basis of separator-phase data

	-	G			
Component	Separator gas, mol fraction, Y	Vapor phase required, 0.415,50 Y	Liquid phase required	Composition of fluid	Fluid, mol fraction
Carbon dioxide	0.011,55	0,004,799	0.000,013	0.004,812	0.011,127
Nitrogen .	.021,28	.008,842	.000,024	.008,866	.020,501
Methane	.882,66	.366,745	.002,574	•369,319	•853 , 99 0
Ethane	.0 48 ,0 5	• 0 19,965	.000,783	.020,748	.047,976
Propane	.0 19 , 62	.00 8 , 152	•000,956	.009,108	•021,061
Iso butane	.004,92	.002,044	.000,607	•002,651	.006,130
Normal butane	.004,20	•001,745	.000,973	.002,718	.006,285
Iso pentane	.002,50	.001,039	•001,089	.002,128	.004,921
Normal pentane	.001,00	.000,416	•000,625	.001,041	.002,407
135-56 hexane	.001,10	.000,457	•001,176	•001,633	•003,776
56-35 hexane	.000,72	.000,299	•000,995	.001,294	•002,992
C ₇₊ residue	.002,40	•000,997	•007,148	.008,145	.018,834
	1.000,00	•415,500	•016,963	.432,463	1.000,00

TABLE 11. - Estimated composition of the reservoir liquid phase

		(gm i			
Component	Separator gas, mol fraction, Y	Gas added, 1.255,09 y	Subsurface liquid sample	Ideal reservoir liquid	Ideal liquid, mol fraction, X
Carbon dioxide	0.011,55	0.014,50	0.078,22	0.092,72	0.003,69
Nitrogen	.021,28	.026,71	•144,11	.170,82	•006,80
Methane	.882,66	1.107,82	11.320,75	12.428,57	•494,66
Ethane	. 048 ,0 5	.060,31	1.897,86	1,958,17	•077,94
Propane	•019,62	, .024,62	1.200,31	1,224,93	•048,75
Iso butane	.00 4 , 92	.006,18	•533,50	•539,68	.021,48
Normal butane	•004,20	.005,27	•708,94	•714,21	•028,43
Iso pentane	•002,50	•003,14	•570,29	•573,43	•022,82
Normal pentane	.001,00	.001,25	•331,22	•332,47	•013,23
135-56 hexane	•001,10	•001,38	•535,29	•536,67	.0 21,36
56-35 hexane	.000,72	.000,90	•14141,114	.442,04	.017,59
Sum		1.252,08	17.761,63	19.013,71	•756,75
C ₇₊ residue	•002,40	.003,01	6.108,73	6,111,74	•243,25
Total	1.000,00	1.255,09	23.870,36	25.125,45	1,000,00

TABLE 12. - Estimated composition of the reservoir-vapor phase

	Reservo	oir liquid	Flowing fluid,	Reservo	ir vapor
Component	gm mols gm C7+	gm·mols gm R	gm mols gm R	.gm mols gm R	Mol fraction
Carbon dioxide	0,000,093	0.000,065	0.004,812	0.004,747	0.011,444
Nitrogen	.000,171	.000,120	.008,866	.008,746	.021,085
Methane	.012,429	.008,735	•369,319	.360,584	.869,290
Ethane	.001,958	.001,376	.020,748	.019,372	.046,701
Propane	.001,225	.000,861	.009,108	.008,247	.019,882
Iso butane	.000,540	.000,380	.002,651	.002,271	.005,475
Normal butane	.000,714	.000,502	.002,718	•002,216	.005,342
Iso pentane	.000,573	.000,403	.002,128	.001,725	•004,159
Normal pentane	.000,332	.000,233	•001,01	.000,808	•001,948
135-56 hexane	.000,537	.000,378	.001,633	.001,255	003,025
56-35 hexane	.000,442	.000,311	.001,294	•000,983	002,370
C ₇₊ residue	.006,112	.004,296	•008,145	.003,849	• 00 9,279
Total	•025,126	.017,660	•432,463	•414,803	1.000,00

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TABLE 13. - Equilibrium data on the high-pressure separator and reservoir phases, values of the ratio y/x

Component	High-pressure separator phases at 525.3 lb./in. ² absolute and 71.4°F.		Estimated reservoir phases at 3,192 lb./in. ² absolute and 228°F.		
1	Well M, fluid	K. and H.1/	Well M, fluid	K. and $H.1/$	
Nitrogen -	15•3	←	3.10	•••	
lethane .	5.82	6•95	1.76	2.03	
Ethane	1.04	1.12	•60	•98	
ropane	• 348	•3 ⁴ 5	• 47	•71	
so butane	•137	128	. 25	,48	
Tormal butane	•073	. } •120	•19	J •40	
so pentane	•039	042			
Jormal pentane	•027) •042]			
.35-56 hexane	•016	017			
56-35 hexane	•012	> •017			

^{1/} The values of equilibrium constants determined by Katz and Hachmuth on Oklahoma City reservoir-fluid samples are offered here only as a means of comparison with data obtained on well M reservoir-fluid samples.

SUMMARY AND CONCLUSIONS

The present report is limited to preliminary results of field and laboratory tests on one well in one field; therefore, general statements and conclusions regarding high-pressure "combination" wells are not justified. Although the results of the present study are subject to verification by additional field and laboratory work, it is believed that the conclusions herein presented apply reliably to well M, which has been studied.

Ratios of gas to hydrocarbon liquid, pressures, and temperatures within the well and the surface-recovery system and other well-flow data were observed over a considerable range of operating conditions in the well. Gas and liquid samples from the high-pressure separator and liquid samples from the well bore and stock tank were obtained for laboratory study to determine fluid-phase relations in the reservoir and recovery system. Operating conditions in the well were exceptionally favorable for a study of the well's productivity and to sampling procedure. The laboratory methods employed in treatment of the samples taken were designed particularly to give information concerning the phases of the hydrocarbon fluid in the reservoir.

The results of the field and laboratory work described in the foregoing sections of this report indicate the following conclusions.

- 1. Comparisons of ratios of gas to hydrocarbon liquid obtained under different rates of fluid recovery did not indicate conclusively the phase relations in the reservoir.
- 2. Pressure data on the flowing well showed that liquid and gas were present simultaneously in the well bore.
- 3. The composition of the subsurface liquid sample, which had a saturation pressure within 200 pounds per square inch of formation pressure, as compared with the compositions of surface liquid samples having much lower saturation pressures, does not indicate that the liquid likely would be formed entirely by condensation as a result of the 200 pounds per square inch decrease in pressure.
- 4. Restoration of the saturation pressure of the subsurface sample to the value of the formation pressure by the addition of the amount of gas likely to be liberated by a drop of pressure of 200 pounds per square inch did not prevent it from remaining in the liquid phase at formation pressure and temperature. It is concluded, therefore, that part of the liquid recovered from the well was present in the reservoir in the liquid phase, and the remainder was formed during the process of production by condensation of heavy components from the original reservoir vapor phase.

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