Application of Vaporization Equilibrium Constants to Production Engineering Problems

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(Oklahoma City Meeting, October, 1937)

The equilibrium constants developed by Souders, Selheimer and Brown[17] have been very useful tools in predicting vapor-liquid equilibria during the past five years. Their equilibrium constants were computed by assuming ideal solutions and recognizing the deviations of vapors from ideal gas laws. The same fundamental concepts were used by Lewis and co-workers[8] for predicting vaporization phenomena by means of fugacities.

The equilibrium constant is defined by equation 1:

$$\frac{y}{x} = K \tag{1}$$

in which K = equilibrium constant,
y = mol fraction of a constituent in the vapor phase,
x = mol fraction of the constituent in the equilibrium liquid phase.

The equilibrium constants are a function of temperature and pressure and might be considered as replacing the ratio of the vapor pressure to the total pressure of Raoult's law. They may be used to compute the vapor or saturation pressure of a liquid or the dew point of a vapor for any pressure or temperature from the analysis of the mixture much as Raoult's law is used. Likewise, the quantity of a mixture that will vaporize at any equilibrium temperature and pressure and the composition of the vapor and liquid may be calculated.

The purpose of this paper is to review the available equilibrium data of interest in petroleum production, to discuss the auxiliary physical properties of the hydrocarbons, and to present typical uses of the equilibrium constants. The particular applications chosen are the computation of the results of stage separation of crude oil and natural gas, the calculation of a pressure-volume curve of a crude oil-natural gas mixture, and information gleaned from a consideration of reservoir equilibria.

Manuscript received at the office of the Institute Sept. 8, 1937.

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[17] References are at the end of the paper.

EQUILIBRIUM DATA

Conditions encountered in crude-oil production are in the range from atmospheric pressure to above 3000 lb. per sq. in. and from about 30° to above 200° F. Under these conditions, the primary vaporization occurring in the natural mixtures consists of nitrogen, methane, ethane, propane, etc., through the compounds predominant in natural gasoline such as heptane or octane. The initial equilibrium constants[17] did not cover the desired pressure range and neither Brown's equilibrium constants nor Lewis' fugacities were of the desired accuracy in crude-oil mixtures for methane, the most prolific compound. Therefore only recently have satisfactory equilibrium data been available with the presentation of the experimental equilibrium constants obtained in the laboratories of Phillips Petroleum Company.[3]

Equilibrium constants were determined on a naturally occurring mixture of crude oil and natural gas at 40°, 120°, and 200° F. at pressures from atmospheric to 3400 lb. per sq. in. The vapors and liquids in equilibrium were analyzed by low-temperature fractionation for methane, ethane, propane, butanes, pentanes, hexanes and heptanes and heavier, the analyses providing the values of y over x or K for the constituents. Fig. 1 shows the data obtained at 120° F. as points with the smoothed curves inserted. Similar data were obtained at 40° and 200° F. and general plots were made of equilibrium constants versus temperature (−30° to 270° F.) lines of constant pressure (5 to 3000 lb. abs.) for the several constituents methane through heptane.

The light straight lines of Fig. 1 represent the equilibrium constant based on vapor pressures and Raoult's law. The latter is inaccurate at pressures above 300 lb. and at all times for constituents above the critical temperature of the pure compound.

The rise of the equilibrium constants to unity at a critical pressure of 5000 lb. for the particular mixture studied explains clearly the occurrence of constituents of high molecular weight in appreciable quantities in the vapor phase at high pressures. For instance, pentane is as volatile in the mixture studied at 3000 lb. and 120° F. as at 135 lb. and 120° F. The critical pressure is the pressure at which the vapor density equals the liquid density and only one phase exists.

This converging of the K's to a critical pressure injects another variable in addition to temperature and pressure on the value of K for a particular case. Fig. 1 also shows the equilibrium data of Sage and Lacey[12] on methane and propane in a binary system and indicates that the systems agree, but that equilibrium constants for mixtures having widely different critical pressures should not be expected to agree. Kay's[5] recent data on the ethane-heptane system is also shown on Fig. 1, giving good agreement of ethane K's but lower values for heptane than the extrapolated heptane values in crude oil primarily because Kay used n-heptane and the crude-oil heptanes contain a large proportion of lower boiling isomers. However, these binary systems and other data point to the probability that mixtures having intermediate critical pressures between the binary systems and the crude oil would have K's corresponding to curves converging to unity at the critical pressure for the particular system and possibly symmetrical with the systems shown.

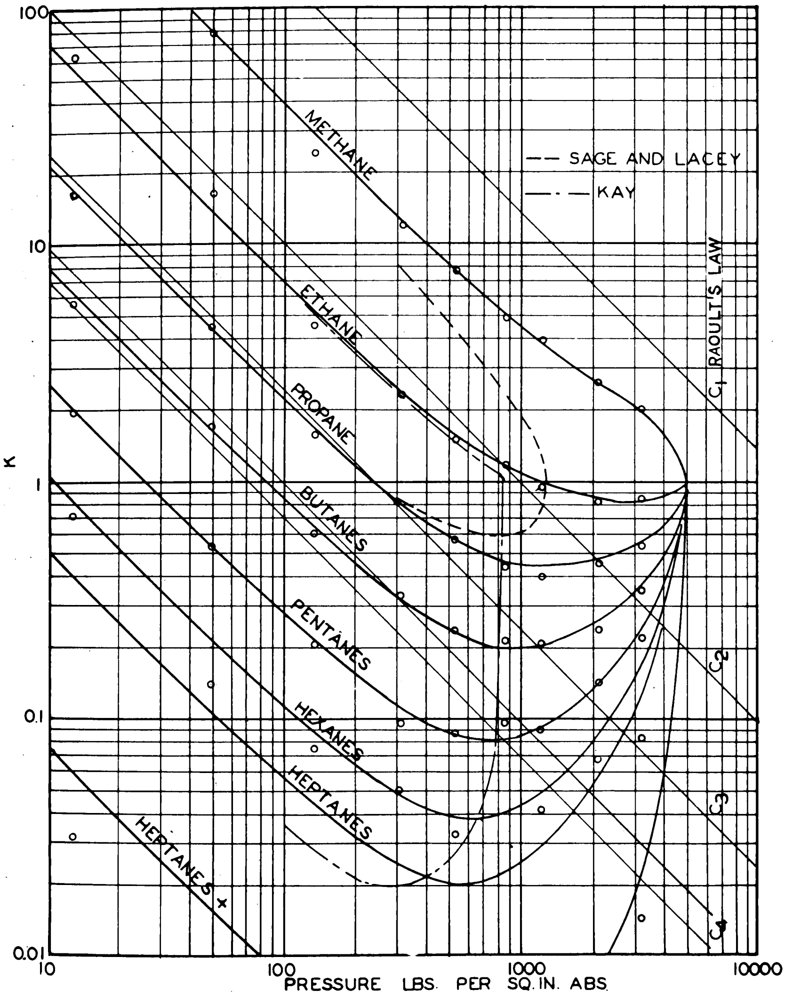


FIG. 1.—EQUILIBRIUM CONSTANTS AT 120° F.

Two sets of gas and liquid analyses of trap samples have been reported by Sage and Lacey[13,14] and trap samples properly taken are known to be representative of equilibrium conditions. The comparison of the K's with those of the charts for the crude oil-natural gas system are given by Table 1. The Kettleman Hills sample checks reasonably well and shows that although the critical of the mixture is likely to be less than that for crude oil, the convergence at 510 lb. is not significant. The ethane *K* of Kettleman Hills sample shows a subnormal value when *K* is plotted as log *K* versus temperature of atmospheric boiling point of constituent. The Conroe data differ considerably from those of the charts, possibly because of differences in chemical nature of the solvent or crude oil. However, discrepancies between individual sets of equilibria should not be used to form conclusions, as shown by irregularities of the data of Fig. 1 from the smoothed curves.

The recommended procedure for selecting equilibrium constants for a mixture is to use the crude-oil natural-gas data with adjustments for critical pressure of the mixture. It may also be necessary to adjust the constant for methane if the base of the crude oil is of a vastly different chemical constitution from that of the Oklahoma City crude. Cyclic compounds tend to raise the equilibrium constant for methane over similar paraffins.

TABLE 1.—*Comparison of Equilibrium Constants*

Constituent	Equilibrium Constants	
	Kettleman Hills Trap Samples at 510 Lb. Abs., 148° F.	Charts of Crude Oil Natural Gas, 510 Lb., 148° F.
Methane	7.9	8.0
Ethane	1.38	1.86
Propane	0.816	0.72
i-butane	0.34	
n-butane	0.251	0.305
i-pentane	0.148	
n-pentane	0.074	0.12

	Conroe Trap Samples 42.4 Lb. Abs., 68° F.	Charts 42.4 Lb. Abs., 68° F.
Methane	149	84
Ethane	16	10.6
Propane	3.15	2.8
Butanes	0.97	0.92

PHYSICAL PROPERTIES OF THE HYDROCARBONS

The calculation of the behavior of hydrocarbon mixtures from a molal analysis and the equilibrium constants results in the molal quantities present in each phase and the molal composition of the phases. This approach to the problem of understanding the properties of hydrocarbon mixtures is quite different from the direct measurement of the specific volume of a mixture, as done by Sage and Lacey,[13] or the differential vaporization of a high vapor-pressure liquid as initiated by Lindsly.[9] The later methods give accurate information for particular cases but fail to give a method of predicting the behavior of other mixtures. Also, the methods are not particularly concerned with the individual phases if two phases are present and do not follow the behavior of one phase if it is separated from the other. If the equilibrium constants and the physical properties of the volatile hydrocarbons were known when the constituents are present in all types of mixtures, it would be possible to compute the results of all the physical measurements made, in addition to the following of a particular phase and a knowledge of the constituents present. This ultimate goal is the objective of Sage and Lacey in their research project for the American Petroleum Institute.

At the present time reasonable estimates may be made of the volumetric properties of a hydrocarbon mixture under many conditions in either the liquid or gaseous phase. These computations require a knowledge of the partial volumes or apparent densities of the several constituents in either phase. The viscosity and specific-heat data primarily from Sage and Lacey are also approaching the stage that will permit the estimation of those properties from the analysis.

As an example of the computation of liquid densities, assume that a vaporization calculation resulted in the molal analysis of the Kettleman Hills trap sample of Sage and Lacey.[13] The molal analysis can be converted to the weight fractions reported by means of the molecular weights also reported. Table 2 shows such a conversion using the liquid densities at 60° F. to obtain the density of the mixture by assuming additive volumes. The change in density with temperature of the mixture at saturation pressure is best obtained by comparison with this variation for other saturated hydrocarbon liquids, as shown by Fig. 2. If the density of the trap sample at saturation pressure is assumed to follow a curve parallel to normal hexane, the values tabulated as calculated values in Table 2 are obtained. This check and the behavior of the saturated densities of Conroe depth sample,[14] natural gas in Dominguez crude,[16] methane in crude oil[15] and methane in Crystal oil,[11] as compared to pure hydrocarbons and the National Standard Petroleum oil tables, show that the saturated liquid density of a normal petroleum mixture at any temperatures existing in crude production may be estimated from the density at 60° F. and data such as shown in Fig. 2.

The choice of apparent densities at 60° F. of the more volatile hydrocarbons, especially methane, is not an easy task, as they may vary with saturation pressure and composition of the mixture. The value of the density for methane used in Table 2 was taken from earlier data of Lacey, Sage and Kircher[7] and the values of other pure hydrocarbons are the actual pure compounds. The check on the Kettleman Hills trap sample may be fortuitous but enough data are now available so that some correlation of the densities could be made.

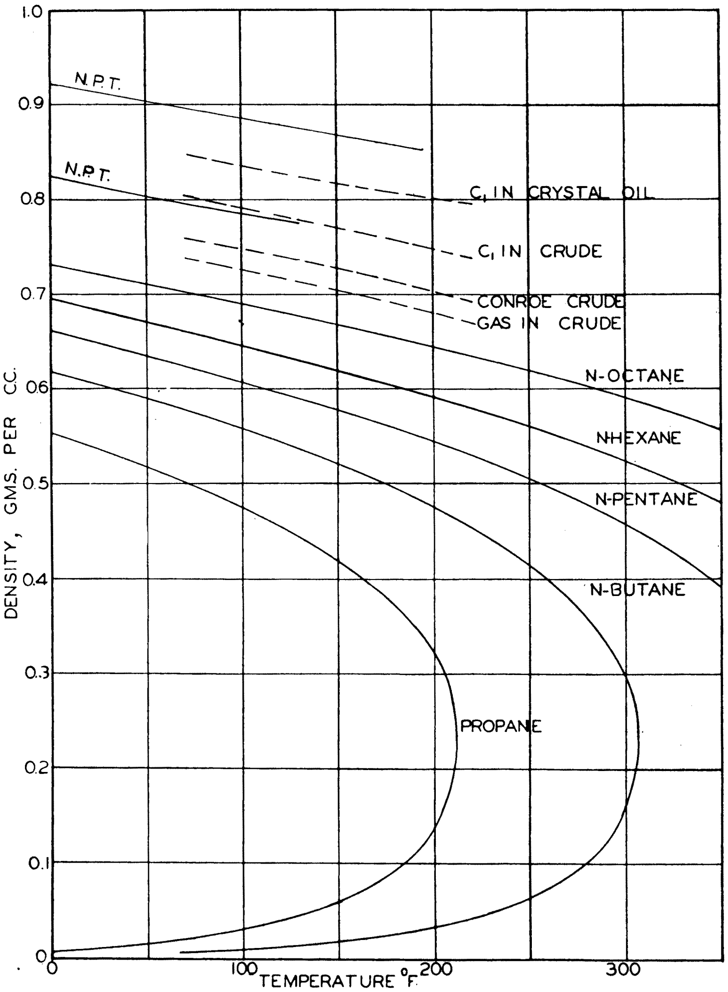


FIG. 2.—SATURATED DENSITIES OF THE HYDROCARBONS.

The densities of saturated and of superheated vapors may be approximated by finding the deviation of the mixture from ideal gas laws. The method presented by Kay[6] of calculating pseudocritical temperatures and pressures of gases by weighing the critical conditions of the pure compounds on a molal basis and using the deviation of the gas from ideal gases equal to methane (preferably) or ethylene at the same reduced conditions appears satisfactory. Also, the method[4] of using the deviation from ideal gases of a mixture of methane and propane of the same molecular weight as the gas and at the desired temperature and pressure is convenient. Both of these methods will permit the computation of the densities of the Kettleman Hills trap-gas sample within about 3 per cent of the experimental values over the entire range investigated from 70° to 220° F. and atmospheric to 3000 pounds.

TABLE 2.—*Computation of Liquid Densities of Kettleman Hills Trap Sample*[13]

Constituent	Weight Fraction	Specific Gravity at 60° F.	Cubic Centimeters per Gram
Methane	0.0193	0.33	0.0585
Ethane	0.0221	0.40	0.0552
Propane	0.0282	0.509	0.0554
i-butane	0.0156	0.564	0.0277
n-butane	0.0464	0.584	0.0795
i-pentane	0.0332	0.625	0.0531
n-pentane	0.0372	0.631	0.0590
Hexanes	0.0705	0.668	0.1056
152°–180° F. boil. pt.	0.0740	0.7019	0.1054
180°–206°	0.0772	0.7223	0.1070
206°–218°	0.0796	0.7347	0.1087
218°–240°	0.0797	0.7466	0.1069
240°–259°	0.0809	0.7515	0.1077
259°–280°	0.0819	0.7607	0.1077
280°–301°	0.0831	0.7720	0.1078
301°–338°	0.0839	0.7788	0.1080
Residue	0.0873	0.8110	0.1076
	1.0000		1.4608 density = 0.6846

Temperature, Deg. F.	Calculated Density Grams per C.C.	Experimental Density Grams per C.C.
60	0.6846	
70	0.681	0.6831
100	0.666	0.6700
130	0.652	0.6543
160	0.637	0.6379
190	0.621	0.6211
220	0.604	0.6043

These two properties, gas and liquid densities, when known will permit the conversion of molal gas and liquid analyses and molal percentages vaporized into volume per cent vaporized or shrinkage on flashing. Also, pressure-volume curves may be computed and the densities of either gas or liquid streams may be calculated when desired.

The compressibility of liquids and viscosity of gases at low pressures may also be estimated from analyses by comparing with data on mixtures of comparable molecular weight and density. The viscosity of liquid mixtures can only be roughly estimated with present correlations but added data by Sage and Lacey should provide a reliable method for predicting this property.

Stage Separation

Stage separation is the equilibrium vaporization of natural gas from crude oil in two or more successive steps at different pressures. By separating a crude oil from the natural gas at a high pressure, the gas is available at a high pressure and the vaporization of the natural gasoline hydrocarbons are suppressed at the high pressure. The equilibrium constants enable the computation of the gas quantity and composition as well as the oil composition and gravity for any series of vaporizations from the analysis of the mixture vaporized. Computations will show the effect of using any system considered and often they will give results where experimental methods are impractical.

The commonest method of separating crude oil and natural gas is a single separator with the liquid going to a lease tank at atmospheric pressure. Table 3 gives the complete calculations of the separation of gas from an oil at 34.7 lb. abs. (20-lb. gauge) and 80° F. in a separator and subsequent flashing of the separator liquid at 14.7 lb. abs. and 80° F. The crude oil (column 1) used is a liquid from the equilibrium experiments[3] and is similar to saturated crude oil at 140° F. and 2175 lb. abs. The equilibrium constants (column 2) were taken from the data based on Oklahoma City crude oil. Columns 3 and 4 and columns 5 and 6 are solutions of equation 2[2] to find a calculated value of the mols vaporized equal to an assumed value.

$$\sum x = \frac{F}{v}\sum \frac{z}{K + \frac{1-v}{v}} = 1 \qquad [2]$$

in which x = mol fractions of constituents in separator liquid,
F = mols of feed mixture to a separator—taken as unity,
v = mols vaporized,
z = mol fractions of constituents in mixture going to separator,
K = equilibrium constant at separator temperature and pressure.

Equation 2 may be written:

$$\sum \frac{z}{K + \frac{1-v}{v}} = \frac{v}{F} = v \qquad [2a]$$

TABLE 3.—*Vaporization Calculation*

VAPORIZATION OF WELL FLUID AT 80° F., 34.7 LB. ABS.

Constituent	1 Mol Fraction (z) Well Fluid	2 K at 80° F., 34.7 Lb. Abs.	3 $K + 0.7$	4 $\frac{z}{K + 0.7}$
Methane	0.3398	105	105.7	0.0032
Ethane	0.0672	14.8	15.5	0.0043
Propane	0.0672	4.1	4.8	0.0140
Butanes	0.0515	1.35	2.05	0.0251
Pentanes	0.0414	0.395	1.095	0.0378
Hexanes	0.0414	0.148	0.848	0.0488
Heptanes and heavier	0.3915	0.010	0.71	0.5510
				0.6842
			v assumed	0.5882

Constituent	5 $K + 0.98$	6 $\frac{z}{K + 0.98}$	Mol Fractions 7 Liquid	 8 Vapor
Methane	106.	0.0032	0.0063^5	0.6675
Ethane	15.48	0.0043	0.0084^1	0.1245
Propane	5.08	0.0132	0.0261	0.1070
Butanes	2.33	0.0221	0.0437	0.0590
Pentanes	1.375	0.0301	0.0595	0.0235
Hexanes	1.128	0.0367	0.0726	0.0107
Heptanes and heavier	0.99	0.3958	0.7834	0.0078
		0.5054	1.0000	1.0000
	v assumed	0.5051		

VAPORIZATION OF SEPARATOR LIQUID AT 80° F., 14.7 LB. ABS.

Constituent	7 Liquid (z) Mol Fraction	9 K at 80° F., 14.7 Lb. Abs.	10 $K + 49$	11 $\frac{Z}{K + 49}$	12 $K + 75$	13 $\frac{z}{K + 75}$
Methane	0.0063	250	299	0.00002	325	0.000019^5
Ethane	0.0084	34	83	0.00010	109	0.000077
Propane	0.0261	9.3	58.3	0.00045	84.3	0.000309
Butanes	0.0437	3.1	52.1	0.00084	78.1	0.000559
Pentanes	0.0595	0.91	49.91	0.00119	75.91	0.000784
Hexanes	0.0726	0.34	49.34	0.00147	75.34	0.000964
Heptanes and heavier	0.7834	0.022	49.022	0.01598	75.022	0.010442
				0.02005		0.013155
			v assumed	0.02000	v assumed	0.013158

Constituent	Mol Fractions 14 Liquid	 15 Vapor	16 Corrected Vapor	17 Mol Wt.	18 Grams per Mol	19 Specific Gravity at 60° F.	20 Cubic Centimeters per Mol
Methane	0.00148	0.3710	0.364	16	0.02		
Ethane	0.00587	0.1995	0.196	30	0.18	0.40	0.44
Propane	0.02353	0.2188	0.215	44	1.03	0.509	2.03
Butanes	0.0425	0.1318	0.129	58	2.46	0.578	4.26
Pentanes	0.0596	0.0542	0.0541	72	4.29	0.628	6.83
Hexanes	0.0732	0.0249	0.0245	86	6.30	0.665	9.47
Heptanes and heavier	0.7938	0.0174	0.0171	225	178.6	0.855	209.00
	1.0000	1.0176	1.000		192.87		232.03

Mol per cent vaporized at 80° F., 34.7 lb. = 50.5; 14.7 lb. = 1.37.

$$\frac{192.9 \text{ grams}}{232 \text{ c.c.}} = 0.831 \text{ density corresponding to } 38.8^\circ \text{ A.P.I. gravity or 291 lb. per bbl. crude at } 60^\circ \text{ F.}$$

$$1 \text{ mol well fluid} \left\{ \begin{array}{l} 0.505 \text{ mol vapor} \\ 191 \text{ cu. ft. at } 60^\circ \text{ F. 14.7 lb.} \\ 0.495 \text{ mol liquid} \end{array} \right. \left\{ \begin{array}{l} 0.00675 \text{ mol vapor} \\ 2.55 \text{ cu. ft. at } 60^\circ \text{ F. 14.7 lb.} \\ 0.4883 \text{ mol liquid} \end{array} \right.$$

To convert to barrels and cubic feet gas:
0.505 mol × 378 = 191 cu. ft. gas
0.4883 mol × 192.9 lb./291 = 0.323 bbl. crude per mol well-head fluid
1.0/0.321 = 3.09 mols well fluid per barrel crude oil.

$$3.09 \text{ mols well fluid} \left\{ \begin{array}{l} 1.56 \text{ mols vapor or 589 cu. ft. gas} \\ 1.53 \text{ mols liquid} \end{array} \right. \left\{ \begin{array}{l} 0.021 \text{ mol gas} = 7.9 \text{ cu. ft.} \\ 1.509 \text{ mol liquid, 291 lb. 1 bbl. crude oil} \end{array} \right.$$

Calculated shrinkage (reservoir crude = 108 mol wt., 0.743 sp. gr. at 60° F.)
0.743 density at 60° F. = 0.718 at 140° F. from Fig. 2 = 251 lb. per bbl.
3.09 mols × $^{108}/_{251}$ = 1.33 bbl. reservoir crude
Shrinkage = 33.0 per cent based on residual crude.

A value of $\frac{1-v}{v}$ is assumed and added to the K for each constituent. When the correct fraction vaporized has been chosen, the summation will equal the assumed v. It is always advisable to plot v assumed against the summation, or v calculated as small differences may still mean a rather large error in v. When the correct value of v has been found, division of summation of $\frac{z}{K+\frac{1-v}{v}}$ by v gives $\sum x$ or liquid mol fraction (column 7). Multiplication of x by corresponding K will give mol fraction in vapor (column 8) by equation 1.

The vaporization occurring in the lease crude tank is computed by a similar computation using the separator liquid as the feed mixture z. This second stage of vaporization is slightly more difficult to solve than the former merely because the trial and error solution requires a closer check between v assumed and v calculated at low percentages vaporized. Fourth-place checks are not always perfect and a plot should be made with points on either side of the line of equality. Errors in v calculated will be reflected in the sum of the y's, or vapor mol fractions not equaling unity. A discrepancy of one or two mol per cent (column 15) at low percentages vaporized is satisfactory and the sum may be reduced or expanded to unity if desired (column 16). It is necessary to carry the methane and ethane of the liquid to three figures if the correct gas analysis is to be computed. Also, the fact that the K for heptanes plus is considered constant may give too high percentages of heptanes plus vaporized, especially at high vaporizations with high gas-oil ratios.

The calculation of molecular weight and density of resultant liquid is necessary to compute the cubic feet of gas per barrel of crude from the mol percentages vaporized; likewise, the shrinkage of the reservoir crude may be computed as shown in Table 3. In any series of separations, the liquid gravities and weight or liquid volume percentages vaporized may be computed. Fig. 3 shows the results in the usual units.

A so-called "two-stage" separation consisting of vaporizations at 315, 34.7 and 14.7 lb. abs. at 80° F. was computed for the same crude oil, and the results are given by Fig. 4. The calculation of the liquid gravities and shrinkages must be done with precision when making comparisons like those between Figs. 3 and 4, and slide-rule work, which was used in this case, should not be trusted to give gravity results to an accuracy of 0.1° A.P.I.

These calculations have been made to represent the vaporization of a reservoir crude sample when the well produces saturated liquid from a reservoir, as when new pools are flowing. If the crude analysis represents the reservoir liquid but the well is flowing at a higher gas-oil ratio than solution ratio, vaporization computations may be made upon a new mixture. As an example, consider the case of Fig. 3, with an experimental gas-oil ratio of 1500 cu. ft. per bbl., and assume that the crude analysis represents reservoir liquid at 2175 lb. abs. and 140° F. The gas in equilibrium with the reservoir crude is computed by the vapor-pressure calculation of the crude, or where

$$\Sigma xK = \Sigma y = 1 \qquad [3]$$

Table 4 shows the vapor-pressure calculation of the crude oil at 140° F., using close to the correct pressure and obtaining summation of

	MOL	GAS FRACTION
METHANE	.6675	.364
ETHANE	1245	.196
PROPANE	.1070	.215
BUTANES	.0590	.129
PENTANES	.0235	.054
HEXANES	.0107	.0245
HEPTANES	0078	.0171

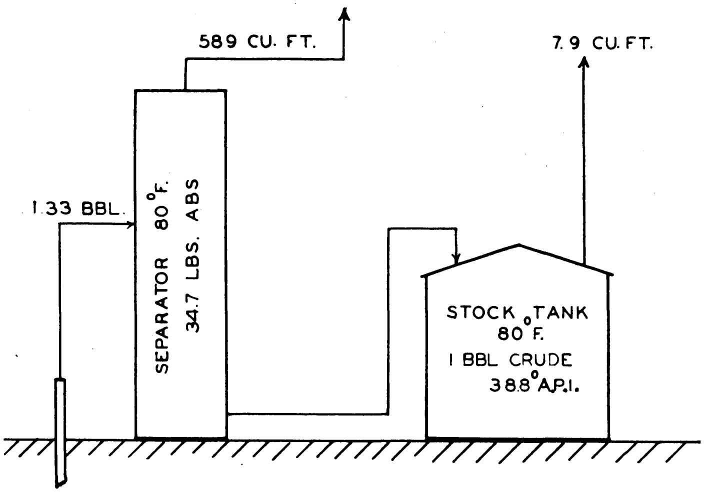


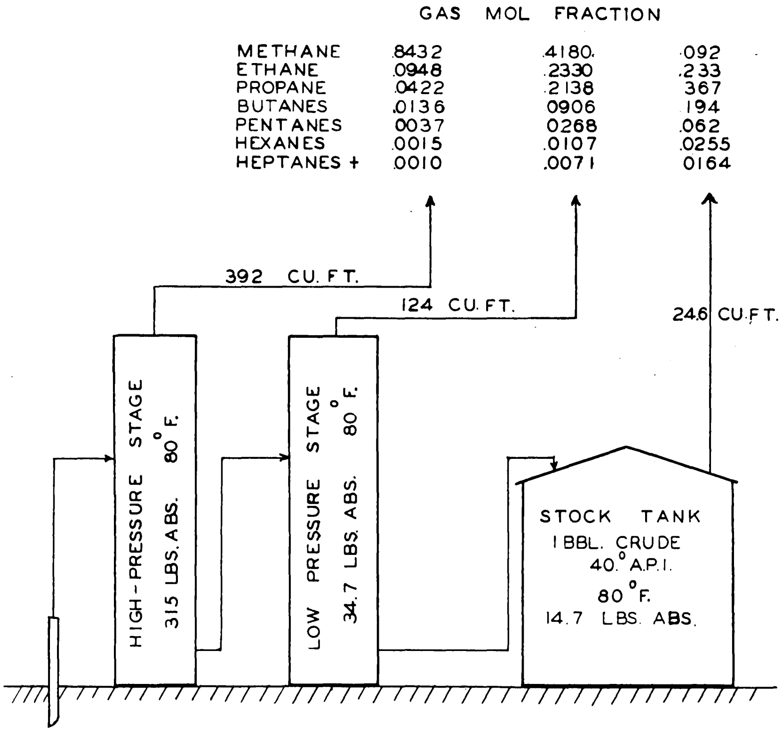
Fig. 3.—Single-stage separation.

Kx to 0.999, or the gas composition in equilibrium with the liquid. The reservoir gas may not be exactly in equilibrium with crude but error is small in most cases. As the experimental gas-oil ratio is about 900 cu. ft. above the saturated gas-oil ratio, as computed, 800 cu. ft. of reservoir gas might be estimated as accompanying the saturated crude oil when allowing for the extra vaporization to occur for some constituents at the higher separator gas-oil ratio. The 800 cu. ft. convert to 2.12 mols of gas for 3.09 mols reservoir liquid for the 1 bbl. crude, so 0.68 mol of gas accompanies 1 mol of liquid. The addition of 0.68 mol gas (column 4) to 1 mol of reservoir liquid (column 1) gives the mixture comprising the well fluid, and when converted to mol fractions (column 6) is the feed analysis for

TABLE 4.—*Calculation of Well Fluid for Gas-oil Ratios above Solution Gas*

Constituent	1 Reservoir Liquid	2 K at 140° F., 2175 Lb. Abs.	3 $\left(\frac{Kx}{y}\right)$	4 0.68 Mol Fraction Reservoir Gas	5 Total Mols	6 New Mol Fraction Well Fluid
Methane	0.3398	2.57	0.8736	0.594	0.9338	0.5565
Ethane	0.0672	0.90	0.0605	0.0411	0.1083	0.0645
Propane	0.0672	0.52	0.0350	0.0238	0.0910	0.0541
Butanes	0.0515	0.295	0.0152	0.0103	0.0618	0.0368
Pentanes	0.0414	0.160	0.0066	0.0045	0.0459	0.0273
Hexanes	0.0414	0.100	0.0041	0.0028	0.0442	0.0263
Heptanes and heavier	0.3915	0.0102	0.0040	0.0027	0.3942	0.2345
			0.9990			

separator computations at the higher gas-oil ratio. A vaporization of this mixture was computed at 34.7 lb. abs. and the liquid again at 14.7 lb. abs., to give the results shown in Fig. 5.



GAS MOL FRACTION

METHANE	.8432	.4180	.092
ETHANE	.0948	.2330	.233
PROPANE	.0422	.2138	367
BUTANES	.0136	0906	194
PENTANES	0037	0268	.062
HEXANES	.0015	.0107	.0255
HEPTANES +	.0010	.0071	0164

FIG. 4.—TWO-STAGE SEPARATION.

The calculation of stage separations from crude analyses applicable to the system will give results as close as most experimental analyses of the fluids. This statement is based on the fact that liquid analyses are likely to be more accurate than gas analyses and the equilibrium-constant data show that any one analysis may be in error. Thus K from smoothed data may compute vaporizations more accurately than routine measurements are made and for future conditions for which experimental measurements are impractical. The gas analyses may be converted to natural gasoline contents by dividing the cubic feet of a constituent in a 1000 cu. ft. of gas by the cubic feet of vapor per gallon of condensate. The gas gravity is the ratio of its molecular weight to that of air.

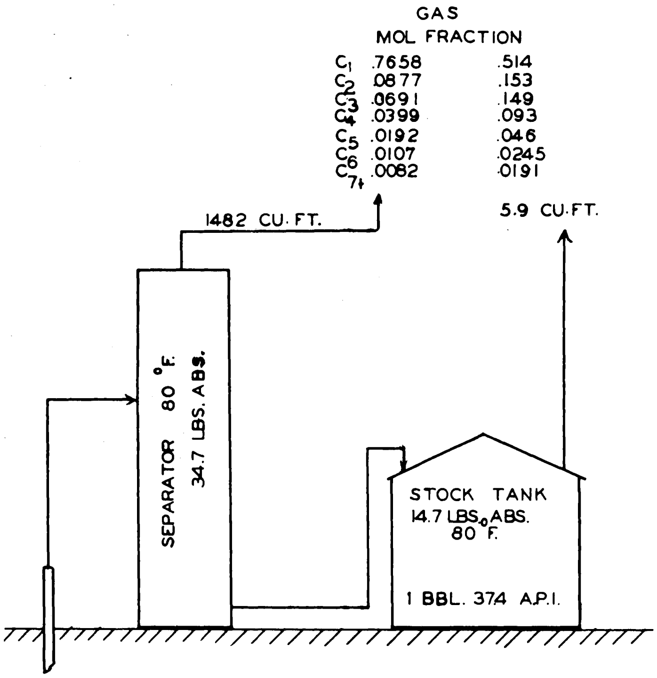


FIG. 5.—VAPORIZATION OF MIXTURE OF RESERVOIR LIQUID AND GAS.

A study of the problems of oil and gas separation will continually raise questions that can be solved by variations of the examples given. The crude-oil gravity or natural gasoline lost as a function of separator pressure may be computed. It may be shown that for low reservoir pressures saturated crude oil flashed at 60 lb. gauge in system of Fig. 3 may lose more natural gasoline in the stock-tank vapors than in the 60-lb. gas leaving the separator. The effect of gas-lift gas on oil gravity or gasoline content may also be computed for any gas-oil ratio.

PRESSURE-VOLUME CURVE OF OIL-GAS MIXTURE

Pressure-volume curves are often measured for reservoir fluids when studying such problems as fluid flow in tubing or oil and gas reserves. It may happen that such curves are desired when the oil to gas ratio has changed since the measurements were made or when no measurements have been made. In such cases a reservoir crude-oil analysis, the desired conditions of oil to gas ratio, temperature, and equilibrium constants will permit the computation of this curve.

The calculation of points on the P-V curve of the Conroe depth sample[14] was made as an example calculation. Unfortunately, the failure to publish the density of the hexane and heavier liquid of the analyzed sample makes the computation only a partial check with experimental results. The calculation of the bubble point or vapor pressure is usually made as one point on the curve. Table 5 shows this computation for the Conroe depth sample A at 160° F., with the result of 1875 ± 25 lb. abs. as compared to an experimental value of 1881 lb. abs.

The depth sample A was vaporized at 500 lb. abs. and 160° F. to obtain the volume of the mixture at these conditions. Column 6 is a successful trial for solving equation 2 and columns 7 and 8 give the composition of the phases present. The volume of the 0.279-mol vapor is computed by ideal gas laws and then corrected for the deviation. The method presented by Kay[6] of computing the pseudocritical temperature and pressure by weighting the critical values of the pure compounds (temperatures column 9, pressures column 10) according to the analysis is shown. The absolute temperature and absolute pressure divided by the pseudocritical temperature and pressure, respectively, give the reduced temperature (T_R) and reduced pressure (P_R). The gas was considered to have the same deviation from ideal gas laws as methane at the same T_R and P_R, or a value of $z = \frac{PV}{RT} = 0.952$. This correction when applied to the ideal gas volume gives 3.52 cu. ft. of gas per mol of mixture vaporized.

The calculation of the liquid volume per mol vaporized consists of finding the molecular weight and density of the liquid as shown by columns 13 to 16. The density of the liquid at 60° F. is converted to density at 160° F. by Fig. 2. The 0.729 mol of liquid becomes 2.17 cu. ft. liquid, or a total volume of 5.69 cu. ft. per pound-mol of mixture. As a partial check on the accuracy of the method, the ratio of calculated volume of one mol of the mixture at 500 lb. to the volume of one mol at 1875 lb. is compared with the experimental ratio. The check of 2.42 volumes computed to 2.39 volumes experimental is very good but the use of 0.83 as density of hexane and heavier as noted may have assisted in bringing the ratio closer together.

Reservoir Engineering

There are many uses of equilibrium constants in every-day reservoir engineering problems if analyses of reservoir gases or liquids are available.

TABLE 5.—*Computation of Pressure-volume Curve*

VAPOR PRESSURE OF CONROE RESERVOIR CRUDE

Constituent	1 Mol Fraction Subsurface Sample	2 K at 160° F. 1875 Lb. Abs.	3 Mol-fraction Vapor Kx or y
Methane	0.3225	2.85	0.919
Ethane	0.0424	1.01	0.0427
Propane	0.0335	0.55	0.0184
Butanes	0.0256	0.31	0.0079
Pentanes	0.0218	0.167	0.0036
Hexanes and heavier	0.5542	0.015	0.0083
			0.9999

FLASH VAPORIZATION OF CONROE CRUDE AT 500 LB. ABS. AND 160° F.

Constituent	1 Mol Fraction Reservoir Crude	4 K at 160° F. 500 Lb. Abs.	5 $K + 2.6$	6 $\frac{z}{K + 2.6}$	Mol Fraction 7 Liquid	 8 Vapor
Methane	0.3225	8.3	10.9	0.0296	0.1065	0.884
Ethane	0.0424	2.01	4.61	0.0092^{0}	0.0331	0.067
Propane	0.0335	0.81	3.41	0.0098^{2}	0.0353	0.030
Butanes	0.0256	0.35	2.95	0.0086^{8}	0.0312	0.011
Pentanes	0.0218	0.14	2.74	0.0079^{6}	0.0286	0.004
Hexanes and heavier	0.5542	0.0048	2.605	0.2125	0.7653	0.004
		v assumed		0.2777	27.9 per cent vaporized	

VOLUMETRIC CALCULATIONS FOR VAPOR

Constituent	8 Mol F. Vapor	9 Critical Conditions Deg. Rankine	10 Lb. Abs.	11 Pseudo Temperature	12 Critical Pressure
Methane	0.884	345	673	305	595
Ethane	0.067	552	708	37	47.4
Propane	0.030	668	646	20	19.4
Butanes	0.011	750	536	8.7	5.9
Pentanes	0.004	840	484	3.3	1.9
Hexanes and heavier	0.004	915	435	3.6	1.7
				377.6° R	672.1 lb. abs.

160° F = 620° R

$$\frac{620}{377.6} = 1.64T_R$$

$$^{500}/_{672} = 0.745P_R$$

$$\frac{PV}{RT} = 0.952 \text{ from } CH_4 \text{ chart.}$$

$$0.279 \times 378 \times \frac{620}{520} \times \frac{14.7}{500} \times 0.952 = 3.52 \text{ cu. ft. gas phase}$$

VOLUMETRIC COMPUTATIONS FOR LIQUID

Constituent	7 Mol Fraction Liquid	13 Mol Wt.	14 Grams per Mol	15 Density at 60° F.	16 Cubic Centimeters per Gram-mol
Methane	0.1065	16	1.7	0.35	4.8
Ethane	0.0331	30	1.0	0.40	2.3
Propane	0.0353	44	1.5	0.509	3.0
Butanes	0.0312	58	1.8	0.578	3.1
Pentanes	0.0286	72	2.1	0.628	3.3
Hexanes and heavier	0.7653	172	131.7	0.83[a]	158.8
			139.8 mol wt.		175.3

$$\text{Density } \frac{139.8}{175.3} = 0.796 \text{ at } 60° \text{ F. corresponding to } 0.755 \text{ at } 160° \text{ F.}$$

$$\frac{0.729 \times 139.8}{0.755 \times 62.4} = 2.17 \text{ cu. ft. liquid phase}$$

1 lb. mol at 1875 lb. = 106. lb. 106 × 0.02218 = 2.35 cu. ft. liquid
1 lb. mol at 500 lb. = 2.17 + 3.52 = 5.69 cu. ft.
Calculated volume at 500 lb. per 60° F. divided by volume at 160° F.
1875 lb. = 5.69 + 2.35 = 2.42
Experimental value = 2.39

[a] Assumed as corresponding to mol wt. and to computation of gravity of reservoir crude and equal to experimental.

A full understanding of equilibrium relations and the properties of the phases that may be estimated will prompt many applications of K.

The most evident relation is that if a reservoir liquid is obtained and analyzed in a new well of a pool, the analysis of the gas-cap gas if present can be computed for the reservoir temperature and pressure. Similarly, if a gas well is discovered and thought to be situated on the gas cap of an oil field, the dew point can be compared with the reservoir pressure and temperature, a calculation that gives the reservoir crude-oil composition if it is present. If a question should arise as to whether a crude oil from one well and gas from another well were in contact in the reservoir, an analysis of the two mixtures and comparison with equilibrium data would indicate the likelihood of present or previous contact. Such applications of equilibrium data assist geological information in showing the course of reservoirs or possible migrations of fluids.

The ability to calculate the quantity and composition of the reservoir phases during the life of the pool has advantages over the measurement of the combined volume. For instance, if there were segregation of the separating phases in a reservoir of unbalanced pressures, it would be possible to make rough estimates of the migration of either phase from the sand properties, physical properties of fluid, and pressure gradients. The viscosity and densities may be computed from the analyses of gases and liquids, or at least this will be possible shortly. This use of equilibrium constants and the physical properties of the hydrocarbons will also assist the engineer in solving problems of fluid flow into the well bore and in the flow string.

The study of the "productivity" of wells as initiated by Moore[10] and continued by Haider[1] may be aided by the use of equilibrium constants and the physical properties of the hydrocarbons. The "productivity index" is defined as the rate of production of crude oil in barrels per day for one pound drop in bottom-hole pressure, and has been shown to be a constant for wells producing entirely a liquid phase at the operating bottom-hole pressure. The vaporization of natural gas from crude oil at the bottom-hole pressure, or the accompanying of the crude by varying amounts of free gas, should be expected to vary the productivity index of a well for various conditions at the sand face. The radial permeability formula[18] may be used to show this effect of the gas volume accompanying the crude oil:

$$Q = \frac{cKt\Delta P}{\mu \log_e \frac{R_1}{R_2}} \qquad [4]$$

in which Q = barrels of fluid per day,
k = permeability, millidarcy,
t = sand thickness, ft.,

ΔP = pressure differential from reservoir to well bore, lb. per sq. in.,
μ = viscosity of fluid at mean pressure, centipoises,
R_1 = distance from well to position where substantially reservoir pressure is maintained, ft.,
R_2 = radius of well bore,
C = constant.

To illustrate the use of vapor-liquid equilibria data as applied to productivity index, assume that the solid curve of Fig. 6 is the productivity curve of a well producing saturated Conroe reservoir crude with no free gas. The PV curve of Sage and Lacey[14] would permit the computation of the barrels of residual crude which were represented by the Q for various average pressures as shown in Table 6. Columns 1, 2 and 3 are assumed data, column 4 is the arithmetical mean pressure from sand face to reservoir body, column 5 shows values from reported PV curve, and column 8 gives the actual barrels of fluid flowing at mean pressure. If K, t, μ, R_1 and R_2 were known, the value of C could be computed, but this discussion is limited to variations in residual crude oil for a given value of Q at various conditions.

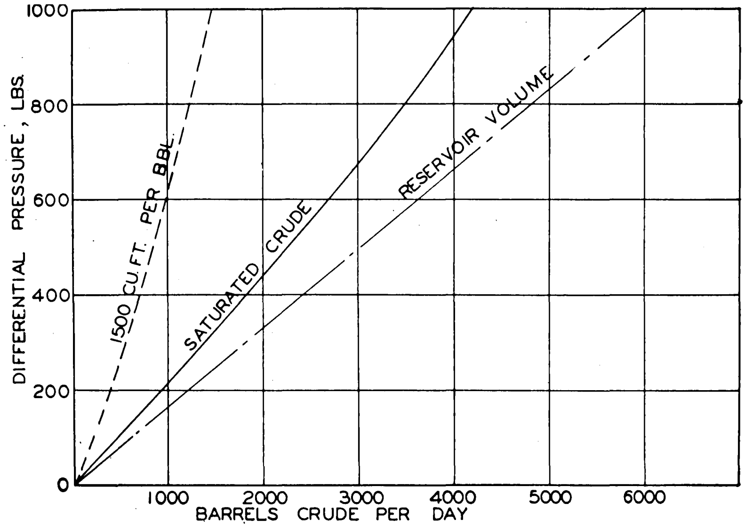


FIG. 6.—PRODUCTIVITY CURVES.

Let us further assume that the well in question changed from solution gas-oil ratio to 1500 cu. ft. per bbl. What is the productivity curve of the well at this condition? Theoretically the values of μ and R will change, which along with surface-energy effects would give a different relationship between Q and the differential bottom-hole pressure. However, let us neglect these factors for purposes of illustration and show the volumetric effect of the gas-oil ratio on the productivity curve. The 1500 cu. ft. of gas is divided into 443 cu. ft. of solution gas and 1057 cu. ft. of free gas at the shut-in reservoir pressure. The free gas may be added to the reservoir crude oil as shown in Table 4 and the *PV* curve computed for this new mixture at 160° F., the assumed reservoir temperature. These volumes of one barrel of residual crude with accompanying gas at the mean pressures are given by column 7, Table 6. The conversion of the reservoir fluid volume to residual crude is shown in column 8, values that are plotted on Fig. 6 as the new productivity curve.

TABLE 6.—*Productivity Computations*

Assumed Data			Saturated Crude Oil		
1	2	3	4	5	6
Bbl. Crude per Day	Bottom-hole Pressure, Lb. Abs.	ΔP, Lb. per Sq. In.	Mean Pressure, Lb. Abs.	Volume of One Barrel Residual Crude at P_m, Bbl.	Q for Eq. 4
0	1875	0	1875	1.23	0
945	1675	200	1775	1.27	1200
1850	1475	400	1675	1.30	2400
2690	1275	600	1575	1.34	3600
3480	1075	800	1475	1.38	4800
4200	875	1000	1375	1.43	6000

CONDITIONS OF 1500 CU. FT. PER BBL. RESIDUAL CRUDE

6	4	7	8
Q of Eq. 4	Mean Pressure, Lb. Abs.	Volume of One Barrel Residual Oil + Gas at Mean Pressure	Residual Crude Corresponding to Q
0	1875		
1200	1775	3.25	370
2400	1675	3.45	696
3600	1575	3.62	995
4800	1475	3.85	1250
6000	1375	4.10	1464

Although other factors than volume have been neglected, this computation would allow the checking to see whether other factors will change the productivities under various conditions. Also, this illustration might have taken the direction of computing the values of Q, or reservoir fluid, for an experimental productivity curve with gas-oil ratio changing with the flow rate. These computations on actual productivity curves will eliminate the volumetric factor and should bring the results closer to constant values for productivity index based on reservoir fluid rather than residual crude oil.

CONCLUSION

Equilibria data for the volatile constituents in crude oil-natural gas systems have been reviewed and the auxiliary physical properties of the hydrocarbons have been discussed. Methods of computing equilibrium vaporizations of mixtures of crude oil and natural gas have been illustrated. Examples of the many uses of this information in petroleum engineering were given; stage separation, *PV* curves, and reservoir engineering problems.

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DISCUSSION

(T. V. Moore presiding)

S. E. BUCKLEY,* Houston, Tex. (written discussion).—Rapid strides are being made in the field of calculating the behavior of the lighter hydrocarbons under the various conditions in which they occur underground and in the changes of phase which they undergo during and after production. The excellent experimental work being done by Lacey, Sage, and coworkers under the auspices of the American Petroleum Institute is adding substantially to the store of knowledge concerning the behavior of both simple and complex mixtures. This paper by Dr. Katz is very timely in that it shows the practical uses to which the accumulating mass of data may be put. The possibility pointed out by Dr. Katz of using a knowledge of the composition of the fluids entering a well to calculate the compositions of the gas and of the oil separated at various stages is not only intriguing but is already proving extremely practical. The necessary data are secured from examination of subsurface samples of the reservoir fluids. The technique of calculation outlined by Dr. Katz permits the accurate and complete determination of the effects of various production practices and is a valuable tool for use in studying both the physical and economic sides of many field operations.

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