

Calculation of Equilibria in Hydrocarbon Mixtures

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THE application of hydrocarbon equilibrium data to various problems encountered in refining and in natural gasoline recovery is an old and well established practice. Both generalized data and data on specific hydrocarbon systems have been made available by a number of investigators. More recently such data have been applied to the relations governing the separation of oil and gas both in the reservoir and at the surface. Most of the applications to production problems, however, have been based upon examinations of surface samples of oil and gas. This paper describes a technique that has been used satisfactorily in a number of cases to calculate directly from the hydrocarbon analysis of and auxiliary laboratory data on a subsurface sample of the reservoir fluid the behavior of the oil and gas during the various stages of separation at the surface incident to production.

TYPES OF INFORMATION CALCULATED

The system of calculations is not designed to supplant field data, but rather to correlate with them laboratory data obtained under controlled conditions in order to obtain a more complete and exact picture than usually is possible through the use of field data alone. The chief advantage of the calculations is the possibility of their use at a minimum of both time and expense to determine completely the effect of any possible operating technique upon each of the following: (1) The gas-oil ratio resulting from liberation of the dissolved gas; (2) the composition and gasoline content of the liberated gas; (3) the composition and gravity of the residual oil; (4) the amount and composition of the gas liberated upon flashing the oil from the separator to the stock tank; (5) the shrinkage of the oil in passing from the reservoir to the stock tank.

This information is frequently essential to the correct determination of the advisability of installing a natural gasoline plant, to design such a plant to take care of seasonal production, and to determine the optimum separator pressures to carry in various parts of a field.

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EXPERIMENTAL DATA REQUIRED

Carefully selected laboratory data, all of which are secured from a subsurface sample of the reservoir fluids, are necessary for the correct application of the calculations to any specific field. The following information is usually obtained: (1) Hydrocarbon analysis of the saturated reservoir fluid through the hexanes; (2) fractional distillation of the residual oil through nonane; (3) the molecular weights and specific gravities of the hexane-free material, the nonane-free material, and the intermediate fractions; (4) hydrocarbon analyses of the gases liberated from the oil by flash or equilibrium vaporization at atmospheric pressure at a minimum of two elevated temperatures; (5) the respective volumes and gravities of the gas and the oil obtained by flashing the reservoir fluid at room temperature at several controlled pressures; (6) the density, thermal expansion, and compressibility of the saturated reservoir fluid.

One subsurface sample usually suffices for all of the determinations, although two samples are usually used to obtain check results.

EQUILIBRIUM BETWEEN GAS AND OIL

The fundamental assumption involved in the calculations is that, owing to intimate mixing in the flow string, the oil and associated gas are at all times in instantaneous equilibrium at the existing temperature and pressure. Thus, the temperature and pressure at the final point of separation determine the compositions of the separated streams. While it has been observed that under some conditions equilibrium is not completely attained in the separator, sufficient data have been obtained to indicate that equilibrium is closely enough approached for the calculations to have wide application.

The equations that serve as the basis for the calculation of the qualities and relative quantities of gas and oil resulting from equilibrium vaporization of a mixture of known composition may be derived in the following manner:

Let X_o = total mols of original material.

L = total mols of liquid at equilibrium.

V = total mols of gas at equilibrium.

x = mol fraction of any component in the liquid.

y = mol fraction of any component in the gas.

$K = y/x$ = equilibrium constant, unique for each component, function of temperature and pressure.

By a material balance on the whole

$$X_o = L + V \quad [1]$$

A material balance on any particular component n gives

$$x_n X_o = x_n L + y_n V \quad [2]$$

TABLE 1.—Analytical Data on Saturated Reservoir Fluid

Component		Wt. Per Cent in Original Saturated Fluid	Specific Gravity at 60° F.	Molecular Weight
Methane.....	C ₁	7.45		
Ethane.....	C ₂	1.22		
Propane.....	C ₃	1.06		
Iso-butane.....	i-C ₄	0.91		
N-butane.....	n-C ₄	0.73		
Iso-pentane.....	i-C ₅	0.50		
N-pentane.....	n-C ₅	0.79		
Hexanes.....	C ₆	2.11		
Heptanes.....	C ₇	3.27	0.7255	100
Octanes.....	C ₈	3.21	0.7425	114
Nonanes.....	C ₉	4.21	0.7635	128
Heavier.....	C ₁₀₊	74.54	0.8342	203
Total.....		100.00		

TABLE 2.—Conversion of Analysis of Original Material from Weight to Mol Basis

Component	Wt. Per Cent	Molecular Weight	Mols per 100 Lb.	Mol Fraction
Methane.....	7.45	16.03	0.4645	0.4380
Ethane.....	1.22	30.05	0.0406	0.0382
Propane.....	1.06	44.06	0.0241	0.0227
Iso-butane.....	0.91	58.08	0.0157	0.0148
N-butane.....	0.73	58.08	0.0126	0.0119
Iso-pentane.....	0.50	72.09	0.0069	0.0065
N-pentane.....	0.79	72.09	0.0110	0.0104
Hexanes.....	2.11	86.11	0.0245	0.0231
Heptanes.....	3.27	100.	0.0326	0.0307
Octanes.....	3.21	114.	0.0281	0.0265
Nonanes.....	4.21	128.	0.0328	0.0309
Heavier.....	74.54	203.	0.3672	0.3463
Total.....	100.00		1.0606	1.0000

MOLS PER BARREL OF ORIGINAL OIL

From *P-V-T* data: 1 bbl. original saturated oil at reservoir temperature and pressure weighs 232.2 lb.

$$\text{Therefore, 1 bbl. original oil} = \frac{232.2(1.0606)}{100} = 2.463 \text{ mols}$$

TABLE 3.—Calculation of Flash Vaporization at 130° F. and 0 Lb. per Sq. In. Gauge

Component	Mol Fraction in Original Oil, x_o	Equilibrium Constant, $K = y/x$	Kx_o	$K - 1$	$V(K - 1)$ at $V = 0.551$	Mol Fraction in Gas: $y_n = \frac{Kx_o}{V(K - 1) + 1}$	Mol Fraction in Oil: $x_n = \frac{x_o}{V(K - 1) + 1}$	Gal. at 60° F. per Mol Oil	Lb. per Mol Oil
Methane.....	0.4380	256.	112.2	255.	140.6	0.7925	0.0031	0.022	0.050
Ethane.....	0.0382	28.	1.07	27.	14.88	0.0673	0.0024	0.022	0.072
Propane.....	0.0227	13.	0.2953	12.	6.61	0.0387	0.0030	0.031	0.132
Iso-butane.....	0.0148	6.7	0.0991	5.7	3.14	0.0239	0.0036	0.044	0.209
N-butane.....	0.0119	4.9	0.0584	3.9	2.149	0.0185	0.0038	0.045	0.221
Iso-pentane.....	0.0065	2.1	0.01364	1.1	0.606	0.0085	0.0041	0.057	0.296
N-pentane.....	0.0104	1.66	0.01728	0.66	0.364	0.0126	0.0076	0.104	0.548
Hexanes.....	0.0231	0.63	0.01457	-0.37	-0.204	0.0183	0.0290	0.451	2.497
Heptanes.....	0.0307	0.245	0.00753	-0.755	-0.416	0.0129	0.0525	0.870	5.257
Octanes.....	0.0265	0.087	0.002332	-0.913	-0.503	0.0047	0.0533	0.984	6.084
Nonanes.....	0.0309	0.032	0.000989	-0.968	-0.533	0.0021	0.0661	1.333	8.471
Heavier.....	0.3463	0.0		-1.0	-0.551		0.7715	22.543	156.615
Total.....	1.0000					1.0000	1.0000	26.506	180.416

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$$\text{Gas-oil ratio} = \frac{0.551}{0.449} \frac{\frac{\text{mols/mol residual oil}}{379} \frac{\text{cu. ft./mol residual oil}}{42}}{26.506} = 737 \text{ cu. ft. measured at } 60^\circ \text{ F., } 14.7 \text{ lb. per sq. in. abs. per barrel residual oil corrected to } 60^\circ \text{ F.}$$

$$\text{Gravity of residual oil} = \frac{180.416}{26.506} = 6.807 \text{ lb. per gal.} = 41.6^\circ \text{ A.P.I. at } 60^\circ \text{ F.}$$

$$V_R/V_S = \frac{26.506}{42} \frac{\frac{\text{bbl./mol residual oil}}{0.449} \frac{\text{bbl./mol original oil}}{2.463}}{26.506} = 0.698 \text{ bbl. residual oil corrected to } 60^\circ \text{ F. per barrel original saturated oil measured at reservoir temperature and pressure.}$$

It was found that a value of $V = 0.551$ satisfied the requirements that $\Sigma y_n = 1$ or $\Sigma x_n = 1$, giving correct solutions of the equilibrium equations. The analysis of the liberated gas is determined as mol fractions, but since, for a gas, volume and mol percentages are identical, a shift of the decimal point converts the analysis to per cent by volume.

The weight and volume of a mol of the residual oil were obtained by multiplying the mol fraction of each component by its molecular weight and by its molal volume, respectively. The molal volumes of the heptanes and heavier materials were obtained from their determined molecular weights and specific gravities, while the molal volumes of the other constituents, except methane, were taken from published data. The molal volume of methane in a particular oil is a characteristic of the

TABLE 4.—*Comparison of Calculated and Determined Analyses of Gas Liberated at 0 Lb. per Sq. In. Gauge at 130° F.*

Component	Per Cent by Volume	
	Calculated	Determined
Methane.....	79.25	79.59
Ethane.....	6.73	6.60
Propane.....	3.87	3.89
Butanes.....	4.24	4.04
Pentanes.....	2.11	2.11
Hexanes.....	1.83	1.77
Heptanes plus.....	1.97	2.00
Total.....	100.00	100.00

oil and must be determined for each case. For the oil under consideration, it was determined by difference in the following manner: The total volume of a unit weight of the original oil if it were possible to maintain it in the saturated state at 0 lb. per sq. in. gauge and 60° F. was determined by extrapolation of the laboratory data on the pressure-volume-temperature relations of the saturated fluid. The volume of the known weight of the dissolved methane was then obtained from the difference between the volume of the total fluid and the calculated volume of the other components. It was assumed for the subsequent calculations that the factor so derived for the dissolved volume of the methane would not be affected by changes produced in the oil by the release of gas from solution.

The calculations of the gas-oil ratio and the gravity of the residual oil, shown also in Table 3, are self-explanatory. The "shrinkage" factor of the oil, expressed as barrels of residual oil corrected to 60° F. per barrel of original saturated fluid measured at the reservoir temperature

and pressure, was obtained by multiplying the calculated volume of a mol of the residual oil by the number of mols of residual oil obtained from one barrel of the original saturated fluid.

Before proceeding further with the calculations, it is usual to compare the calculated analysis of the gas with that of the gas flashed from

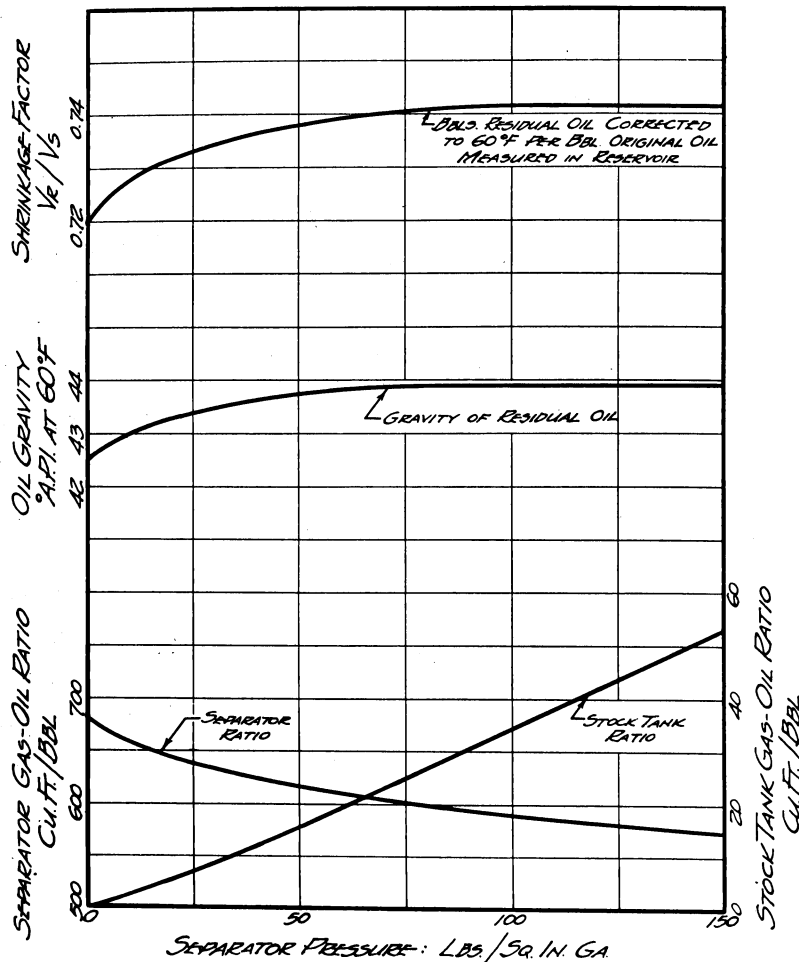


FIG. 2.—EFFECT OF SEPARATOR PRESSURE ON PROPERTIES AND RELATIVE AMOUNTS OF OIL AND GAS AT 70° F.

the original fluid in the laboratory at the same temperature and pressure. This comparison is made for the purpose of checking the equilibrium constants used and to determine the degree to which the particular mixture deviates from the ideal. The comparison is made at high temperature to take advantage of the greater concentration of heavier

hydrocarbons present in the gas. This greater concentration permits a more accurate hydrocarbon analysis and tends to magnify any absolute discrepancies between the calculated and the determined results. When the results check at high temperatures, it is possible to proceed with the assurance that the calculated analyses at normal temperatures and moderate pressures will be satisfactory.

Table 4 contains a comparison of the calculated analysis of the gas liberated at 130° F. with that actually obtained in the laboratory. The

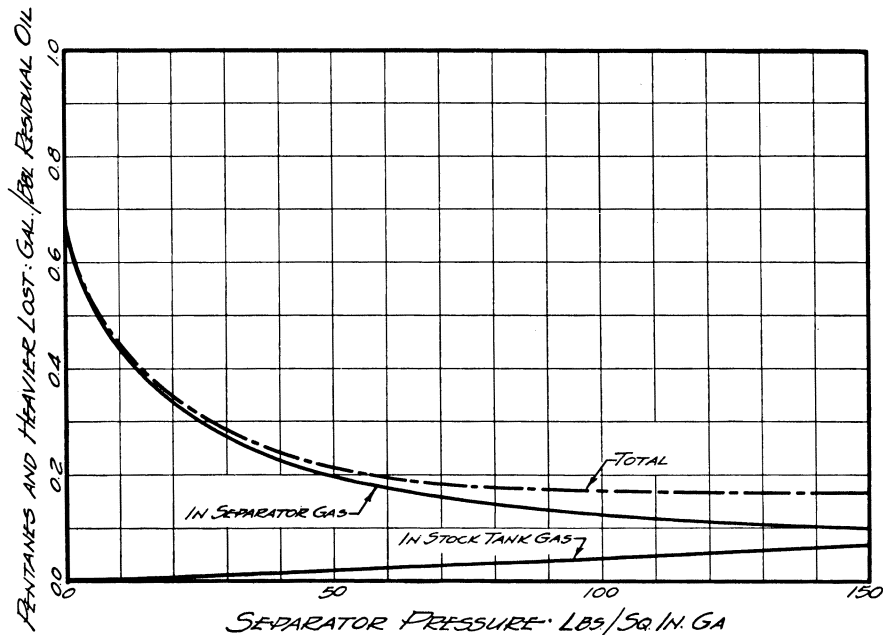


FIG. 3.—EFFECT OF SEPARATOR PRESSURE ON LOSSES OF PENTANES AND HEAVIER AT 70° F.

agreement in this particular case was such that no correction to the equilibrium constants was necessary.

Two complete sets of calculations are necessary for the condition of a separator operating at a pressure greater than atmospheric. The first calculation is similar to the one in Table 3, involving merely the calculation of the flash vaporization of the original fluid at the conditions existing in the separator. This calculation yields the compositions of the separator oil and gas. The separator oil, however, undergoes a second vaporization upon being released to atmospheric pressure in the stock tank, and the composition and relative amount of the final stock tank oil is dependent upon the conditions at each of the liberations. The calculation of the second vaporization is similar to that of the first with the exception

that the separator oil rather than the reservoir fluid is the material being flashed.

The effects of increasing gas-oil ratio due to the production of excess free gas from the reservoir, or the effects of gas lift upon the qualities of the resultant oil and gas, may be determined by similar calculations. In such cases, it is necessary to determine the composition of the excess gas. The fluid to be flashed consists of the mixture of oil and associated gas

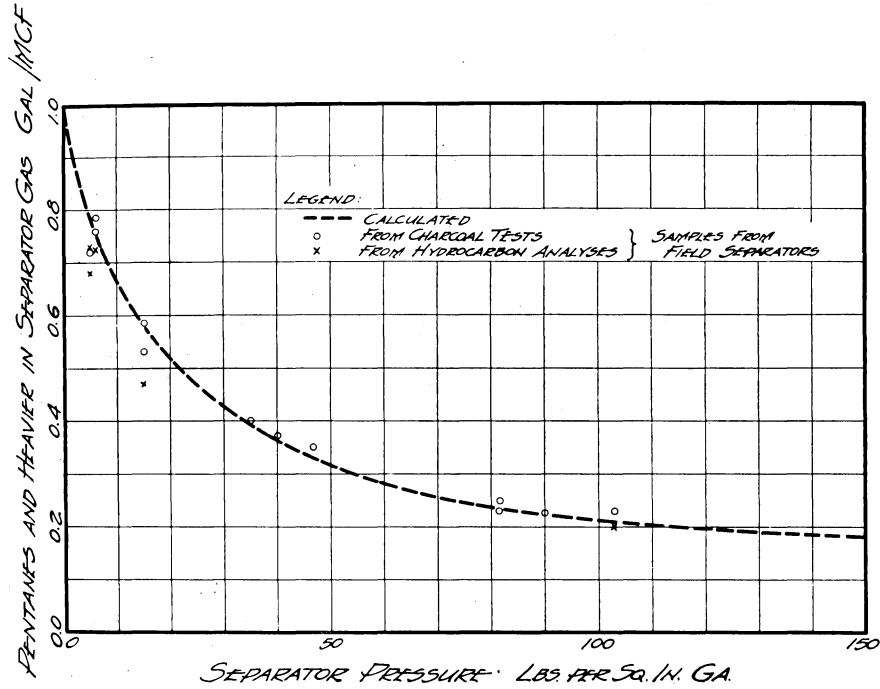


FIG. 4.—EFFECT OF SEPARATOR PRESSURE ON GASOLINE CONTENT OF SEPARATOR GAS.

and has a composition determined by the relative quantities of original oil and gas present.

CORRELATION OF CALCULATED RESULTS

It is customary to calculate all of the desired information at three temperatures, corresponding to the seasonal extremes and the yearly average for the particular region involved, and at a series of separator pressures from atmospheric to 150 lb. per sq. in. gauge. The data are then plotted to give a composite picture of the effect of production technique in the particular field. Figs. 2, 3 and 4 illustrate the effect of separator pressure on items of particular significance. Fig. 2 shows the effect of separator pressure at 70° F. on the separator and stock tank gas-oil ratios, the gravity of the residual oil, and the barrels of stock tank

oil obtained per barrel of original saturated oil measured in the reservoir. Fig. 3 illustrates the effect of separator pressure on the losses of pentanes and heavier hydrocarbons per barrel of residual oil, both in the separator and in the stock tank gases. Fig. 4 shows the effect of separator pressure at 70° F. on the gasoline content (pentanes and heavier) of the separator gas. Data obtained by hydrocarbon analyses and by charcoal tests on separator-gas samples from a number of wells in the field are included for comparison. The agreement between the calculated values and the field data in this instance was excellent.