EQUILIBRIUM CONSTANTS FOR A GAS-CONDENSATE SYSTEM

A. E. HOFFMANN, J. S. CRUMP AND C. R. HOCOTT, MEMBER AIME, HUMBLE OIL AND REFINING CO., HOUSTON, TEX.

ABSTRACT

Planning of the efficient operation of a gas-condensate reservoir requires a knowledge not only of the gross phase behavior of the system but also of the equilibrium distribution of the various components between the gas and condensate phases. This equilibrium distribution can be calculated with appropriate equilibrium constants. In this paper are presented equilibrium constants determined experimentally for the oil and gas phases initially present in the same reservoir and for the gas and condensate phases of the gas cap material at a series of pressures below the original reservoir pressure. Also presented is a method for the correlation of the experimentally determined equilibrium constants. The utility of the correlation is demonstrated further by an example of its use in adjusting the equilibrium data to permit their application to another gas-condensate system of similar composition.

INTRODUCTION

Planning of the efficient operation of a gas-condensate reservoir requires a thorough knowledge not only of the gross phase behavior of the particular hydrocarbon system but also of the equilibrium distribution of the various components between the gas and condensate phases. At the initial conditions of reservoir temperature and pressure, the original hydrocarbon materials in a gas-condensate reservoir or in the gas-cap of an associated reservoir exist in a single, homogeneous vapor phase. However, some condensation of hydrocarbons to a liquid phase usually occurs in the reservoir as pressure declines incident to production. Because of this condensation, the produced gas changes composition continuously. The composition of the produced gas, as well as that of the condensed liquid, can be calculated from the composition of the original reservoir material through the application of appropriate equilibrium constants or "K"-values provided these values are known.

Equilibrium constants have been used for many years in problems of surface separation of gas and oil and natural gasoline recovery. However, no satisfactory equilibrium data at reservoir conditions have been available for the higher boiling hydrocarbons which acquire abnormal volatility at high pressure and are therefore present in the gas phase in condensate reservoirs. Early work in this field indicated that the behavior of the higher boiling hydrocarbons largely determines the behavior of gas-condensate systems at high pressure.[1] Consequently, a portable test unit was designed to permit determination of the distribution of the heavier hydrocarbons between the gas and liquid phases of a gas-condensate system. This paper describes the test equipment and presents the results of an investigation of the reservoir fluids from an associated oil and gas reservoir in the Frio formation in Southwest Texas. Also presented is a method for correlation of the experimentally determined equilibrium constants, together with an example of the use of the method in adjusting these data for application to another gas-condensate system of similar composition.

FIELD TESTING AND SAMPLING

In order to determine the compositions of the reservoir fluids, field samples were secured from two different wells, one completed in the oil zone, and one completed in the gas cap.

The oil well was completed through perforations in 5½-in. casing at a depth of 6,822-6,828 ft subsea. Pressure and temperature traverses made in the well indicated the pressure and temperature to be 3,831 psig and 201°F, respectively, at a depth of 6,828 ft subsea. Subsurface samples were taken from this well after a four-hour shut-in period.
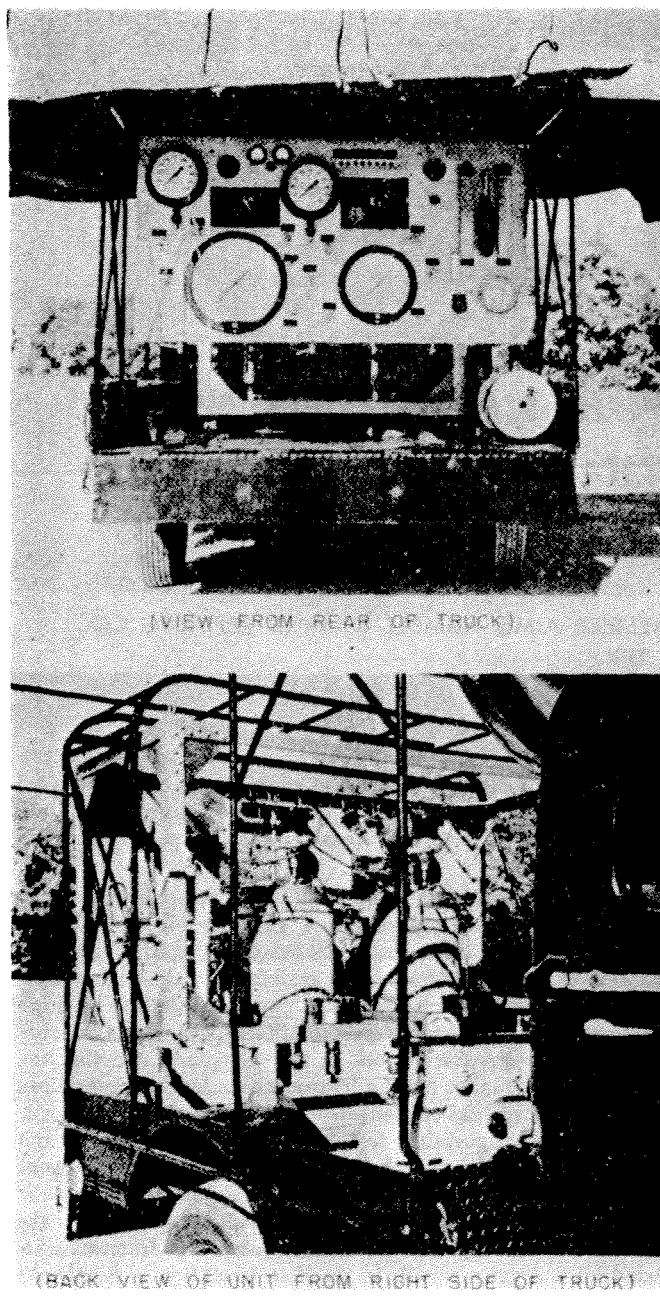
FIG. 1 — PORTABLE APPARATUS FOR GAS-CONDENSATE TESTING.

The gas well was completed through perforations in 7-in. casing at a depth of 6,760-6,788 ft subsea. For testing, the well was placed on production and the rates of gas and condensate production were determined at frequent intervals with carefully calibrated equipment. After the rates of production had become constant, samples of gas and liquid were taken from the separator. In addition to the conventional gas samples, separate portions of the gas were passed through charcoal tubes for adsorption and subsequent analysis of the butanes and heavier hydrocarbon content of the gas.

At the time of sampling, the well was producing at a rate of 5,718 Mcf of gas and 162.8 bbl of separator liquid per day. The tubing pressure was 3,100 psig, and the separator pressure and temperature were 785 psig and 83°F, respectively.

At the conclusion of the sampling the well was shut in, and about 36 hours later pressure and temperature traverses were made in the well. The pressure and temperature were indicated to be 3,822 psig and 201°F, respectively, at a depth of 6,788 ft subsea.

For further testing of the gas well a specially designed portable test unit was used for the determination of the phase behavior and for the sampling incident to the determination of equilibrium constants at reservoir temperature at various pressures for the gas-cap material.

PORTABLE TEST EQUIPMENT

The portable equipment used in the investigation was designed for operation at pressures up to wellhead pressure and was constructed for 10,000 psi maximum working pressure. Oil baths are used for temperature control. They are heated with immersion heaters powered by a portable, gasoline engine driven, 2,500 watt, 110 volt, 60 cycle AC generator, which also provides power for stirrers, lights, and relays. All electrical equipment is provided with ample safty devices to minimize spark hazard. Insofar as possible, 18-8 stainless steel was used throughout the pressure system to reduce corrosion and for safety during low temperature operation. The equipment is assembled on an aluminum panel and framework equipped with rollers and mounted on a half-ton pickup truck. Photographs of the unit are shown in Fig. 1.

The test equipment consists essentially of two gas-liquid separators, together with auxiliary equipment for measuring the rates of gas flow and of liquid accumulation and for the sampling of each phase. A flow diagram of the equipment is shown in Fig. 2. The first separator, referred to as the high pressure separator, is operated at reservoir temperature at a series of pressures. The second separator, referred to as the low pressure separator, is usually operated at pressures and temperatures in the range of those of the field separator. The usual test procedure involves the operation of these separators in series, with the gas from the first separator flashed into the second separator. The heavy hydrocarbon fractions in the gas phase from the high pressure separator are condensed to the liquid phase in the low pressure separator. By this procedure, these heavy hydrocarbon fractions may be concentrated sufficiently to permit the securing of an adequate sample for an analysis of these fractions. From a composite of this liquid analysis with that of the gas leaving the low pressure separator, an extended analysis can be obtained of the gas leaving the high pressure separator. Such a complete analysis is not possible with conventional gas samples or charcoal samples.

TESTING AND SAMPLING GAS-CAP MATERIAL

The method used in obtaining a continuous representative sample of the well stream is essentially that described by Flaitz and Parks.[2] By this method an aliquot of the well stream is obtained through a special line sampler inserted in the flow line near the well head. For accurate testing it is essential that the well be producing at a rate sufficient to prevent accumulation of liquid in the tubing and to insure homogeneous flow. The proper sampling rate is determined by by-passing the high pressure separator, operating the low
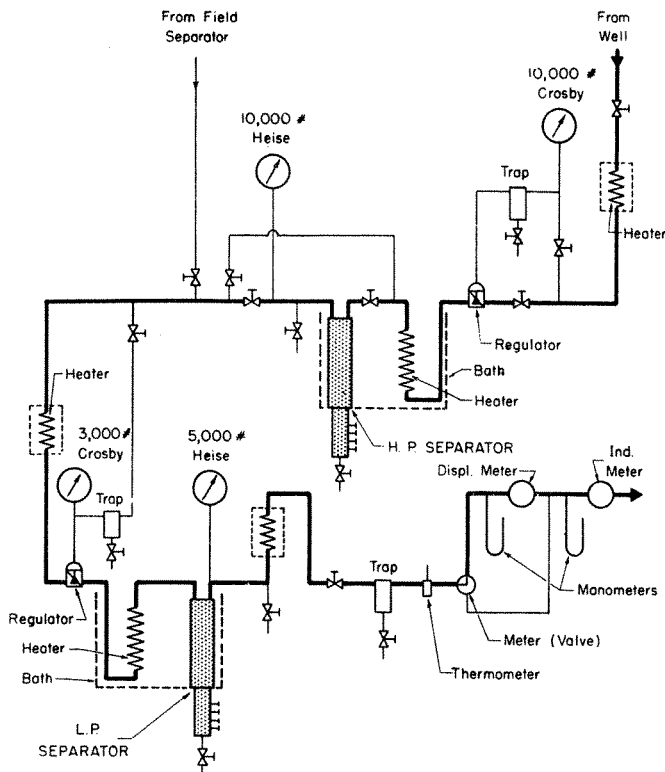
FIG. 2—FLOW DIAGRAM, PORTABLE APPARATUS FOR GAS-CONDENSATE TESTING.

the rates of production of gas and liquid in each separator. These measurements were used to determine the phase behavior of the system. Data on the gas/liquid ratios and the density of the separator liquid are presented in Table 1. These data, presented as condensate/gas ratio as a function of pressure, are shown in Fig. 3. The data were extended to a dew point of 3,822 psig on the basis of laboratory measurements.

At each of the selected conditions approximately three liters of liquid were obtained from each of the separators for laboratory examination. Conventional gas samples were also obtained from the low pressure separator. In addition, separate portions of the gas from the low pressure separator were passed through charcoal tubes for the adsorption and subsequent analysis of the butanes and heavier hydrocarbons.

LABORATORY EXAMINATION OF SAMPLES

Subsurface Oil Sample

Laboratory examination of the subsurface oil samples indicated the reservoir oil to have a saturation pressure of 3,825 psig at 201°F and a specific volume at those conditions of 0.02401 cu ft per lb. The gas/oil ratio of the reservoir oil when flashed to atmospheric pressure at 77°F was 910 cu ft/bbl of residual oil corrected to 60°F. The corresponding residual oil volume was 0.678 volume corrected to 60°F per volume of saturated oil at 3,825 psig and 201°F.

The hydrocarbon analysis of the subsurface oil sample is presented in Table 2. A low temperature Podbielniak apparatus was used for the analysis of the low-boiling fractions up to and including n-pentane. A "hypercal" (high temperature) distillation was used as a basis for extending the analysis to include the hydrocarbon fractions heavier than pentane. The procedure followed in the application of the hypercal distillation data to the distribution of the heavier fractions was as follows: The boiling points, specific gravities, and molecular weights of approximately two per cent cuts were plotted against the volume distilled. The distillation curve was then divided arbitrarily into fractions with mid-boiling points roughly equivalent to those of the respective normal paraffin hydrocarbons. Thus, from the volume, average molecular weight, and specific gravity of each fraction, the higher boiling hydrocarbons were divided into an equivalent series of indi-

pressure separator of the test unit at the same temperature and pressure as the field separator, and varying the sampling rate until the two separators yield identical gas/liquid ratios and identical gravities for the separator liquids flashed to atmospheric pressure.

During testing, the sampled aliquot passes through 3/16 in. OD stainless steel tubing to the first heater, where the fluids are restored to reservoir temperature, and then is flashed into the high pressure separator maintained at reservoir temperature and the desired pressure. The gas from the high pressure separator is further flashed into the low pressure separator, and the gas off this separator is measured. In this study, the high pressure separator was operated successively at pressures of 2,900, 2,500, 2,000, 1,500, 1,000, and 500 psig. The low pressure separator was maintained at approximately 250 psig and 80°F. At each pressure, measurements were made of

Table 1 — Phase Behavior of Gas-Condensate System
Separator Temperature: 201°F

Separator Pressure psig	Separator Gas/Liquid Ratio*		Density of Separator Liquid g/cu cm
	cu ft/bbl	bbl/MMcf	
2,900	110,264	9.07	0.6565
2,500	80,406	12.44	0.6536
2,000	64,279	15.56	0.6538
1,500	58,904	16.98	0.6753
1,000	59,016	16.94	0.7160
500	66,293	15.08	0.7209

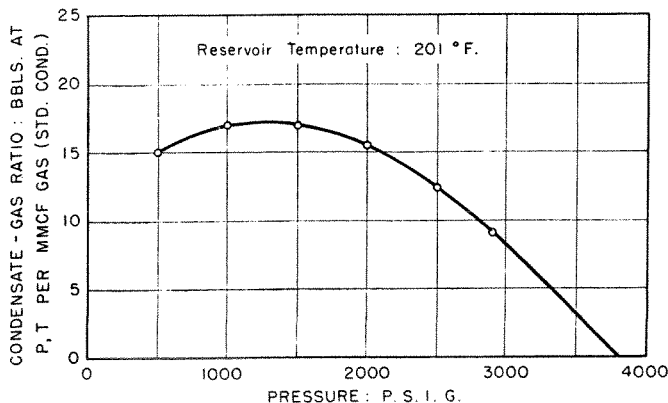*Separator gas volumes corrected to 14.7 psia, 60°F; separator liquid volumes at indicated pressure and temperature.

FIG. 3 — EFFECT OF PRESSURE ON CONDENSATE FORMATION.

Table 2 — Hydrocarbon Analyses of Reservoir Fluids

Component	Mol %	Reservoir Oil Liquid Density g/cu cm at 60°F	Molec- ular Wt.	Mol %	Reservoir Gas Liquid Density g/cu cm at 60°F	Molec- ular Wt.
Methane	52.00			91.35		
Ethane	3.81			4.03		
Propane	2.37			1.53		
Iso-butane	0.76			0.39		
N-butane	0.96			0.43		
Iso-pentane	0.69			0.15		
N-pentane	0.51			0.19		
Hexanes	2.06			0.39		
Fraction 7	2.63	0.749	99	0.361	0.745	100
Fraction 8	2.34	0.758	110	0.285	0.753	114
Fraction 9	2.35	0.779	121	0.222	0.773	128
Fraction 10	2.240	0.786	132	0.158	0.779	142
Fraction 11	2.412	0.798	145	0.121	0.793	156
Fraction 12	2.457	0.812	158	0.097	0.804	170
Fraction 13	2.657	0.826	172	0.083	0.816	184
Fraction 14	3.262	0.846	186	0.069	0.836	198
Fraction 15	3.631	0.854	203	0.050	0.840	212
Fraction 16	2.294	0.852	222	0.034	0.839	226
Fraction 17	1.714	0.838	238	0.023	0.835	240
Fraction 18	1.427	0.846	252	0.015	0.850	254
Fraction 19	1.303	0.851	266	0.010	0.865	268
Fraction 20	1.078	0.871	279	0.006	0.873	282
Fraction 21	0.871	0.878	290	0.004	0.876	296
Fraction 22	0.715	0.884	301	0.002	0.878	310
Fraction 23	0.575	0.889	315			
Fraction 24	0.481	0.893	329			
Fraction 25	0.394	0.897	343			
Fraction 26	0.335	0.900	357			
Fraction 27	0.280	0.903	371			
Fraction 28	0.250	0.906	385			
Fraction 29	0.232	0.908	399			
Fraction 30	0.195	0.910	413			
Fraction 31	0.170	0.912	427			
Fraction 32	0.156	0.914	441			
Fraction 33	0.143	0.916	455			
Fraction 34	0.130	0.917	469			
Fraction 35	0.118	0.918	483			
Total	100.000			100.000		

vidual hydrocarbons. This procedure was applied in extending the analyses of all liquid samples reported in this paper.

Field Separator Samples

Hydrocarbon analyses were made of the gas and liquid samples and of the contents of the charcoal samples obtained from the field separator. A detailed description and discussion of the technique involved in the analysis of such samples have been given by Buckley and Lightfoot.[1]

The composition of the produced gas-cap material was computed from the analyses of the separator samples by compositing on the basis of the produced ratio of 35,120 cu ft of separator gas per bbl of separator liquid. This composition, together with the average molecular weights and specific gravities of the heavier fractions, are also presented in Table 2.

Laboratory measurements at 201°F on a composite sample of the separator gas and liquid, recombined in accordance with their produced ratio, indicated the dew point of this gas-condensate system to be approximately 3,822 psig. This is in agreement with the measured shut-in pressure of the gas cap and compares favorably with the saturation pressure of 3,825 psig for the reservoir oil.

Portable Test Equipment Samples

Hydrocarbon analyses were made of the liquid samples obtained from the high pressure separator of the portable test unit when operated at reservoir temperature and successively at pressures of 2,900, 2,500, 2,000, 1,500, 1,000, and 500 psig. Also, hydrocarbon analyses were made of the companion gas and liquid samples and of the contents of the charcoal samples obtained from the low pressure separator when operated in series with the high pressure separator at each of the above pressures. From the analyses of both gas and liquid samples from the low pressure separator, extended composite analyses were obtained of the equilibrium gas from the high pressure test separator at each of the above pressures. The compositions of the equilibrium gas and liquid from the high pressure separator at the various pressures are reported in Table 3.

CORRELATION OF EXPERIMENTAL DATA

The accuracy with which analyses can be made of the composition of the equilibrium phases has generally necessitated the use of correlation procedures to smooth the scatter of the data and to develop from the data mutually consistent equilibrium constants. The procedure presented here was developed some years ago by S. E. Buckley and has proved
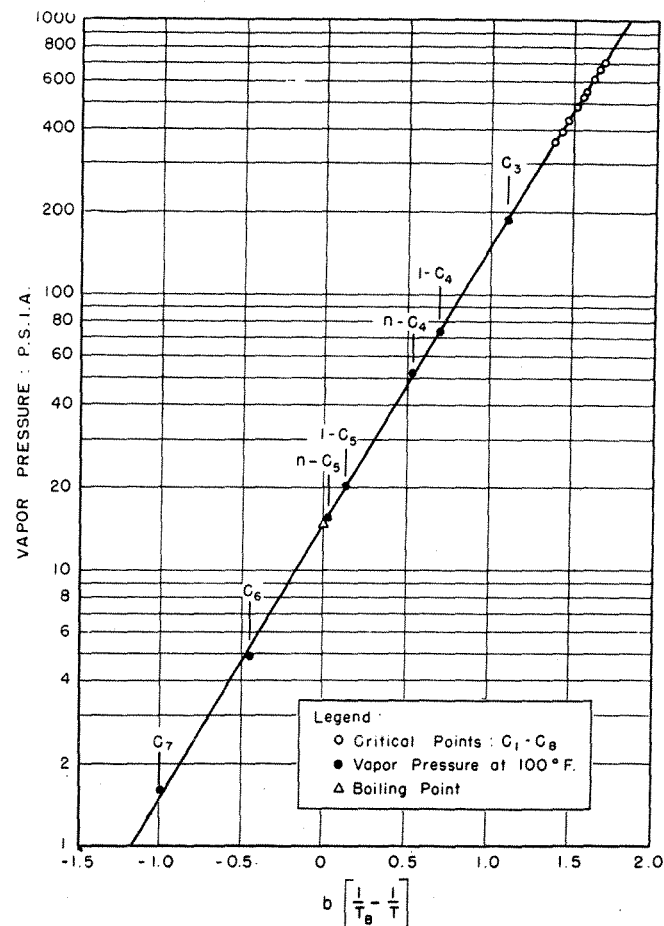

FIG. 4 — GENERAL VAPOR PRESSURE CURVE FOR HYDROCARBONS.

Table 3 — Hydrocarbon Analyses of Test Samples

Separator Temperature: 201°F

Pressure: psig Component	2900 Gas Mol %	2900 Liquid Mol %	2500 Gas Mol %	2500 Liquid Mol %	2000 Gas Mol %	2000 Liquid Mol %	1500 Gas Mol %	1500 Liquid Mol %	1000 Gas Mol %	1000 Liquid Mol %	500 Gas Mol %	500 Liquid Mol %
Methane	91.65	46.45	92.05	41.16	92.18	34.19	92.00	27.32	91.89	19.55	92.09	10.43
Ethane	4.17	4.36	4.01	3.92	4.03	3.62	4.11	3.56	4.25	2.96	4.02	2.09
Propane	1.56	2.86	1.53	2.71	1.57	2.87	1.60	2.89	1.66	2.59	1.56	1.97
Iso-butane	0.33	0.93	0.33	0.94	0.34	1.02	0.35	1.09	0.35	0.99	0.35	0.75
N-butane	0.47	1.25	0.43	1.32	0.44	1.55	0.46	1.70	0.46	1.66	0.44	1.30
Iso-pentane	0.16	0.90	0.18	1.04	0.15	0.97	0.16	1.09	0.16	0.98	0.14	0.65
N-pentane	0.19	0.65	0.17	0.67	0.17	1.06	0.19	1.15	0.19	1.20	0.20	1.15
Hexanes	0.38	3.14	0.37	3.07	0.33	3.65	0.37	4.50	0.37	4.47	0.36	4.24
Fraction 7	0.301	3.69	0.278	5.48	0.238	5.34	0.260	7.03	0.238	6.39	0.312	7.88
Fraction 8	0.228	3.81	0.218	5.08	0.191	6.09	0.213	7.32	0.183	8.27	0.235	9.29
Fraction 9	0.167	3.56	0.154	4.32	0.142	5.62	0.127	6.84	0.115	9.20	0.156	8.83
Fraction 10	0.119	3.099	0.101	4.035	0.089	5.242	0.069	6.211	0.063	8.927	0.073	8.553
Fraction 11	0.089	2.978	0.067	3.975	0.052	5.245	0.038	5.674	0.031	7.934	0.035	8.178
Fraction 12	0.061	3.085	0.043	4.071	0.030	5.226	0.024	5.238	0.017	6.424	0.018	7.839
Fraction 13	0.045	3.557	0.026	4.673	0.019	4.971	0.015	5.182	0.010	5.177	0.009	7.603
Fraction 14	0.034	4.452	0.019	4.644	0.013	4.718	0.009	4.690	0.007	4.217	0.002	6.719
Fraction 15	0.022	3.302	0.015	3.156	0.009	3.133	0.005	3.081	0.004	3.067		4.519
Fraction 16	0.014	2.063	0.009	1.979	0.005	1.861		1.923	0.002	2.037		2.776
Fraction 17	0.010	1.453		1.364	0.002	1.249		1.064		1.327		1.813
Fraction 18		1.191		1.023		0.832		0.811		0.914		1.246
Fraction 19		1.001		0.718		5.583		0.629		0.642		0.857
Fraction 20		0.856		0.509		0.432		0.421		0.493		0.593
Fraction 21		0.742		0.143		0.307		0.350		0.316		0.372
Fraction 22		0.621				0.221		0.236		0.265		0.239
Fraction 23												0.113
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000

Table 4 — Values of $b\left(\dfrac{1}{T_B} - \dfrac{1}{T}\right)$ for 201°F

Hydrocarbon	T_B Boiling Point °R	$\dfrac{1}{T_B}$	T_c Critical Temperature °R	$\dfrac{1}{T_c}$	P_c Critical Pressure psia	b^*	Smoothed Values b†	$b\left(\dfrac{1}{T_B}-\dfrac{1}{T}\right)$
Methane	201.01	0.0049749	343.3	0.0029129	673.1	805	805	2.786
Ethane	332.16	.0030106	549.77	.0018189	708.3	1,412	1,412	2.114
Propane	415.96	.0024041	665.95	.0015016	617.4	1,799	1,799	1.602
Iso-butane	470.58	.0021250	734.65	.0013612	529.1	2,037	2,037	1.245
N-butane	490.79	.0020375	765.31	.0013067	550.7	2,153	2,153	1.128
Iso-pentane	541.82	.0018456	829.8	.0012051	483.	2,368	2,368	0.786
N-pentane	556.62	.0017966	845.60	.0011826	489.5	2,480	2,480	0.702
N-hexane	615.42	.0016249	914.1	.0010940	439.7	2,780	2,780	0.309
N-heptane	668.86	.0014951	972.31	.0010285	396.9	3,068	3,068	−0.057
N-octane	717.89	.0013930	1,024.9	.0009757	362.1	3,335	3,335	−0.402
N-nonane	763.12	.0013104	1,071.	.0009337	331.	3,590	3,590	−0.729
N-decane	805.11	.0012421	1,114.	.0008977	306.	3,828	3,828	−1.039
N-undecane	844.27	.0011845	1,152.	.0008681	282.	4,055	4,055	−1.335
N-dodecane	880.99	.0011351	1,186.	.0008432	263.	4,291	4,291	−1.624
N-tridecane	915.54	.0010923	1,219.	.0008203	250.	4,524	4,500	−1.896
N-tetradecane	948.15	.0010547	1,251.	.0007994	230.	4,678	4,715	−2.164
N-pentadecane	979.02	.0010214	1,278.	.0007825	220.	4,919	4,919	−2.421
N-hexadecane	1,008.38	.0009917	1,305.	.0007663	200.	5,030	5,105	−2.664
N-heptadecane	1,036.30	.0009650	1,323.	.0007559	190.	5,315	5,290	−2.902
N-octadecane	1,062.97	.0009408	1,350.	.0007407	180.	5,440	5,470	−3.133
N-nonadecane	1,088.48	.0009187	1,368.	.0007310	170.	5,664	5,630	−3.349
N-eicosane	1,112.91	.0008986	1,395.	.0007169	160.	5,706	5,790	−3.561
N-heneicosane	1,136.3‡	.0008801					5,945§	−3.766
N-docosane	1,158.8‡	.0008630					6,095§	−3.965

*Computed from relation $b = \dfrac{(\log P_c - \log 14.7)}{\left(\dfrac{1}{T_B} - \dfrac{1}{T_c}\right)}$

†Values of b for normal hydrocarbons smoothed by plot of b vs number of carbon atoms.
‡Estimated from extrapolation of boiling point data.
§Estimated from extrapolation of plot of b vs number of carbon atoms.
NOTE: Physical constants of hydrocarbons taken from publications released by API Research Project 44.

Table 5 — Smoothed Values of KP at 201°F

System:	Gas-Oil	Condensate					
Pressure, psig:	3,822	2,900	2,500	2,000	1,500	1,000	500
Component				KP: psia			
Methane	6,750	5,751	5,623	5,432	5,100	4,769	4,544
Ethane	3,740	2,790	2,510	2,170	1,800	1,515	1,260
Propane	2,420	1,620	1,375	1,100	840	650	490
Iso-butane	1,790	1,130	907	682	495	360	253
N-butane	1,610	990	790	582	414	295	203
Iso-pentane	1,200	690	525	367	247	165	107
N-pentane	1,110	630	472	323	217	142	90.5
Hexanes	795	415	298	190	120	74.1	43.3
Fraction 7	582	283	192	118	69.7	40.3	21.9
Fraction 8	434	197	128	74.3	41.5	22.5	11.5
Fraction 9	326	139	87.0	47.6	25.1	13.0	6.23
Fraction 10	250	101	60.3	31.5	15.7	7.73	3.50
Fraction 11	193	73.5	42.6	21.1	10.1	4.72	2.00
Fraction 12	153	54.7	30.7	14.7	6.65	2.96	1.19
Fraction 13	122	41.3	22.3	10.2	4.47	1.89	0.730
Fraction 14	96.5	31.2	16.4	7.20	3.02	1.22	0.445
Fraction 15	74.7	23.3	11.9	4.96	2.00	0.780	
Fraction 16	59.5	18.2	9.05	3.64		0.527	
Fraction 17	47.1	14.5		2.72			
Fraction 18	37.9						
Fraction 19	30.2						
Fraction 20	23.8						
Fraction 21	19.4						
Fraction 22	15.1						

very satisfactory. In this procedure, the data are smoothed by plotting for each hydrocarbon the log of the product KP (the equilibrium constant times the absolute pressure) against a function $b\left(\dfrac{1}{T_B} - \dfrac{1}{T}\right)$, where b is a constant, characteristic of the particular hydrocarbon, T_B is its boiling point in °R, and T is the temperature in °R. It has been found empirically that for the equilibrium between a gas and a liquid at any given pressure, the logarithms of the KP products for the individual hydrocarbons so plotted yield reasonably straight lines against the function $b\left(\dfrac{1}{T_B} - \dfrac{1}{T}\right)$.[*] In Fig. 5 the KP products obtained from the experimental data are plotted against this function. On the whole, the relationship drawn to define the behavior of the KP products represents the experimental data well within the limits of reproducibility.
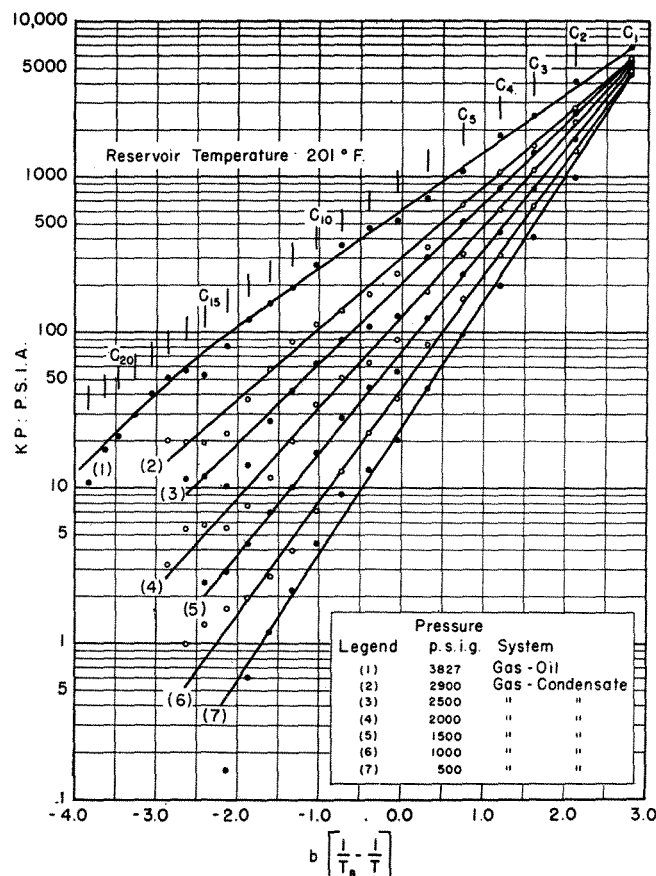
FIG. 5 — EXPERIMENTALLY DETERMINED K-VALUES AT 201°F.

---

[*]The basis for this method of correlation is as follows:

1. There is an analogy between the product KP and the pure liquid vapor pressure of a dissolved component.[3]

2. The logarithms of the vapor pressures of pure substances when plotted against the reciprocal of the absolute temperature yield approximately straight lines over reasonable temperature intervals.

3. The vapor pressures of pure hydrocarbons on a conventional Cox chart[4] converge to a common point of intersection.

These facts have long been known. Although the Cox chart has a temperature scale that differs slightly from $\dfrac{1}{T}$ the convergence of the vapor-pressure lines suggests that they might be rotated into a single line by appropriate changes in slope, which can be done by employing a single constant for each line. This approach was therefore employed to construct a single vapor-pressure curve for all hydrocarbons by plotting $\log \dfrac{p}{14.7}$ vs $b\left(\dfrac{1}{T_B} - \dfrac{1}{T}\right)$, where b is the factor required for each hydrocarbon to rotate its vapor-pressure curve to the common line. This vapor-pressure curve is shown in Fig. 4. This single line was found to represent the vapor-pressures of hydrocarbons with reasonable accuracy over a substantial temperature range.

Values of the required constant b may be computed from the vapor pressures at any two temperatures from the equation $\log \dfrac{p_2}{p_1} = b\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$. Experience has indicated that values of b computed from the critical pressures and temperatures and the normal boiling points are satisfactory for correlation purposes for most condensate reservoirs. Values of b calculated in this manner for the various hydrocarbons are presented in Table 4. Values for the high molecular weight hydrocarbons were determined from a smooth curve of a plot of b vs number of carbon atoms in the molecule.

The aforementioned analogy between KP and vapor pressure led then to the correlation technique of plotting $\log KP$ vs $b\left(\dfrac{1}{T_B} - \dfrac{1}{T}\right)$ for the various components of an equilibrium mixture of oil and gas.

Table 6 — Hydrocarbon Analysis of Upper Reservoir Gas

Component	Mol %	Liquid Density g/cu cm at 60°F	Molecular Weight
Methane	90.74		
Ethane	4.35		
Propane	1.69		
Iso-butane	0.36		
N-butane	0.54		
Iso-pentane	0.20		
N-pentane	0.21		
Hexanes	0.42		
Fraction 7	0.419	0.741	100
Fraction 8	0.292	0.752	114
Fraction 9	0.245	0.770	128
Fraction 10	0.167	0.775	142
Fraction 11	0.116	0.783	156
Fraction 12	0.090	0.793	170
Fraction 13	0.067	0.807	184
Fraction 14	0.049	0.835	198
Fraction 15	0.028	0.837	212
Fraction 16	0.014	0.843	226
Fraction 17	0.003	0.847	240
Total	100.000		

The smoothed values of KP taken from the above plot are presented in Table 5. These data are further presented in Fig. 6 as a cross plot of KP against pressure at reservoir temperature. Where possible, the data have been extended below 500 psig by extrapolation to the vapor pressures of the particular hydrocarbons at 201°F.

FIG. 6 — EFFECT OF PRESSURE ON K-VALUES AT 201°F.

SELECTION OF EQUILIBRIUM CONSTANTS FOR ANOTHER RESERVOIR

To determine the utility of the above correlation in developing equilibrium constants for another gas-condensate system of similar composition, a second reservoir in the same Southwest Texas field was selected for investigation. On a production test, this reservoir produced gas and condensate at a rate of 36,199 cu ft/bbl of separator liquid from a well completed at a depth of 6,200 to 6,205 ft subsea. During testing, the field separator was operating at a pressure of approximately 780 psig and a temperature of 73°F. The reservoir pressure and temperature were 3,117 psig and 189°F, respectively. The composition of the reservoir material was obtained from anal-
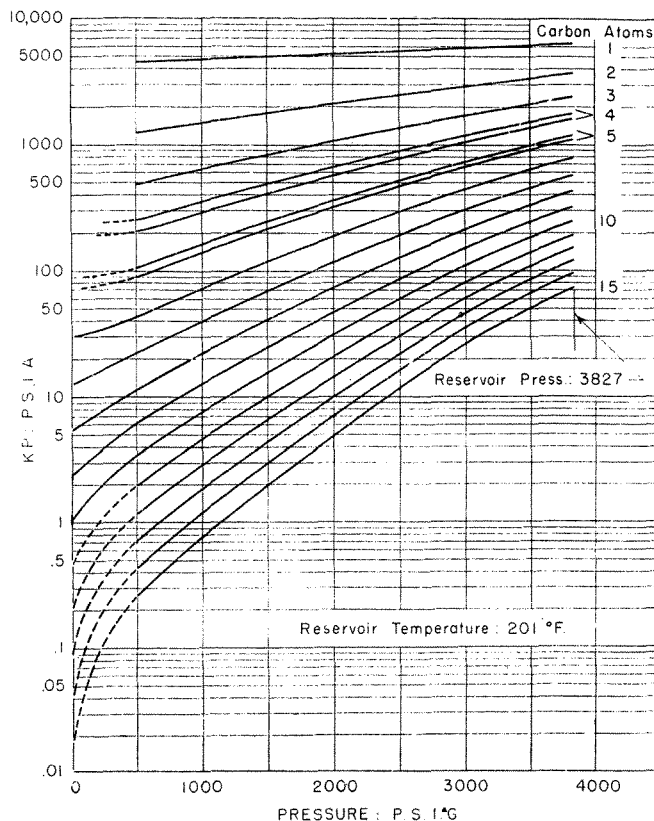
yses of field separator gas and liquid samples in the same manner as that described above. This composite hydrocarbon analysis is presented in Table 6. A dew-point determination on a composite sample of separator gas and liquid recombined in accordance with their produced ratio was also made in the laboratory. This dew point was indicated to be approximately 3,117 psig, the reservoir pressure at the time of sampling.

In order to select equilibrium constants appropriate for this reservoir, the function $b\left(\dfrac{1}{T_B} - \dfrac{1}{T}\right)$ was computed for each

Table 7 — Smoothed Values of KP at 189°F

| Pressure, psig: Component	2,900	2,500	2,000	1,500	1,000	500
			KP: psia			
Methane	5,580	5,450	5,220	4,860	4,550	4,310
Ethane	2,690	2,410	2,070	1,715	1,430	1,190
Propane	1,540	1,290	1,030	782	595	447
Iso-butane	1,055	845	630	455	325	228
N-butane	925	730	535	377	265	180
Iso-pentane	640	482	333	223	147	94.0
N-pentane	585	437	298	196	127	79.5
Hexanes	383	272	173	107	65.3	37.8
Fraction 7	258	175	105	61.5	35.0	18.7
Fraction 8	178	114	65.4	36.1	19.2	9.62
Fraction 9	125	77.0	41.7	21.7	11.1	5.20
Fraction 10	90.0	53.3	27.2	13.5	6.50	2.87
Fraction 11	65.0	37.2	18.0	8.60	3.90	1.61
Fraction 12	47.5	26.1	12.2	5.47	2.36	0.930
Fraction 13	35.4	18.8	8.35	3.59	1.48	0.555
Fraction 14	26.5	13.7	5.77	2.39	0.945	0.332
Fraction 15	20.1	10.0	4.08	1.61	0.610	0.204
Fraction 16	15.5	7.45	2.91	1.11	0.402	0.128
Fraction 17	11.9	5.60	2.10	0.770	0.269	0.0810
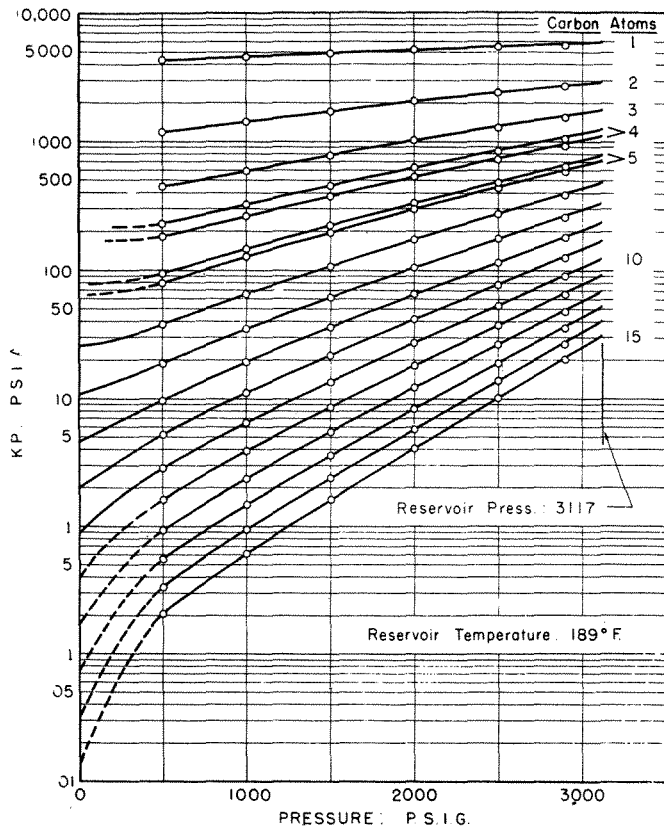
FIG. 7 — EFFECT OF PRESSURE ON K-VALUES AT 189° F.

component of the system at a temperature of 189°F, the reservoir temperature. Then, using the graph in Fig. 5, KP products for each hydrocarbon were determined at the corresponding $b'\left(\dfrac{1}{T_{B}} - \dfrac{1}{T}\right)$ from the curves at the various pressures. These KP products are presented in Table 7. These data are illustrated in Fig. 7 in a plot of KP against pressure for each component of this particular hydrocarbon system. The points indicated on the graph at each pressure are those determined from Fig. 5 for that pressure.

At pressures above 2,500 psig the curves were extended to 3,117 psig by trial and error in such a manner as to satisfy dew-point conditions. The differences between the extended curves and the points shown at 2,900 psig indicate the adjustment in the smoothed experimental data required for application to the reservoir fluids in the second reservoir. The extent of this deviation is such that no adjustment appears necessary at pressures lower than 2,500 psig, and the corresponding equilibrium constants should be satisfactory for computations of the phase behavior of this gas-condensate system.

Although calculations made with equilibrium constants correlated in this manner have not been checked by following the actual depletion of a gas-condensate reservoir, comparisons of such computations with depletion-type experiments on recombined samples in the laboratory have yielded results that appeared to be entirely adequate.

It should be pointed out that the method of correlation presented here is designed solely for the correlation of equilibrium constants for a particular system. Since it is well known that equilibrium constants, particularly at high pressure, are quite sensitive to composition, it is obvious that the particular equilibrium constants presented in this paper would not be applicable to another gas-condensate system of substantially different composition. In no sense are they offered as being generally applicable. The method of correlation, however, as distinct from the particular equilibrium constants, is one that has been found useful for many gas-condensate systems covering a wide range of composition. For each system experimental data are required for that particular system. For the smoothing of and detection of errors in analyses of equilibrium mixtures, the method has been rather rigorously tested. The limits to which the method can be employed to extend equilibrium constants for a particular system into regions of temperature and pressure beyond those experimentally employed have not been fully determined.

REFERENCES

1. Buckley, S. E., and Lightfoot, J. H.: "Effects of Pressure and Temperature on Condensation of Distillate from Natural Gas," *Trans.* AIME, (1941), 142, 232.
2. Flaitz, J. M., and Parks, A. S.: "Sampling Gas-Condensate Wells," *Trans.* AIME, (1942), 146, 13.
3. Nysewander, C. N., Sage, B. H., and Lacey, W. N.: "The Propane-n-Butane System in the Critical Region." *Ind. and Eng. Chem.*, (1940), 32, (1), 118.
4. Cox, Edwin R.: "Pressure-Temperature Chart for Hydrocarbon Vapors." *Ind. and Eng. Chem.*, (1923), 15, (6), 592. ★ ★ ★

DISCUSSION

By Fred H. Poettmann, Phillips Petroleum Co., Bartlesville, Okla., Junior Member AIME

The authors have made an excellent contribution by making available equilibrium data at reservoir conditions of the high boiling hydrocarbon fractions in a gas-condensate system. It is the high boiling hydrocarbon fractions which have the greatest effect in calculating the dew point of a gas condensate system, and the more information we have on these fractions, the more accurate will be our predictions. The procedure used by the authors for obtaining equilibrium vaporization ratios for the high boiling fractions is very good.

We shall divide our discussion of the authors' correlation procedure into two parts, (1) the origin of the correlation, and (2) the authors' application of the correlation.

The relationships used by the authors in correlating their equilibrium vaporization ratios can be found in any good text on thermodynamics. Equation (1) can be derived assuming only ideal solutions in the vapor and liquid phases.

$$ln\, K = b'\left(\frac{1}{T_{B}} - \frac{1}{T}\right) \qquad \ldots \ldots \ldots (1)$$

where

$$b' = \frac{\triangle\overline{H}}{R}$$

$\triangle\overline{H}$ = heat of solution of component
R = gas constant
T_{B} = normal boiling point of component in degrees Rankine
T = equilibrium temperature degrees Rankine

The relationship used in Equation (2) is that employed by the authors. In addition to the assumption of ideal solutions
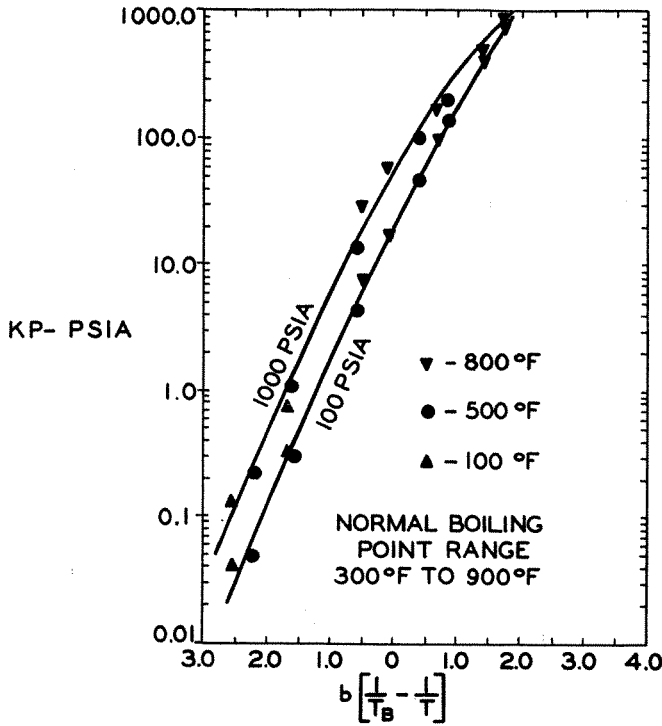
FIG. 1 — EQUILIBRIUM VAPORIZATION RATIOS, HIGH BOILING HYDRO-CARBON FRACTIONS. CHARACTERIZATION FACTOR 10.5.
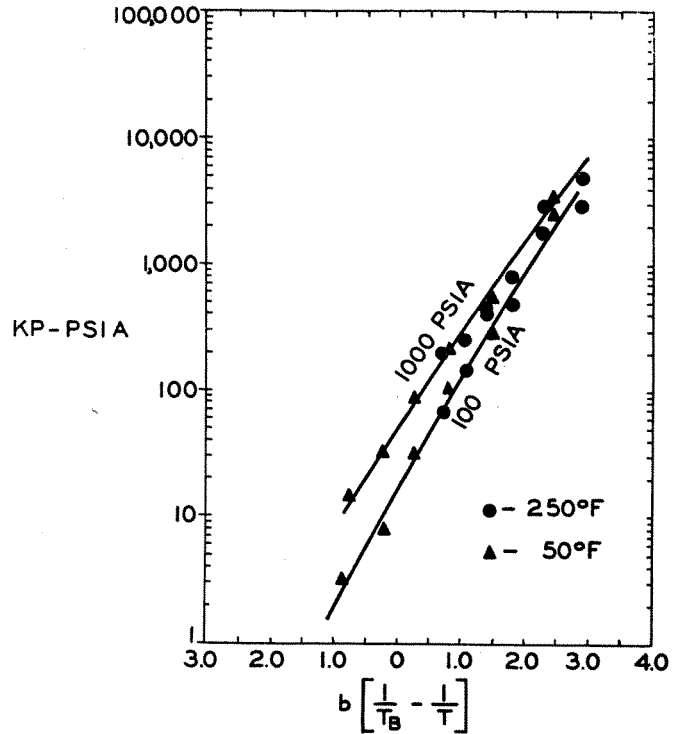

FIG. 2 — EQUILIBRIUM VAPORIZATION RATIOS, C_1 TO C_6. ROLAND, SMITH AND KAVELER.

in the vapor and liquid phases, the added assumption of the vapor being a perfect gas was also made in its derivation.

$$ ln \frac{KP}{14.7} = b \left(\frac{1}{T_b} - \frac{1}{T} \right) \qquad \cdots \cdots \cdots \quad (2) $$

where

$$ b = \frac{L}{R} $$

P = psia

L = heat of vaporization of the component as a pure material

R = gas constant

Thus a plot of $ln\ KP$ vs

$$ b \left(\frac{1}{T_b} - \frac{1}{T} \right) $$

will serve as a generalized correlation for K data at any temperature, pressure, and component for any system under conditions in which the relationship of the components in that system are compatible to the assumptions made. As expected, this has been found to be true for only very limited ranges of temperature and pressure for systems we have considered.

Fig. 1 shows K's for high boiling hydrocarbon fractions correlated in this manner.[1] Fig. 2 shows Roland, Smith, and Kaveler's condensate K's, and Fig. 3, Katz and Hackmuth K's.[2,3] For pressures higher than those shown on the diagrams, the correlation fails completely. We feel that Equation (1), where b' is determined from experimental K data should give a slightly better correlation than the case used by the authors where b is determined from the vapor pressures of the com-
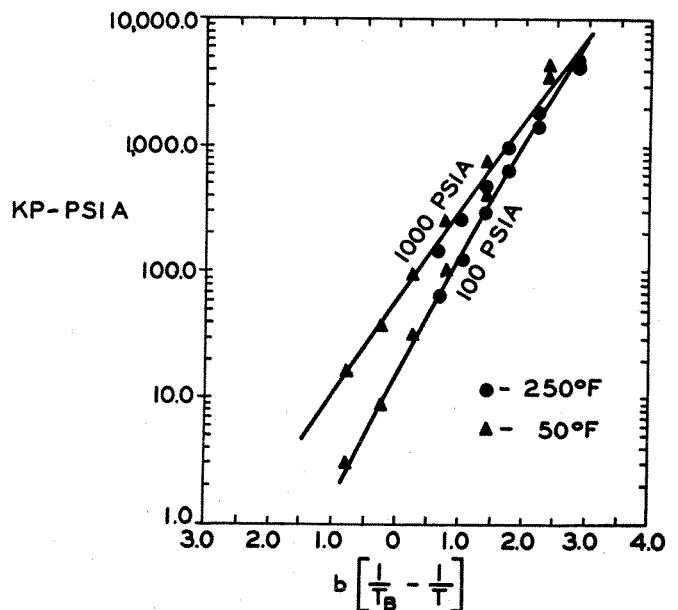

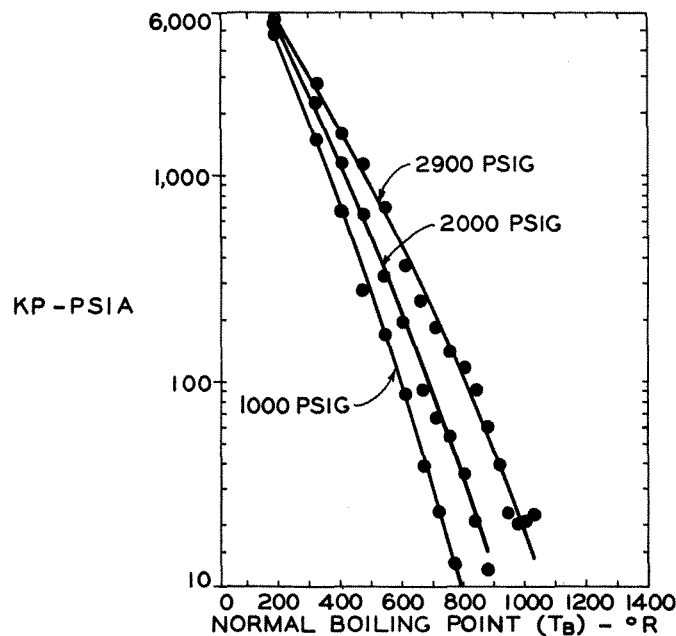FIG. 3 — EQUILIBRIUM VAPORIZATION RATIOS. KATZ AND HACKMUTH.

FIG. 4 — EQUILIBRIUM VAPORIZATION RATIOS VS NORMAL BOILING POINT OF COMPONENT. TEMPERATURE, 201°F.

ponents in the pure state. In neither case, will the K data correlate in the range of high temperatures and pressures which include retrograde behavior.

In the application of the correlation, the authors first justify the use of the correlation as a means of smoothing their experimental data. The authors' Fig. 5 is restricted to a constant temperature, the reservoir temperature. The variables on this plot are K, P, and T_B, b is not an independent variable, but a function of T_B, only. The petroleum industry has for years correlated K's at constant temperature by simply plotting $ln\ K$ or $ln\ KP$ vs the normal boiling point for lines of constant pressure. Fig. 4 is a plot of three of the constant pressure lines shown on the authors' Fig. 5. The curves are identical to those shown on the authors' Fig. 5. The experimental data are also indicated. We cannot see any advantage of using the authors' correlation as a means of smoothing K data at constant temperature.

In extending equilibrium vaporization ratios to another temperature, the authors actually use the correlation as a general method for obtaining K data. This procedure will give reasonable results at low pressures and temperatures but, as stated previously, at high temperatures and pressures, and especially in the region of retrograde behavior, the K data will not correlate. The authors warn that the procedure should not be applied to widely different conditions of temperature and composition. This warning is well taken. Fig. 5 gives an indication of what can occur if the temperature variation alone is too large. It is a plot of

$$ln\ KP\ vs\ b\left(\frac{1}{T_B} - \frac{1}{T}\right)$$

at 3,000 psia and 150, 201, and 250°F. The data were obtained from the condensate system of Roland, Smith, and Kaveler.[2] Fig. 5 shows that the K data do not correlate as a single curve at 3,000 psia and 150, 201, and 250°F. Tabulated below are the differences in the actual values of K at 250°F and K values at 250°F adjusted from the 201°F curve, all taken at 3,000 psia. Only K values of methane through pentane were compared.

Component	K_{250} Adjusted from 201°F	K_{250} Actual	K_{250} Deviation	Per Cent Deviation
C_1	2.10	2.02	+0.08	+ 3.96
C_2	1.14	1.04	+0.10	+ 9.62
C_3	.73	0.62	+0.11	+17.7
C_4	.49	0.40	+0.09	+22.5
C_5	.37	0.30	+0.07	+23.3

As can be seen, the higher the boiling point, the greater the percentage deviation in the K value.

REFERENCES

1. Poettmann, F. H., and Mayland, B. J.: "Equilibrium Constants for High Boiling Hydrocarbon Fractions of Varying Characterization Factors," *Petroleum Refiner*, (July, 1949), **28**, (7), 101.
2. Roland, C. H., Smith, D. E., and Kaveler, H. H.: "Equilibrium Constants for a Gas-Distillate System," *Oil and Gas Jour.*, (1941), **39**, (46), 128.
3. Katz, D. L., and Hackmuth, K. H.: "Vaporization Equilibrium Constants in Crude Oil-Natural Gas System," *Ind. and Eng. Chem.*, (1937), **29**, 1072.   ★ ★ ★
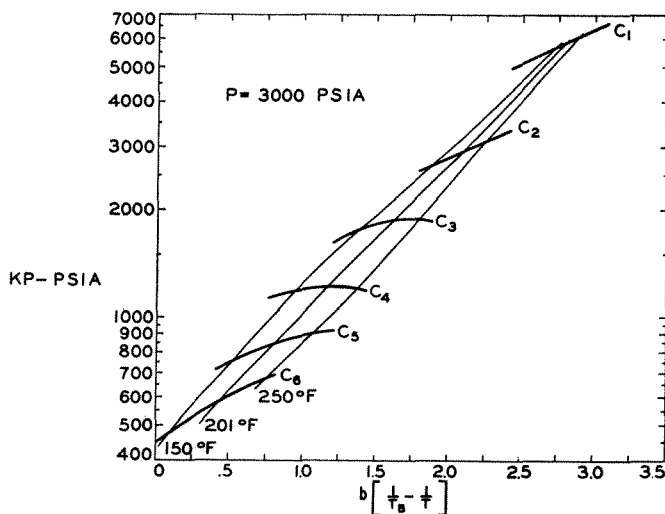
FIG. 5 — EFFECT OF TEMPERATURE ON CORRELATION. ROLAND, SMITH AND KAVELER K DATA.[2]