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Equilibrium Vaporization Ratios

Hydrocarbon Mixture Containing Two Concentrations of Heptanes and Heavier Fraction

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Equilibrium vaporization ratios have been obtained for the components, methane through heptanes-plus, in two combined natural gas-crude oil mixtures of a common source. The mixtures contained 20.13 and 11.20 mole % of heptanes-plus with relative amounts of the remaining components held constant. The data were obtained at 190° F. and cover a pressure range of 1000 to 6000 pounds/square inch.

The results of this investigation are compared with those of related work. A brief description of the apparatus and procedures used are included.

Generalized equilibrium vaporization-ratio (K value) charts, applicable to the light hydrocarbons for pressures up to 600 pounds/square inch and based on the early work of Brown (17), Katz (8), and Sage (16) are available in the literature and various handbooks. Subsequent work by Katz (9), who used a 225 molecular weight crude oil, showed the behavior of equilibrium ratios at pressures above 1000 pounds/square inch to be theoretically unpredictable. The over-all composition of these mixtures varied as the pressure was decreased to reproduce the depletion behavior of an oil reservoir.

Webber (20) reported equilibrium ratios resulting from an investigation of a natural gas-absorber oil system. The gas-oil ratio of Webber's system increased with pressure. Subsequently Eilerts (3) pointed out the importance of holding the over-all composition constant, particularly with respect to the heptanes-plus fraction. Similar data have been reported by Kirkbride and Bertetti (10).

Roland, Smith, and Kaveler (14) obtained equilibrium ratio data for gas-distillate mixtures of 50, 75, 85, and 90 mole % methane at 40°, 120°, and 200° F. Isothermal comparison of the data for the various mixtures showed that, for this particular system, the effect of varying over-all composition was not large.

Standing and Katz (18) presented considerable volumetric data on four natural gas-gasoline-crude oil mixtures. Two mixtures had sufficient equilibrium ratio data to make an isothermal-isobaric comparison at 200° F. The relative amounts of methane, ethane, and propane in these mixtures were held constant. The gas-oil ratios of the mixtures were 7180 and 3660 cubic feet per barrel.

Roland (13) investigated a fixed gas-oil ratio, natural gas-crude oil system at 120° and 200° F. over a pressure range of 1000 to 9500 pounds/square inch. Data were also given for nonfixed gas-oil ratio mixtures and a mixture derived from a high pressure vapor phase.

More recent experimental work (5, 6, 12, 19) has been concerned with equilibrium ratios for the nonhydrocarbons, nitrogen, carbon dioxide, and hydrogen sulfide in natural gas-crude oil and natural gas-distillate systems. These components, often occurring in natural petroleum reservoir mixtures, are of considerable interest and pose special analytical and experimental problems.

The amount of published experimental data on the heptanes-plus fraction, compared with those on lighter hydrocarbons, was found to be limited (1). Hence, the primary object of this investigation was to show the effect of varying the amount of heptanes-plus components while holding the relative amounts of the other components constant. Most of the previous investigators varied the composition by changing the gas-oil ratio. If the fluids used to make up the mixtures contained components which were common to both fluids, the relative amounts of these components would not remain constant in the resulting mixtures. In this investigation the mixtures were recombined in such a manner that this effect would be eliminated.

The data obtained may be divided into two groups: in the first, the liquid and gas samples were recombined in a fixed gas-oil ratio; the second group was handled in the same manner, except that the number of moles of heptanes-plus component per mole of the remaining components was decreased by a factor of one-half. Since this investigation was mainly concerned with the effects of the heptanes-plus fraction, special attention was paid to this component in analyzing the various phase samples.

MATERIALS USED

The reservoir materials used to make up the recombined equilibrium mixtures A and B in Table I were obtained from a Chitwood-Boatwright sand unit in Grady County, Oklahoma. The liquid sample was taken from a high-pressure separator operating at 98° F., and 357.3 pounds/square inch. The gas samples were taken at the same pressure from another point in the same field.

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TABLE I. ANALYSIS OF OIL AND GAS MIXTURES

Hydrocarbon	Composite Composition, Mole % Recombined Mixture A	 Recombined Mixture B
Methane	60.88	67.69
Ethane	7.38	8.21
Propane	5.03	5.59
Butanes	2.78	3.09
Pentanes	1.96	2.18
Hexanes	1.84	2.04
Heptanes and heavier	20.13	11.20
Moles heptanes-plus/ moles remaining[a]	0.252	0.126

[a] Mol. wt. 191; A.P.I. gravity at 60° F., 37.7.

Preliminary checks with a mass spectrometer and Burrell gas analysis apparatus showed the presence of carbon dioxide in concentrations less than 1%. This was removed by means of caustic packed filters.

The composite analyses in Table I were the result of several analyses of both equilibrium mixtures in a single phase condition. To characterize the higher boiling-point fractions of the liquid separator-sample, a portion of each sample was flashed at atmospheric pressure. The resulting liquid was subjected to a U. S. Bureau of Mines distillation (Table II).

EQUILIBRIUM APPARATUS

Detailed descriptions of apparatus similar to that used (Figure 1) are available in the literature (2,9,15). Briefly, the apparatus consists of a thermostated mercury pump, charging cell, and 600-cc. rocking equilibrium cell. Temperatures of the thermostats, controlled to within 0.3° F. with suitable devices, were measured by means of mercury in glass thermometers, calibrated with a National Bureau of Standards certified platinum resistance thermometer. Stirrers and pumps provided the necessary agitation. All pressure measurements were made with a dead-weight gage. A high pressure mercury U-tube (2) (a mercury level indicating device) was used to control the position of the mercury and dead-weight gage oil interface at a fixed point to which all mercury head corrections were referred.

CHARGING THE EQUILIBRIUM CELL

The materials were charged in such a manner that the over-all composition of the mixtures could be represented by the analyses in Table I. In addition to this restriction, it was necessary that enough mixture be present to yield sufficient quantities of each phase for representative sampling.

The equilibrium and charging cells were flushed out and evacuated. The charging cell was then filled with mercury (valves A, H, D, and E, Figure 1, closed) with the mercury pump adjusted to read approximately 200 cc. delivered. A reading of the pump at the desired pressure was taken and valve C closed. Valve D was opened and the gas was then admitted to the charging cell. The gas-sample tank was carefully heated before transferring the gas to the charging cell. With valve D closed and C opened a predetermined number of turns, the pump reading was again determined at the same pressure and temperature as the initial reading. The gas was then injected into the evacuated equilibrium cell through valve E. The above process was repeated until the desired amount of gas was charged to the equilibrium cell. The conditions for charging both the gas and liquid separator samples were chosen in such a manner as to avoid making volumetric measurements near the phase boundary conditions of either fluid. The calibrations and formulas suggested by Beattie (2) as well as the data presented by Jessen (7) were used for the fluid charging procedures.

The amount of liquid corresponding to the gas previously charged was then injected into the equilibrium cell. The procedure for charging liquid was the same as that for the gas (except for the charging cell conditions).

TABLE II. U. S. BUREAU OF MINES
Distillation of Chitwood-Boatwright sand crude oil

Temp., ° F.	Per Cent Over	Gravity Fraction, °A.P.I., 60/60
Up to 122	2.8	
167	5.0	79.3[a]
212	9.7	66.6
257	17.9	58.4
302	25.4	54.7
347	31.8	48.8
392	35.8	47.2
437	40.8	44.5
482	46.2	41.7
527	54.7	39.1
Distillation at 40 Mm. Pressure		
Up to 392	57.3	
437	62.0	35.2
482	66.5	33.2
527	71.0	31.8
572	77.3	29.7
Gravity of crude, °A.P.I.		41.3
Gravity of still residue, °A.P.I.		23.3

[a] Cumulative density of first two fractions.

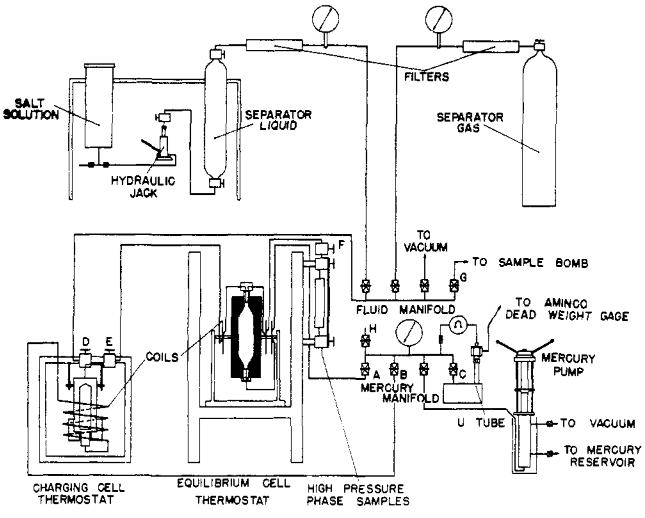


Figure 1. Apparatus used to obtain equilibrium samples

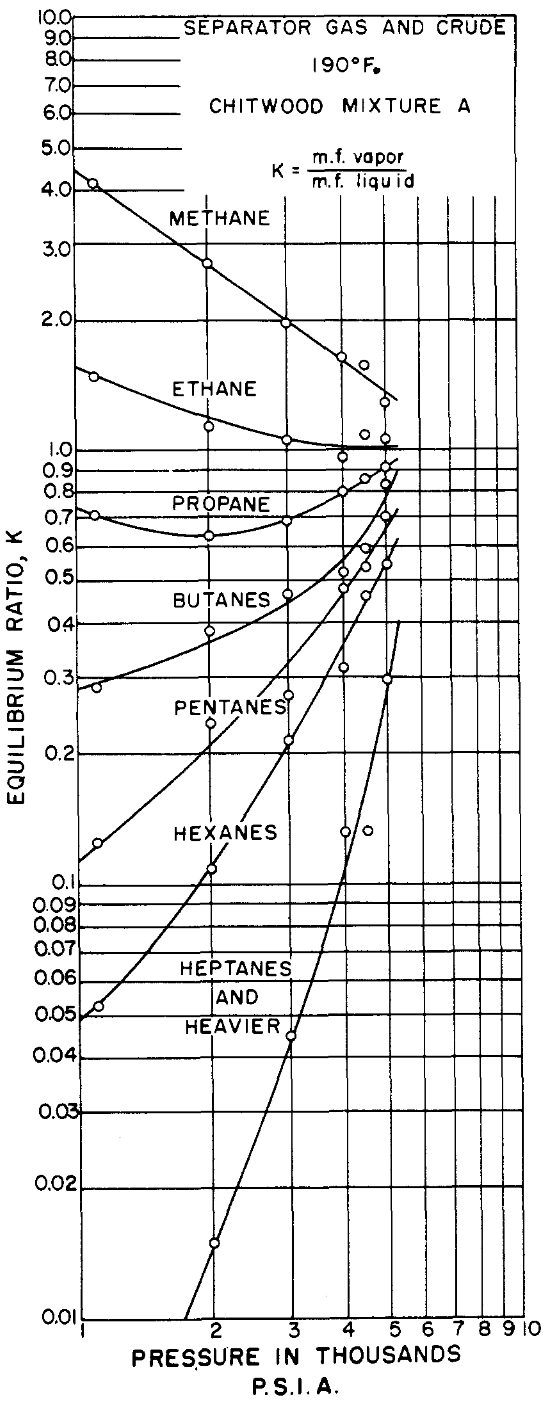


Figure 2. Equilibrium ratios for mixture A at 190° F.

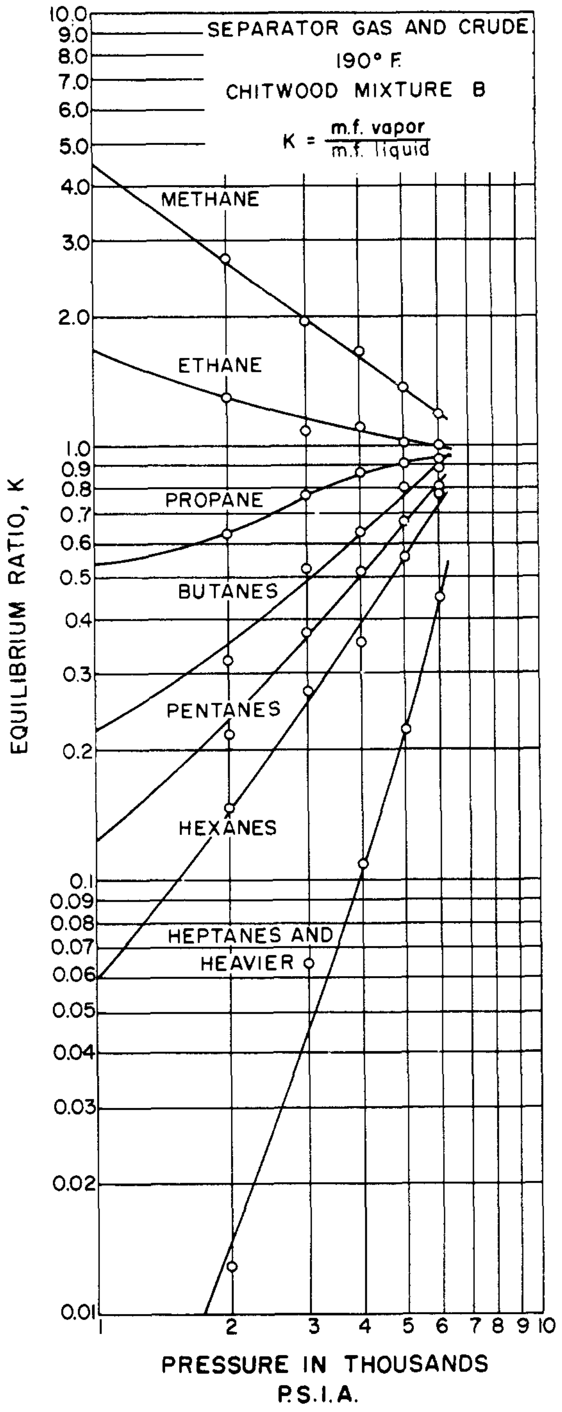


Figure 3. Equilibrium ratios for mixture B at 190° F.

When mixture B was desired, half the amount of liquid which would have been charged for mixture A was displaced through valve G into a mercury filled sample container; the remaining half was charged to the equilibrium cell. The separator liquid in the sample container was "topped" by means of a previously evacuated distillation apparatus that was constructed for this purpose. The volumes of the liquid samples handled ranged from 50 to 100 cc. The distillation could be carried out in this apparatus with special attention to rapid and complete recovery of the lighter fractions, methane through hexanes, which were injected into the equilibrium cell by means of valves F and H (Figure 1).

Before initiating any equilibrium determinations, all coils to the equilibruim cell were filled with mercury to ensure that all fractions of the charge had been placed in the equilibrium cell. Valves B, F, and H (Figure 1) were closed. Valve A was opened; the amount of mercury necessary to bring the mixture to the desired pressure was injected, and the cell was then rocked to ensure equilibrium conditions before sampling procedures were carried out.

SAMPLE DISPLACEMENT

Isobaric-isothermal conditions were maintained during all displacements of the equilibrium mixture. The dead-

TABLE III. PHASE ANALYSES AND EQUILIBRIUM CONSTANTS FOR RECOMBINED MIXTURE A AT 190° F.

	Mole %			Mole %			Mole %		
	Liquid	Vapor	K	Liquid	Vapor	K	Liquid	Vapor	K
	1110 lb. / sq. inch abs.			2000 lb. / sq. inch abs.			3000 lb. / sq. inch abs.		
Methane	20.27	84.22	4.15	31.26	84.90	2.72	42.38	83.52	1.97
Ethane	5.81	8.63	1.49	6.84	7.72	1.129	7.19	7.59	1.06
Propane	6.26	4.45	0.711	6.37	3.94	0.619	6.11	4.18	0.684
Butanes	5.24	1.50	0.286	4.16	1.60	0.385	3.68	1.72	0.467
Pentanes	4.45	0.56	0.126	3.41	0.80	0.235	2.86	0.78	0.273
Hexanes	6.28	0.33	0.053	3.65	0.40	0.110	3.13	0.67	0.214
Heptanes and heavier	51.69	0.31	0.0060	44.31	0.64	0.014	34.65	1.54	0.044
Z = PV/nRT	0.436	0.924	. .	0.690	0.874	. .	0.923	0.846	. .

	Mole %			Mole %			Mole %		
	Liquid	Vapor	K	Liquid	Vapor	K	Liquid	Vapor	K
	4000 lb. / sq. inch abs.			4500 lb. / sq. inch abs.			5000 lb. / sq. inch abs.		
Methane	49.60	80.93	1.63	50.90	79.96	1.57	59.33	76.43	1.29
Ethane	7.73	7.38	0.955	7.07	7.62	1.08	7.52	7.96	1.06
Propane	5.35	4.27	0.798	5.09	4.34	0.853	5.01	4.54	0.906
Butanes	3.47	1.81	0.522	3.59	2.13	0.593	2.84	2.37	0.835
Pentanes	2.02	0.96	0.475	2.21	1.18	0.534	1.99	1.39	0.698
Hexanes	2.39	0.75	0.314	2.15	0.98	0.456	2.14	1.16	0.542
Heptanes and heavier	29.44	3.90	0.132	28.99	3.79	0.131	21.17	6.15	0.291
Z = PV/nRT	1.098	0.903	. .	1.200	0.926	. .	1.207	0.987	. .

weight gage served as the pressure maintenance device while the actual displacement was carried out with a mercury pump. The floating gage-piston acted as a buffer, smoothing out minor pressure fluctuations induced by the various manipulations.

Before sample displacements were initiated, the equilibrium cell-rocking arm was disconnected from the eccentric and the cell was turned into the upright position as shown in Figure 1. The mercury in the cell connecting the equilibrium cell and valve F, plus approximately 20 cc. of gas phase, was carefully displaced from the cell to flush the sampling lines. A phase-sample bomb was then connected at valve F. The sample bombs used had been previously filled with mercury in vacuo, and then pressured. The phase samples were displaced into the sample bombs by slowly injecting mercury into the equilibrium cell and withdrawing mercury from the sample bomb at the same rate. Careful attention to details resulted in the satisfactory determination of the volume of the phase samples.

TABLE IV. PHASE ANALYSES AND EQUILIBRIUM CONSTANTS FOR RECOMBINED MIXTURE B AT 190° F.

	Mole %			Mole %			Mole %		
	Liquid	Vapor	K	Liquid	Vapor	K	Liquid	Vapor	K
	2000 lb. / sq. inch abs.			3000 lb. / sq. inch abs.			4000 lb. / sq. inch abs.		
Methane	30.21	81.93	2.71	40.82	79.36	1.94	46.71	77.70	1.66
Ethane	6.56	8.50	1.30	7.54	8.25	1.09	7.71	8.58	1.11
Propane	8.21	5.17	0.630	6.52	5.04	0.773	6.07	5.23	0.862
Butanes	6.86	2.21	0.322	4.71	2.53	0.537	4.09	2.51	0.614
Pentanes	4.93	1.07	0.217	4.12	1.55	0.376	3.16	1.64	0.519
Hexanes	4.25	0.62	0.146	4.29	1.19	0.277	3.50	1.24	0.354
Heptanes and heavier	38.97	0.50	0.0128	32.00	2.08	0.0650	28.76	3.10	0.108
Z = PV/nRT	0.6557	0.839	. .	0.868	0.819	. .	1.038	0.865	. .

	Mole %			Mole %		
	Liquid	Vapor	K	Liquid	Vapor	K
	5000 lb. / sq. inch abs.			6000 lb. / sq. inch abs.		
Methane	54.91	75.38	1.37	61.01	72.12	1.18
Ethane	8.17	8.28	1.01	8.48	8.52	1.00
Propane	5.95	5.34	0.897	5.81	5.44	0.936
Butanes	3.44	2.76	0.802	3.41	3.03	0.888
Pentanes	2.62	1.75	0.668	2.23	1.72	0.771
Hexanes	2.76	1.55	0.562	2.01	1.61	0.801
Heptanes and heavier	22.15	4.94	0.223	17.05	7.56	0.443
Z = PV/nRT	1.199	0.991	. .	1.365	1.148	. .

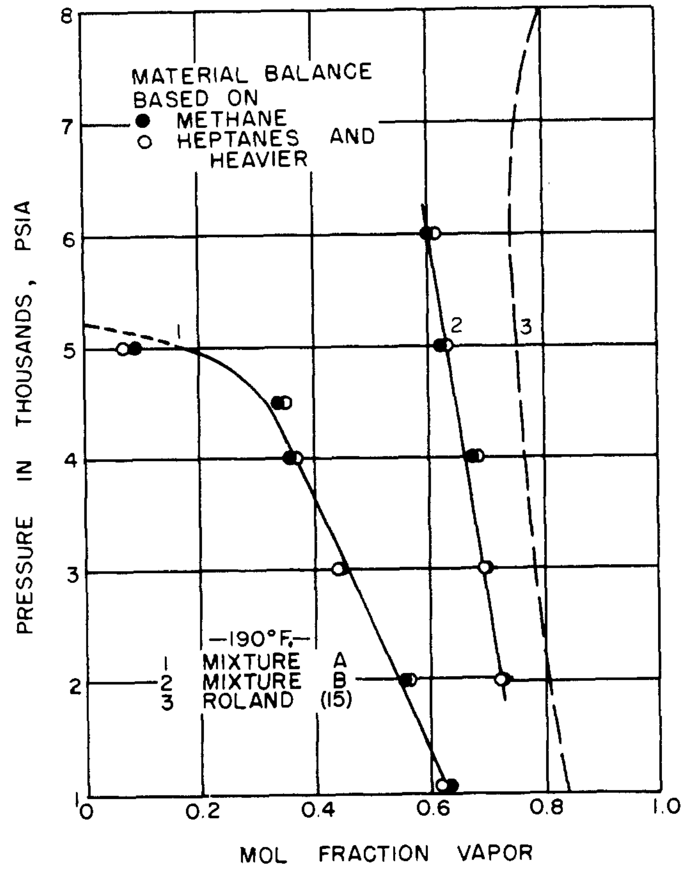
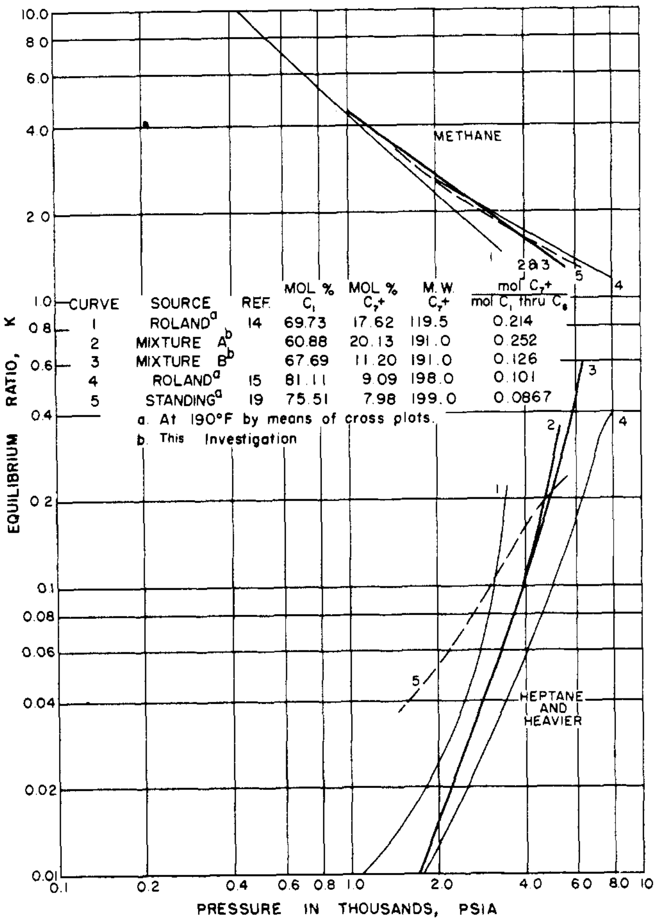


Figure 4. Relative amount of vapor phase present at equilibrium conditions



CURVE	SOURCE	REF.	MOL % C_1	MOL % C_7+	M.W. C_7+	$\frac{\text{mol } C_7+}{\text{mol } C_1 \text{ thru } C_6}$
1	ROLAND[a]	14	69.73	17.62	119.5	0.214
2	MIXTURE A[b]		60.88	20.13	191.0	0.252
3	MIXTURE B[b]		67.69	11.20	191.0	0.126
4	ROLAND[a]	15	81.11	9.09	198.0	0.101
5	STANDING[a]	19	75.51	7.98	199.0	0.0867

a. At 190°F by means of cross plots.

b. This Investigation

Figure 5. Comparison of equilibrium ratio data for various multicomponent mixtures at 190° F.

ANALYTICAL METHODS

The light hydrocarbon fractions of the phase samples, methane through hexanes, were analyzed by means of a Podbielniak Hyd-Robot distillation apparatus. The performance of this device was checked with gas mixtures of known composition and quantity. Each phase-sample bomb was connected to a mercury pump and the sample was displaced into the distillation kettle while the methane fraction was being distilled and recorded. The charging operation was completed well before the methane-ethane break. At this point the remaining fractions through hexanes, were distilled and recorded using standard procedures.

The number of moles of the corresponding heptanes and heavier fractions were determined gravimetrically or by using the freezing point depression of a known amount of benzene. The apparatus and procedures for freezing point determinations were substantially those of Rossini and coworkers (11). Modifications and correlations as suggested in the literature (4) were used to make the above methods applicable to the determination of molecular weights of crude oils. The column packing, connecting tubing, and sample bomb were washed with a known amount of benzene at the completion of each distillation. The number of moles of the nondrainable residue was thus determined. It was found, through multiple blank determinations, that the silicone stopcock-grease used had little effect on the freezing point of pure benzene. Plots of molecular weights as a function of the corresponding density (4) and pressure (13) served as a check of the experimental values for the liquid samples. Complete molecular weight versus pressure plots for the systems studied were not obtained because of the small amount of heptanes-plus material present in the gas samples. In these instances the moles of heptanes-plus were determined directly by the freezing point method as were the nondrainable residues of the liquid samples.

EXPERIMENTAL DATA

The equilibrium ratio of methane closely approximates a simple power function of pressure (Figures 2 and 3). The mole fraction of the total amount of vapor phase present in the equilibrium mixtures (Figure 4) was obtained by means of a mass balance on the major components — methane and the heptanes-plus fraction — utilizing the over-all composition as given in Table I and the experimental values of mole fractions of the components in each phase of the equilibrium mixtures (Tables III and IV).

Compressibility factors (Tables III and IV) show the change in the volumetric behavior of the equilibrium phases as a function of pressure. These data may be utilized in conjunction with the corresponding mole fractions of the components to determine the vapor-liquid volumetric ratio.

Because of the extreme sensitivity with which these systems respond to changes in pressure at the higher pressures, the over-all results are believed to be accurate within 3.0% for methane, 8.0% for heptanes-plus, and a somewhat higher percentage for the remaining components. The estimated accuracies are not the same for all components, since the accuracies depend on the amount of material present in the mixtures investigated.

CONCLUSIONS

The results of this investigation indicate that for this system, the equilibrium ratios for methane and heptanes-plus remain reasonably constant when the concentration of the heptanes-plus fraction is decreased by a factor of approximately 2. The effect of a decrease in the heptanes-plus fraction at the concentrations studied serves mainly to extend the pressure region over which these ratios are defined. This trend could be completely reversed with a continued decrease in the heptanes-plus concentration. Decreasing the amount of the heptanes-plus fraction in this system does have a slight effect on the equilibrium ratios of the intermediate components, ethane through hexanes; the net effect is a small increase at the higher pressures.

Figure 5 shows many interesting trends regarding the equilibrium ratios of different multicomponent systems. The data of other investigators have been cross plotted to yield values at 190° F. With the exception of the C and F mixture data of Standing and Katz (18), the procedure of cross plotting on semilog paper would introduce a relatively small amount of error.

The curves as numbered in Figure 5 generally show an increase in $\frac{\partial K}{\partial p}$, and a decrease in the rate at which they approach their respective "apparent convergence pressure". With the exception of Roland's distillate system, the moles of heptanes-plus per mole of remaining components decrease as the curve numbers increase. The low molecular weight of Roland's heptanes and heavier fraction could over-ride this factor. The molecular weight of the systems shows an increase with respect to curves 1, 2, 3, and 4. The molecular weight corresponding to curve 5 is slightly less than that corresponding to curve 4. Figure 4 compares the phase behavior of the mixtures represented by curves 2, 3, and 4, in Figure 5.

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Critical Properties and Vapor Pressures of Some Ethers and Heterocyclic Compounds

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This report, a continuation of previous work (11), supplies more data on critical properties of newer organic compounds, thus permitting the law of corresponding states to be used in estimating other properties of engineering importance.

Critical properties were determined for five ethers and eight heterocyclic compounds, using the apparatus and technique of the previous work.

Correlations and equations are given for the critical temperatures and pressures of the ethers, heterocyclic compounds, and ketones.

Many organic chemicals, heretofore of only academic interest, are now being produced in tonnage quantities. Frequently engineers need to estimate certain properties of these compounds that are basic to the design of research equipment, pilot plants, and commercial installations.

The law of corresponding states, first proposed by van der Waals, has been used by many investigators for the estimation and correlation of thermodynamic data; Nelson and Obert (14) gave a brief review of various forms that are in common use. One of the more important correlations based on this law are compressibility charts, the most recent of which was prepared by Nelson and Obert (15) from 30 gases. These charts show a maximum deviation of 1.0% in the region below the critical point. In pressure ranges where P_r = 1.0 to 10.0, the maximum deviation is 2.5%, while in the high pressure ranges where P_r = 10.0 to 40.0, the maximum deviation, based on 9 gases, is about 5%.

A knowledge of critical constants permits a correction for the effect of pressure on various thermodynamic properties such as enthalpy, entropy, heat capacity, and fugacity coefficients. The concept of the law of corresponding states is now being advanced toward the calculation of transport properties such as thermal conductivity (3) and diffusion coefficients (1). Attempts are being made to generalize some physical properties on the same basis (23).

A brief review of various methods for the determination of critical properties was given by Kobe and Lynn (9), who also tabulated critical values for many compounds.

APPARATUS

The apparatus (Figure 1) differs in some respect from that described by Kobe, Crawford, and Stephenson (11). Briefly, it consists of a high pressure bomb incased in an