$\overline{W}^+$ = dimensionless average mass fraction
W_{Aw} = mass fraction at the wall
$\overline{W}_A$ = average mass fraction
y_{Bm} = log mean concentration of nondiffusing species, dimensionless
y = distance from the pipe wall, $R - r$, ft.
y^* = dimensionless distance from the pipe wall, $1 - r/R$
y^+ = dimensionless distance from the pipe wall, $y\, U_\tau/\nu$
Z = aspect ratio = z/D
z = axial direction, axial distance
Z^+ = dimensionless axial distance = z/R
ρ = density
μ = viscosity
ν = kinematic viscosity
ϵ = eddy viscosity
τ = shear stress
ϕ = blowing factor, $V_w/U_{\tau 0}$
A = diffusing species
B = nondiffusing species
0 = incoming stream
r = radial direction
w = wall value
z = axial direction

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Phase Equilibria in the Methane-Ethane-Propane-*n*-Pentane-*n*-Hexane-*n*-Decane System

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An experimental facility for vapor-liquid equilibrium measurements at high pressures (100 to 15,000 lb./sq. in. abs.) and ordinary temperatures (100° to 300°F.) on multicomponent mixtures is described. The vapor-liquid phase behavior of a six-component hydrocarbon mixture, which simulated a natural gas and a condensate, was studied with this apparatus. Measurements were made at 150° and 250°F. and pressures ranging from 100 lb./sq. in. abs. to the single-phase pressures for these systems and temperatures.

Vapor-liquid equilibrium K values for the components of natural gas and condensate at high pressures are used by reservoir engineers in making condensate depletion calculations and by process engineers in designing hydrocarbon separation facilities for the gas and condensate production.

The natural gas-condensate system is a multicomponent mixture that is difficult to break down into components. Natural gas compositions can usually be characterized by the names and amounts of specific compounds (that is, hydrocarbons and related gases, such as nitrogen and carbon dioxide). Condensates, on the other hand, are usually characterized in terms of both real and hypothetical components, the latter being identified by atmospheric boiling point ranges.

In this technique of characterization, a hypothetical component contains many actual components, all in small concentration, that fall in the specific boiling point range. For the prediction of thermodynamic properties of such hypothetical components, it is necessary to use average physical properties, such as density, molecular weight, vapor pressures, and vapor-liquid K values. Approximations of this kind may be acceptable in depletion and design calculations, but should not be a part of an experimental study of vapor-liquid equilibria, as was learned in a recent thesis project (9) carried out at Oklahoma State

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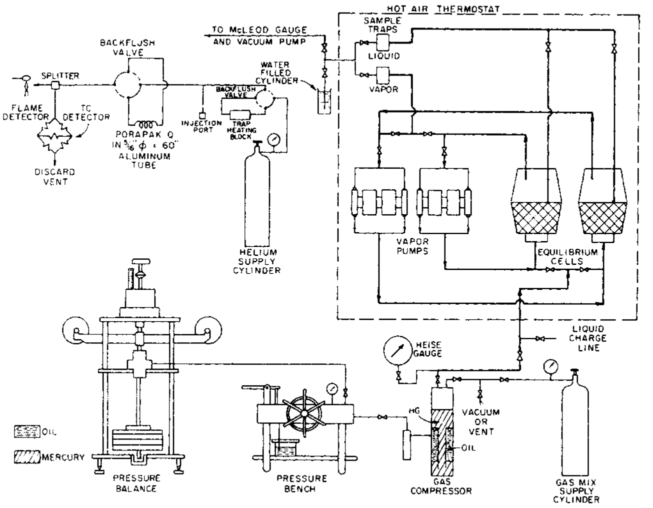

Fig. 1. Schematic diagram of vapor-liquid equilibrium apparatus.

University.

This effort led to a new experimental program, using prepared mixtures of fewer components. The program was designed to reveal effects of hydrocarbon types in the C_{7+} fraction and the effects of inert gases on the K values of the light hydrocarbons. Experimental mixtures studied were a base gas of three components, a base liquid of three components, an inert gas, an aromatic, and a naphthene. The two base mixtures were designed to simulate a natural gas and a condensate, the proportions of methane, ethane, and propane in the base gas and of *n*-pentane, *n*-hexane, and *n*-decane in the base liquid being selected from averages of 85 well-stream analyses. Compositions of the base hydrocarbon mixtures are given in Table 1. These hydrocarbons were furnished by Phillips Petroleum Company. The base gas mixture was prepared by blending 76-14-10 methane-ethane-propane mixture with research grade methane, both from Phillips. The base liquid mixture was prepared by blending research grade *n*-pentane, *n*-hexane, and *n*-decane, all from Phillips.

There were three parts to this experimental work: (1) phase equilibria in the six-component base system, (2) effects of nonparaffins on the K values of paraffin hydrocarbons, and (3) effects of carbon dioxide on K values of paraffin hydrocarbons. The present paper reports the results of the measurements on the base system. In addition, the experimental facilities and procedures, which were the same through all three parts of the investigation, are described herein. Parts 2 and 3 of this investigation are covered in two doctoral theses (*3*, *12*).

The dynamic or flow method of equilibrating vapor and liquid that was used in this work has been used previously by other investigators (*5*, *7*) other than those of this laboratory (*3*, *9*, *12*).

EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus is shown in Figure 1. Details of this and similar apparatus have been described elsewhere (*3*, *9* to *12*). Two equilibrium cells were connected in parallel, as shown, but were operated at different times. These two equilibrium cells are shown in detail in Figures 2 and 3. The cell in Figure 2 was used in the nonparaffinic effects study, while the cell in Figure 3 was used in the inerts effects study. As can be seen in Figure 1, there are two vapor circulating pumps, one for each equilibrium cell, in the thermostat.

The 0 to 3,000 lb./sq.in. Heise Bourdon pressure gauge was added for this work to save operating time and effort at most pressures encountered in these measurements. Above 2,700 lb./sq.in. the dead weight pressure balance was used, even though the high accuracy and precision of the pressure balance were not necessary in this investigation, since measurement of phase compositions was the accuracy controlling factor. Pressure was maintained by the addition of the gas mixture via the gas compressor and the pressure bench, as shown in Figure 1.

The two equilibrium cells differ in mechanical details, as can be seen by Figures 2 and 3. Both are constant volume (150 cc.) cells and designed to operate at 15,000 lb./sq.in. Closures in the Hart cell are lens rings, while O ring seals were used in the Autoclave cell. Considerable difficulty was experienced in making the Autoclave cell leaktight at high pressures. There was no difficulty of this kind with the Hart cell. Vapor and liq-

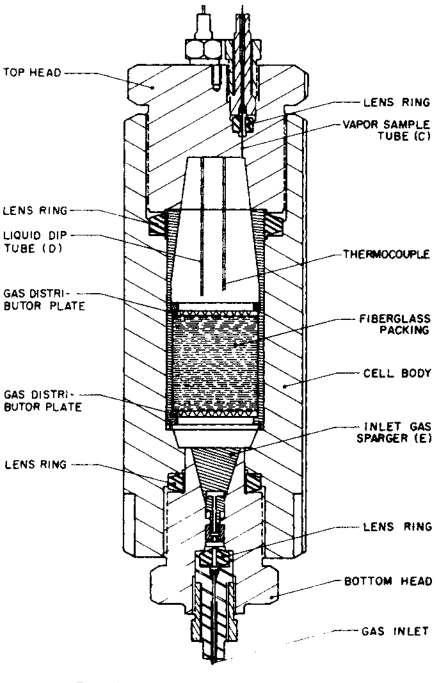

Fig. 2. Equilibrium cell (Hart).

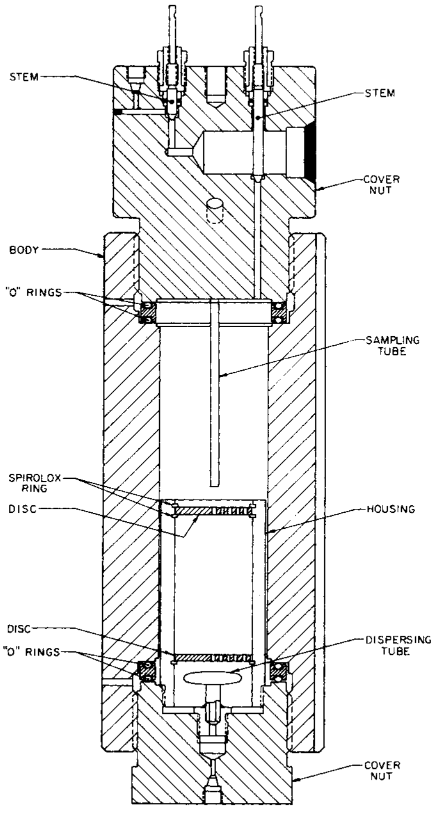

Fig. 3. Equilibrium cell (Autoclave).

uid sample cavities were built into the cap of the autoclave cell, but these were not used in this investigation. Both cells contain devices (dispersion tube, sparger, perforated plate, packing) to break the gas up into small bubbles for better mixing with the liquid.

Two features of these equilibrium cells are undesirable; constant volume and nonvisual. Because of the constant volume, pressure variations must be made by the introduction of more gas, which changes the proportions of the gas and liquid charges that are in the cell. The nonvisual nature of the cell made sampling a blind operation.

The vapor recirculating pumps consist of a magnetic steel, loose fitting piston in a nonmagnetic stainless steel tube. Reciprocating action is provided by two electromagnetic coils to produce double action pumping. Double ball check valves at each end of the cylinder act as inlet and outlet valves. These pumps maintained vapor circulation satisfactorily but the electromagnets liberated considerable heat that had to be removed from the thermostat by cooling.

The temperature in the air thermostat was maintained by circulating air, with a 6-in. squirrel cage blower, across a cooling coil and eight 250-w. finned electric heaters. Four of these heaters were operated in an on-off mode to control temperature to 0.1°F. via a Fisher controller for which the sensing element was a small resistance thermometer. The four other heaters were continuous, for which the power was set manually by a powerstat. Refrigerated water and glycol solution was pumped continuously through the coiling coil to remove heat from the thermostat. Temperature of the coolant was controlled by a Honeywell regulator that operated separately from the Fisher controller of the thermostat.

Equilibrium cell temperature was measured with iron-constantan thermocouples that were calibrated in place by comparison with an NBS calibrated platinum resistance thermometer. The location of the thermocouple, shown on Figure 2, is in the vapor phase. In the other cell the thermocouple is embedded in the cell wall (not shown on Figure 3). Temperatures of the sample traps were also measured by calibrated iron-constantan thermocouples.

The sample traps are flow-through needle type valves with a sample cavity machined into the valve body directly below the stem path in such a way that the fluid will flow through the cavity when the stem is raised and be trapped in the cavity when the stem is lowered. These sample cavities were drilled to be 2 and 40 μliters in volume to get reasonable size samples of the liquid and vapor phases, respectively. These sample traps were made from a design described by Yarborough and Vogel (*8*, *13*).

Connections permitting a direct transfer of the samples from the traps into the chromatograph were made and tried. This involved lines and valves to permit flowing the elution gas, helium, through the sample traps and into the chromatograph. If this had worked successfully, it would have been a great convenience and timesaver. Direct transfer of samples to the chromatograph, by sweeping the elution gas through the sample traps, was not successful because of the long length of tubing.

Sample trap valves were disconnected, removed from the air bath thermostat, and set in a heating block just outside the chromatograph oven. In addition to the heating block for direct injection of the sample, the chromatograph was equipped with back flush valves, stream splitter, two identical columns (one for reference gas and one for unknown), two detectors, and two recorders to permit simultaneous operation of thermal conductivity and flame ionization detectors.

The chromatograph was calibrated, using mixtures of known composition that covered the range of compositions expected in the experimental equilibrium samples. Liquid mixtures, of different proportions, of *n*-pentane, *n*-hexane, and *n*-decane were prepared gravimetrically, while binary vapor mixtures of methane with ethane, propane, *n*-pentane, and carbon dioxide were made up in a glassware assembly located inside a constant-temperature air bath, connected to a vacuum pump and equipped with a Texas Instruments quartz Bourdon tube pressure gauge. These known hydrocarbon mixtures were run through the chromatograph and resulting chromatograms were used to calibrate the columns. *n*-Pentane, being present in both the light and heavy end calibrations, was used as a reference compound. The accuracy of the composition analysis was determined by repeated analyses of several different calibration samples and found to be ± 3%.

TABLE 1. BASE HYDROCARBON MIXTURES USED IN EXPERIMENTAL MEASUREMENTS

Component	Mole % gas	Mole % liquid
C_1	88	—
C_2	7	—
C_3	5	—
n-C_5	—	20
n-C_6	—	20
n-C_{10}	—	60

Calculated initial charge compositions

	150°F.	250°F.
C_1	0.015	0.010
C_2	0.001	0.001
C_3	0.001	0.001
n-C_5	0.196	0.197
n-C_6	0.196	0.197
n-C_{10}	0.590	0.594
	0.999	1.000

EXPERIMENTAL PROCEDURE

There were four major steps in the experimental operations: charging the liquid and the gas mixtures, equilibration at the desired conditions, sampling the equilibrium vapor and liquid, and sample analysis. To begin a series of runs, the equilibrium cell and the gas compressor were isolated from the rest of the system and evacuated. Next the vacuum pump was isolated and the equilibrium cell and the gas compressor were filled with the base gas mixture to a few atmospheres pressure. The gas was bled off and the system evacuated again. This procedure was repeated another time, leaving the cell empty and evacuated.

Next a burette containing a supply of the deaerated base liquid mixture (*n*-pentane, *n*-hexane, and *n*-decane) was connected to the liquid charge line. With the vacuum pump connected and the cell isolated, a small amount of liquid was allowed to flow into the line, which was then evacuated to rinse the line. Then about 100 cc. of the liquid mixture was allowed to flow into the equilibrium cell. Next, the gas compressor was filled with the gas mixture preparatory to pressuring the equilibrium cell. Both cells were used, alternately, in this work.

The equilibrium cell was next heated to the desired operating temperature, 150° or 250°F., and the pressure raised by charging the gas mixture into the equilibrium cell from the compressor. Vapor-liquid equilibrium was then attained by circulating the vapor from the top back to the bottom of the cell by a magnetically driven pump. In preparation for sampling, the magnetic pump was shut off and isolated from the cell. The sampling system (traps and lines) was evacuated and the sample traps closed. After 15 min. of settling, the block valves downstream of the sample traps were closed and the lines were allowed to fill slowly with the equilibrium vapor and liquid fluids from the cell. Pressure in the cell was maintained during this sampling operation by the addition of more gas from the compressor, which in turn was pressured by the oil from the pressure bench. After a second 15 min. of settling, each phase was bled slowly through the trap to ensure the presence of an equilibrium composition in the traps when they were closed to catch the desired sample.

The vapor sample was always taken first by slowly opening the downstream valve and permitting the vapor to bubble slowly in a water-filled graduated cylinder. After 15 min. of bubbling, the vapor line was closed and a sample taken by opening and closing the sample trap. A similar procedure was followed in sampling the equilibrium liquid phase. At low pressure sampling of the liquid phase, liquid decane collected on the water. In both cases pressure was maintained by the injection of more base gas from the gas compressor.

The use of a dynamic sampling technique necessitates the examination of possible effects on the vapor and liquid equilibrium sample compositions. First, the amount of sample material removed and fresh gas injected into the equilibrium cell is small (approximately 250 cu. cm. at ambient conditions) compared to the 150-cu. cm volume of high pressure vapor and liquid contents of the cell. Second, since the sampling was done slowly, the fresh pressuring gas was injected into the equilibrium cell at a low rate having to pass through a sparger causing the stream to split into small bubbles. These bubbles then had to rise through the liquid to the vapor phase. During this slow passage the small gas bubbles will attain almost complete equilibrium with the liquid, thus minimizing any vapor-phase composition upsets. Since the liquid phase is already saturated with the gas, and due to the small volume of fresh gas injected, the change in liquid phase composition resulting from the saturation of this gas with heavier components will be insignificant. Thus the phase sample compositions should be representative of the true equilibrium compositions within the accuracy of the analysis.

After the samples were trapped in the valve cavities, the sampling section was isolated and the sample traps were removed from the thermostat. The sample valve body was then purged with compressed air and placed in the heating block. Helium was allowed to flow through the sample valve body until all hydrocarbon traces disappeared. The above procedure was necessary to remove all adsorbed material in the valve body. Then the sample trap was opened and the sample was swept into the analytical column by the helium elution gas.

The analytical column was a ⅝-in. O.D. aluminum tube 60 in. long and packed with 11 g. of Porapak Q. Each analysis was started by allowing the column to remain at 40°C. (maintained by a cooling coil located in the oven) for 4 min. Methane and ethane were separated during this period at 40°C. After these 4 min. the temperature programmer was started and the temperature was increased at a rate of 10°C./min. to a maximum of 250°C. After the *n*-hexane elution (25 min. after the start of the analysis), the back flush valve was reversed and *n*-decane eluted through the inlet end of the column.

The elution stream was split in 1:3 ratio just before entering the detectors, the smaller fraction going to the flame ionization detector and the larger fraction to the thermal conductivity detector. The flame ionization detector was most sensitive on the small peaks. The analysis time for one sample was 45 min. The coexisting equilibrium liquid sample was always analyzed after the vapor sample.

The procedure for the next data point was the same except that the equilibrium cell was already filled with liquid. Pressure was raised to the desired level by adding more of the gas mixture from the gas compressor. Equilibrium was established and samples taken as in the previous run.

An approximation of the starting overall composition can be made from the knowledge of the amounts of liquid and gas introduced into the cell. The estimates of the initial cell compositions are given in Table 1 for both isotherms. These can be compared with the single-phase compositions presented in Tables 2 and 3 to establish the range of composition change. It is immediately evident that the composition changes between the initial and end points for each isotherm were large.

Sample compositions were found by calculating the weight ratios of each component from the analytical peak area ratios. The weight ratio-area relationships had been determined earlier using known calibration standards at identical operating conditions in the chromatograph.

EXPERIMENTAL RESULTS

Experimental *xy* data are presented in Tables 2 and 3 for the six hydrocarbons in the base system at the indicated temperature and pressure conditions. The mole fractions were rounded off and may add up to 1.000 ± 0.0002. Since the cells were not windowed, the existence of a single phase was judged by the sample compositions. Although the deviations in *K* values were substantial, a single-phase condition could be recognized by the condition of *K* slightly greater than 1 for the intermediate components. This precluded a very accurate determination of the single phase pressure.

The constant temperature bath was maintained at either 150° ± 0.2°F. or 250° ± 0.4°F. During any one pressure run, the bath temperature was not observed to vary by more than 0.3°F. The errors in *K* values due to error in temperature measurement are negligible.

Pressures below 2,700 lb./sq.in.abs. were measured on the Heise gauge to the nearest 1 lb./sq.in.abs. Higher pressures were measured on the Hart pressure balance to the nearest 0.1 lb./sq.in.abs. Errors in *K* values due to pressure measurements are also negligible.

Most of the predictable errors in the *K* values are due to the chromatographic analyses. The disc chart integrator can be expected to produce an error in the peak count. An error analysis was made, using the maximum expected peak area errors

TABLE 2. EXPERIMENTAL *xy* DATA AND *K* VALUES FOR BASE SYSTEM AT 150°F.

Pressure, lb./sq. in. abs.		C_1	C_2	C_3	C_5	C_6	C_{10}
100	*y*	0.8712	0.0216	0.0062	0.0701	0.0269	0.0040
	x	0.0226	0.0025	0.0019	0.2023	0.2004	0.5703
200	*y*	0.9099	0.0263	0.0073	0.0379	0.0162	0.0024
	x	0.0460	0.0054	0.0046	0.1466	0.1713	0.6261
400	*y*	0.8602	0.0617	0.0449	0.0211	0.0103	0.0018
	x	0.0852	0.0228	0.0453	0.1344	0.1486	0.5636
500	*y*	0.9203	0.0340	0.0115	0.0222	0.0103	0.0018
	x	0.1202	0.0172	0.0130	0.1410	0.1629	0.5457
1,000	*y*	0.9370	0.0330	0.0081	0.0120	0.0066	0.0033
	x	0.2612	0.0266	0.0152	0.1089	0.1253	0.4628
1,250	*y*	0.9374	0.0300	0.0099	0.0130	0.0068	0.0029
	x	0.3260	0.0313	0.0226	0.1156	0.1194	0.3851
1,500	*y*	0.9275	0.0370	0.0145	0.0119	0.0069	0.0022
	x	0.3513	0.0409	0.0324	0.0979	0.1049	0.3725
2,000	*y*	0.9202	0.0413	0.0156	0.0120	0.0071	0.0038
	x	0.4903	0.0474	0.0340	0.0824	0.0859	0.2599
2,500	*y*	0.8954	0.0447	0.0201	0.0149	0.0124	0.0124
	x	0.5365	0.0513	0.0366	0.0659	0.0713	0.2384
3,000	*y*	0.8585	0.0414	0.0183	0.0179	0.0172	0.0466
	x	0.5753	0.0409	0.0272	0.0509	0.0616	0.2441
3,999	*y*	0.6502	0.0486	0.0296	0.0435	0.0495	0.1785
	x	0.6575	0.0464	0.0292	0.0397	0.0456	0.1815

TABLE 3. EXPERIMENTAL *xy* DATA AND *K* VALUES FOR BASE SYSTEM AT 250°F.

Pressure, lb./sq. in. abs.		C_1	C_2	C_3	C_5	C_6	C_{10}
100	*y*	0.5986	0.0231	0.0090	0.2103	0.1207	0.0382
	x	0.0177	0.0016	0.0014	0.1694	0.1785	0.6314
200	*y*	0.7736	0.0268	0.0106	0.1092	0.0579	0.0219
	x	0.0461	0.0044	0.0039	0.1643	0.1682	0.6130
300	*y*	0.8019	0.0360	0.0140	0.0861	0.0487	0.0133
	x	0.0644	0.0077	0.0063	0.1574	0.1745	0.5897
500	*y*	0.8416	0.0345	0.0142	0.0640	0.0356	0.0100
	x	0.1130	0.0107	0.0089	0.1415	0.1536	0.5722
702	*y*	0.8612	0.0383	0.0139	0.0486	0.0288	0.0092
	x	0.1476	0.0161	0.0129	0.1425	0.1583	0.5226
1,000	*y*	0.8797	0.0383	0.0165	0.0337	0.0211	0.0105
	x	0.2157	0.0232	0.0180	0.1265	0.1428	0.4737
1,500	*y*	0.8691	0.0386	0.0166	0.0337	0.0229	0.0192
	x	0.3212	0.0294	0.0205	0.1109	0.1207	0.3975
2,000	*y*	0.8510	0.0415	0.0192	0.0363	0.0261	0.0259
	x	0.4122	0.0342	0.0235	0.0947	0.0993	0.3362
2,500	*y*	0.8195	0.0409	0.0195	0.0339	0.0288	0.0575
	x	0.4879	0.0349	0.0236	0.0780	0.0818	0.2938
3,001	*y*	0.8416	0.0396	0.0212	0.0327	0.0289	0.0360
	x	0.8518	0.0366	0.0200	0.0317	0.0270	0.0329

TABLE 4. COMPARISON OF FOUR PREDICTION METHODS WITH UNSMOOTHED EXPERIMENTAL K VALUES

Average absolute % deviation

	Prediction method			
Component	Chao-Seader (*1*)	Gen B-W-R (*2*)	R-K-A et al. (*6*)	NGPA (*4*)
	Temperature = 150°F. (11 points)			4 points
Methane	30.8	66.5	59.5	12.0
Ethane	12.9	57.3	50.5	5.5
Propane	6.6	63.5	40.4	14.5
n-Pentane	13.1	30.3	25.2	17.2
n-Hexane	16.9	18.6	16.6	27.4
n-Decane	54.0	86.4	31.4	47.4
	Temperature = 250°F. (10) points)			4 points
Methane	24.4	50.3	57.8	3.7
Ethane	25.3	31.9	52.2	7.3
Propane	15.2	34.7	44.7	7.3
n-Pentane	12.4	18.4	30.8	16.0
n-Hexane	16.0	12.3	24.0	14.3
n-Decane	42.6	68.9	21.9	25.9

for each peak. From this analysis the maximum possible variations in K values were calculated for each component in each analysis. This error analysis gave the following maximum possible errors in K values at 150°F. and two pressures.

	200 lb./sq. in. abs.	1,000 lb./sq. in. abs.
Methane	18.2 ± 1.64	4.24 ± 0.29
Ethane	4.55 ± 0.65	1.24 ± 0.15
Propane	1.67 ± 0.25	0.545 ± 0.069
n-Pentane	0.206 ± 0.021	0.0969 ± 0.0114
n-Hexane	0.0930 ± 0.0104	0.0453 ± 0.055
n-Decane	0.0037 ± 0.0007	0.0071 ± 0.0016

Possible errors due to sampling cannot be assigned numerical values.

COMPARISONS WITH PREDICTED *K* VALUES

Experimentally measured K values, such as those given in Tables 2 and 3, can be used to evaluate K value prediction methods. Four methods have been applied to the six-component hydrocarbon mixtures and conditions covered in this work. These methods are: The NGPA convergence pressure type K charts (*4*); the generalized B-W-R equation of state (*2*); the Chao-Seader method (*1*); and the Redlich et al. modified R-K equation of state method, R-K-A (*6*).

In Table 4 the results of comparisons among the Chao-Seader, the generalized B-W-R equation of state, and the R-K-A equation of state methods, by direct substitution of experimental data, and the experimental K values, are summarized for each component at both temperatures. Average absolute deviations are given for each component at both temperatures. Percent deviation is defined as [(Calc − Exptl)/Exptl]100.

These results showed that Chao-Seader method predicts smaller deviations in the calculated K values than the equation of state techniques. It also predicts consistently high for methane and low for n-decane, but provides a more evenly distributed range of deviation than the other two methods.

Some of the data points were taken at pressures well above the maximum allowable pressure for the Chao-Seader correlation. If the average absolute percent deviations for the Chao-Seader correlation are calculated for the points of 2,000 lb./sq.in.abs. and less, the values are decreased. At 150°F. they were 18.7% for methane, 7.0% for ethane, 6.7% for propane, 9.7% for n-pentane, 6.7% for n-hexane, and 39.6% for n-decane. At 250°F. they were 13.3% for methane, 18.4% for propane, 8.4% for n-pentane, 10.0% for n-hexane, and 31.9% for n-decane. These values clearly demonstrate that as the correlation limits are approached, the percent deviations increase beyond 10%.

The equation of state methods provide similarly large absolute percent deviations in the K values, with the R-K-A equation having a slightly lower average deviation. However, both equations of state have rather uneven deviation distributions with the R-K-A equation predicting consistently low K values for all components, while the generalized B-W-R equation of state predicts high for all components except n-decane, for which the calculated values are consistently low.

A comparison was made of bubble-point pressures calculated using experimental liquid-phase compositions and system temperature. The comparison indicates that the Chao-Seader method provides the best bubble-point pressure calculation, with the generalized B-W-R equation of state showing the largest deviations. However, convergence could not be obtained in the computer bubble point calculations at the highest pressures for all the three methods.

Also shown in Table 4 is a comparison of the NGPA correlation. Only four points at each temperature were examined at pressures below 2,000 lb./sq.in.abs. The last point for each isotherm was selected as the convergence pressure for that isotherm. Because of the lower pressures the average percent deviations are less for this method than the others. However, a direct comparison can be made with the values for the Chao-Seader correlation below 2,000 lb./sq.in.abs. given in the text previously.

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