

# Density of Hydrocarbon

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**T**HE densities of petroleum gases and vapors under definite conditions of temperature and pressure are constantly required in engineering calculations in the petroleum industry. Thus, in the calculations of pressure drop in pipe lines, orifice-meter correction factors in the metering of high-pressure gas, times of contact of vapors in a cracking furnace, and vapor velocities in bubble towers, an accurate knowledge of the density is essential. Because of the great amount of time, apparatus, and painstaking work necessary in density determinations, few experimental data have been obtained and engineers have relied almost exclusively on various methods of calculation. Until recently the perfect gas law was generally used for this purpose. Cope, Lewis, and Weber (4) and Brown, Souders, and Smith (3), however, showed by means of data on pure compounds that densities calculated in this way are in error by an amount much greater than that allowable in most engineering calculations except at pressures not much above atmospheric or at very high temperatures. The method proposed by them for calculating the deviation of the density from that given by the perfect gas law is satisfactory for the vapors or gases of pure compounds, but calculations of the deviations for vapors of light petroleum distillates by Thiele and Kay (8) indicate that it is not applicable to complex mixtures. In view of the need for a reliable method of calculating the density of petroleum gases and vapors, experimental work was undertaken to obtain the pressure-volume-temperature relations of a number of refinery gases and light distillates which would serve as an experimental basis for the development of such a method. This paper presents the method and

The  $P$ - $V$ - $T$  relations of eleven typical petroleum hydrocarbon mixtures in the gaseous state are determined experimentally over a wide range in temperature and pressure extending from the saturated condition below to the highly superheated condition above the critical region. The  $P$ - $V$ - $T$  data on the mixtures, expressed as deviations from the perfect gas law, are correlated with similar data on pure hydrocarbons by means of the

results of these determinations on eleven petroleum hydrocarbon mixtures. The mixtures were selected for variety as to their physical state, boiling range, and chemical character, and are representative of those encountered in petroleum refining. The method of correlating the experimental data is given, and its application as a general method for calculating the density of any petroleum gas or vapor is indicated.

## Determination of $P$ - $V$ - $T$ Relations of Hydrocarbon Mixtures

**APPARATUS.** The apparatus was a modification of that used by Bahlke and Kay (1) and is shown in Figure 1:

$A$  and  $B$  are legs of a steel U-tube which are partially filled with mercury.  $A$  is fitted with a stuffing box through which passes the thick-walled capillary tube,  $C$ , containing the sample under investigation. The method of fastening the tube in the compressor has already been described (1). To the top of leg  $B$ , closed by steel plug  $D$ , connection is made through copper tubing to the high-pressure gas cylinder,  $G$ , which serves as a means for applying pressure to the system. Control of the pressure is facilitated by increasing the volume capacity of the system by connecting vessel  $H$  in the line and by capillary constrictions  $E$  and  $F$ , consisting of a piece of narrow-bore capillary tubing held in a steel block by litharge and glycerol cement. To prevent the sudden loss of the mercury in the event of the bursting of the capillary tube under high pressure, a simple ball check valve,  $I$ , is placed in the interconnection between  $A$  and  $B$ .

Experimental tube  $C$  is a Pyrex capillary tube of about 2-mm. bore and 3-mm. wall thickness. It is carefully calibrated by weighing the mercury required to fill it to various points and its volume from the sealed end, expressed in terms of the distance from a reference line etched around the tube near the sealed end. For mixtures which are gases at room temperature and atmospheric pressure, a bulb of about 8-cc. capacity is sealed to the lower end of the tube to serve as a gas reservoir. Stirring of the sample in the tube is accomplished by means of a steel ball  $1/16$  inch in diameter which is moved by electromagnet  $K$  surrounding the tube. The liquids used in vapor jacket  $L$  for heating the tube and the method of regulating the pressure on the boiling liquid in order to control the temperature have been described (1). The temperature of the vapor is measured by means of the calibrated copper-constantan thermocouple,  $M$ , using a Leeds & Northrup type  $K$  potentiometer for the e. m. f. measurements.

Pressure gage  $J$  is a precision spring gage with a 16-inch dial, calibrated and marked by hand in 5-pound divisions from 0-2000 pounds. The dial is fitted with a rotating zero adjustment by means of which the pointer can be adjusted to read true zero at atmospheric pressure. The accuracy of the gage was guaranteed by the manufacturer to be within one-third of a scale division up to 400 pounds and 0.25 per cent at the higher pressures. The interpolation of pressures between scale marks is, in most cases, avoided by adjusting the

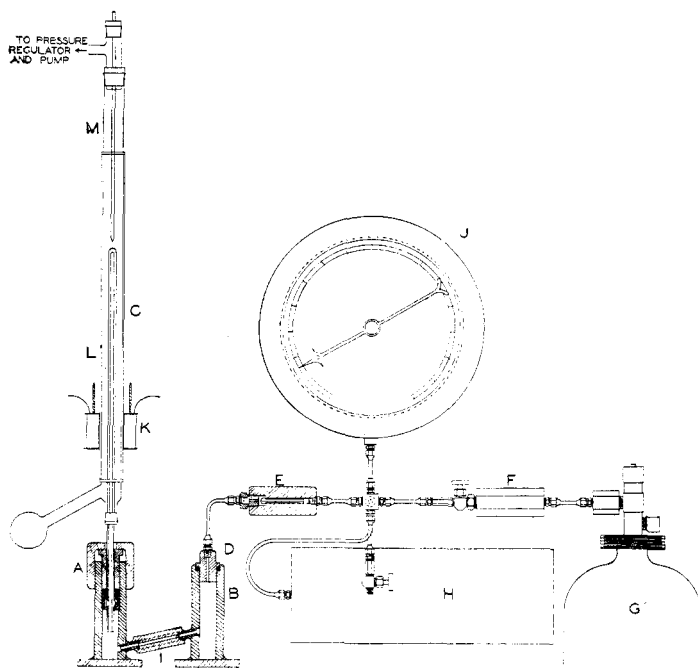


FIGURE 1. APPARATUS FOR DETERMINING  $P$ - $V$ - $T$  RELATIONS

# Gases and Vapors

theorem of corresponding states using a particular temperature and pressure for each mixture, termed the "pseudocritical temperature and pressure," for calculating the corresponding reduced quantities. Methods and charts for estimating the pseudocritical temperature and pressure of a petroleum hydrocarbon mixture are given which make possible the calculation of its  $P$ - $V$ - $T$  relations over a wide range of temperature and pressure.

pressure until the pointer coincides with a mark on the scale. The pressure as determined by the gage is corrected for the difference in levels of the mercury in the experimental tube and in leg  $B$  of the steel U-tube and, when necessary, for the vapor pressure of mercury. The final pressure is expressed as absolute pressure.

## Loading the Experimental Tube with a Sample

In loading the tube with a liquid sample, enough of the liquid was added through a hairlike capillary projecting to the bottom of the tube to fill about 2 inches of its length. The capillary was then withdrawn, the steel ball inserted, and a small amount of mercury added. The capillary was again inserted to remove the entrapped air and excess liquid and to bring the mercury to rest at a point such as to leave the desired amount of liquid in the tip of the tube. The excess liquid on the top of the mercury was then carefully removed by suction, the remainder of the tube completely filled with mercury, and the tube put in place in the compressor. The weight of the sample taken was calculated from its volume and its density (determined in a separate experiment).

In the case of gas samples the experimental tube described above for gases was used. The tube was completely filled with mercury and placed in an upright position with the open end dipping into mercury contained in an open dish. The sample was then introduced into the tube through a small capillary inserted into the end under mercury, and the gas was admitted until the mercury was displaced to a given mark at which the volume of the tube was known. The pressure and temperature of the gas were then measured, and from these data together with the density (determined by a separate experiment) the weight of the sample was calculated.

For mixtures composed of gas and liquid, the liquid was introduced first, measured, and frozen in the top of the tube by means of liquid air. The quantity of gas necessary to make a mixture of the desired composition was then measured out in a micro-gas buret similar to that described by Blacet, MacDonald, and Leighton (2) and introduced into the tube.

## Stocks Studied

Table I contains a list of the stocks, with the customary inspection data, for which the  $P$ - $V$ - $T$  relations were obtained. These stocks cover a wide range in boiling point and may be classified into three groups, according to their physical state at room temperature and atmospheric pressure as (1) gas, (2) liquid, and (3) gas plus liquid. The gases were typical refinery gases. Traces of hydrogen sulfide and moisture were removed by passing them first through concentrated potas-

## At High Temperature and Pressure

sium hydroxide solution, then through concentrated sulfuric acid, and finally over phosphorus pentoxide. The composition was determined by Podbielniak analysis and the density by weighing a known volume of the gas at atmospheric pressure and room temperature. The molecular weight was calculated from the density, taking into account the deviation of the gas from the gas law at atmospheric pressure. The liquids were petroleum distillates selected for variety as to the nature of the crude oil from which they were obtained and the degree of refining—virgin and cracked, treated and untreated. The acid-treated virgin stocks were represented by samples 4, 7, 8, and 9. All except sample 7, which was a distillate from West Texas crude oil, were from Midcontinent crude. Cracked stocks were represented by sample 5 from Midcontinent crude and sample 6 from a crude oil which was more naphthenic in nature than Midcontinent. The former was used without acid treatment; the latter was treated with 75 per cent sulfuric acid in the proportion of 4 pounds per barrel. Traces of moisture were removed by contact with phosphorus pentoxide in the case of the virgin distillates, and by barium perchlorate in the case of the cracked distillates. No attempt was made to remove traces of dissolved air. Molecular weights of all the liquid distillates except samples 4 and 5 were determined by the freezing point method using nitrobenzene as a solvent. The molecular weights of the latter were estimated from curves of molecular weight vs. 50 per cent A. S. T. M. boiling point.

FIGURE 2. COMPARISON OF  $P$ - $T$  DIAGRAM OF MIXTURE AND PURE COMPOUND

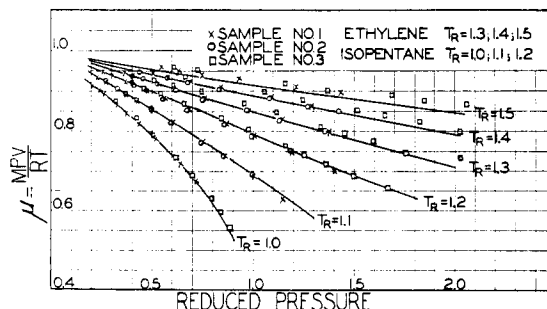
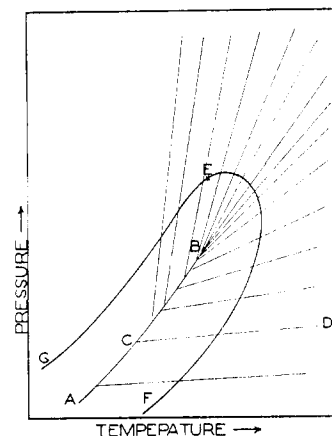


FIGURE 3. COMPARISON OF PLANT GASES WITH ISOPENTANE AND ETHYLENE

TABLE I. PHYSICAL DATA ON STOCKS STUDIED

Sample No.	Mol. Wt.	Gas									
		Podbielniak Analysis								Total	
		Air	C <sub>1</sub>	C <sub>2</sub> =	C <sub>2</sub>	C <sub>3</sub> =	C <sub>3</sub>	C <sub>4</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
1	37.7 <sup>a</sup>	0.70	7.06	5.10	24.90	22.05	30.92	5.85	..	3.42	..
2	39.4 <sup>a</sup>	0.58	0.96	2.35	25.88	19.50	47.11	..	..	3.62	..
3	46.0 <sup>a</sup>	..	..	..	0.83	17.26	64.42	5.75	6.23	2.43	3.08
10-a	...	..	0.55	2.16	19.24	23.80	52.91	..	..	1.34	..

Sample No.	Description	Liquid									
		A. S. T. M. DISTR.								% Evapd.	
		Mol. Wt.	A. P. I.	° F./° C.	10	30	50	70	90	Max.	
4	Straight-run naphtha from Midcontinent crude	86	72.5	143	150	154	158	162	170	198	
5	Cracked dist. from Midcontinent crude	109 <sup>c</sup>	56.0	42	146	240	288	322	358	398	
6	Cracked gasoline from Gulf Coast crude	107	52.0	144	188	221	250	278	318	374	
7	Straight-run dist. from West Texas crude	98	69.9	190	191	192	193	193	193	195	
8	Cut from straight-run dist., Midcontinent crude	104	55.6	219	220	221	222	223	225	231	
9	Cut from straight-run dist., Midcontinent crude	111	59.4	240	243	243	243	244	244	262	
C <sup>b</sup>	Straight-run dist. from Midcontinent crude	110	57.1	211	230	245	258	272	295	326	

Sample No.	Mol. Wt.	Description
10	77	Mixture of 89.9 wt. % of sample 4 + 10.06 wt. % of sample 10-a
11	81.5	Mixture of 26.62 mole % ethane + 73.39 mole % n-heptane

<sup>a</sup> Calculated from density measurements.  
<sup>b</sup> See literature citation 1.  
<sup>c</sup> Corrected for gas in sample.

### Application of Theorem of Corresponding States to Mixtures

Cope, Lewis, and Weber (4) and Brown, Souders, and Smith (3) pointed out that the deviations from the perfect gas law for pure hydrocarbon gases and vapors can be correlated by means of the theorem of corresponding states. They showed that, if the deviations expressed by  $\mu = MPV/RT$  are plotted against the reduced pressures, the resulting curves for the same reduced temperature are practically the same for all pure hydrocarbons. If, then, the density at temperature  $T$  and pressure  $P$  is required and the critical temperature and pressure of the compound are known, the deviation from the perfect gas law can be obtained from such curves and the density calculated. This method of calculation gives results well within the accuracy required in most engineering calculations.

If the data on complex mixtures are plotted in a similar manner, the resulting curves deviate considerably from those for pure compounds, particularly in the critical region. A comparison of the  $P$ - $V$ - $T$  relations of a pure compound and a mixture shows that the reason for the deviation lies in the improper selection of the critical point of the mixture for calculating the reduced pressure and temperature. This is made clear by the diagram in Figure 2.  $AB$  is the vapor pressure curve,  $B$  is the critical point,  $CD$  and similar lines are the isochors (lines of constant density) of a pure compound. If the values of the temperature, pressure, and volume at critical point  $B$  are used for calculating the corresponding reduced quantities, a plot similar to Figure 2 is obtained which, according to the theorem of corresponding states, is the same for all substances. This same diagram for a mixture differs from that for a pure compound in that the vapor pressure line is replaced by the area  $GEF$ , and the portion of the curves within this area do not exist. The critical point is situated on the border curve somewhere in the vicinity of  $E$ . Obviously, if the data in the superheated region are to be compared with those for a pure compound by the theorem of corresponding

states, the logical point for calculating the reduced quantities is not critical point  $E$  but point  $B$  which is the critical point of the pure compound whose  $P$ - $V$ - $T$  relations in the superheated region are identical with those for the mixture. If, then, the pressure and temperature of point  $B$  are known, the  $P$ - $V$ - $T$  relations in the superheated region can be calculated exactly as they would be for a pure compound, regardless of the boiling range of the mixture.  $B$  may be called the "pseudocritical point" of the mixture since it is analogous to the critical point of a pure compound. The difference between this point and the actual critical point is dependent on the width of the border curve which is directly related to the boiling range of the mixture. As the boiling range is diminished, the critical point approaches the pseudocritical, and the two points coincide and are identical in the case of a pure compound. Advantage may be taken of this relation in the correlation of the pseudocritical temperature and pressure with other properties of the mixture by using the available critical data for pure compounds.

### Estimation of Pseudocritical Point

Since the pseudocritical point of a mixture is located within the border curve, it has no real existence and, therefore, cannot be measured. Only for mixtures of very narrow boiling range is it approximately equal to the critical point. However, it may be estimated graphically from the  $P$ - $V$ - $T$  data on the mixture. The following method was found to be satisfactory. A general plot was prepared of the deviation from the perfect gas law *vs.* the logarithm of the reduced pressure for various reduced temperatures of pure isopentane for which accurate  $P$ - $V$ - $T$  data are available (10). The data for the experimentally determined isotherms of the mixture were then plotted on a separate sheet of semi-transparent paper in a similar way except that the temperature and pressure were expressed in the units of measurement—that is, in degrees Rankine and pounds per square inch absolute. Since

$$\log P_r = \log P - \log P_c$$

where  $\log P_c =$  a constant for any given mixture

by laying the plot of the experimental data over the general plot and shifting it along the pressure axis, the two sets of curves could be matched, each isotherm coinciding with the corresponding reduced isotherm. The pseudocritical temperature and pressure could then be readily calculated.

Values of the pseudocritical temperature and pressure cal-

TABLE II. PSEUDOCRITICAL POINTS OF PETROLEUM MIXTURES

Sample No.	Pseudocritical Temp.				Pseudocritical Pressure				Mol. Wt.	K <sup>a</sup>
	Found	Calcd. from analysis	Calcd. from Fig. 8	Difference	Found	Calcd. from analysis	Calcd. from Fig. 8	Difference		
1	150	150	...	0	651	651	...	0	37.7	...
2	188	168	...	0	651	651	...	0	39.4	...
3	219	219	...	0	625	608	...	-17	46.0	...
4	468	...	464	-4	475	...	482	7	86	12.30
5	574	...	575	1	448	...	438	-10	108	11.82
6	573	...	582	9	463	...	456	-7	107	11.52
7	512	...	521	9	440	...	438	-2	98	12.22
8	561	...	565	4	457	...	461	4	104	11.63
9	577	...	577	0	411	...	413	2	111	12.00
10	415	...	415	0	480	...	496	16	77	12.5 <sup>b</sup>
11	413	400	422	...	450	480	450	...	81.5	12.8 <sup>b</sup>
c	580	...	578	-2	406	...	418	12	110	11.94

<sup>a</sup> Watson and Nelson characterization factor.

<sup>b</sup> Calculated from characterization factors of liquid and gas.

<sup>c</sup> Straight-run naphtha from Midcontinent crude (1).

culated in this way for the mixtures that were studied are shown in Table II, columns 2 and 6.

### P-V-T Data for Mixtures and for Pure Hydrocarbons

Figures 3 to 6 show a comparison of the data obtained on the various gases and distillates with data on pure hydrocarbons at the same reduced temperature and pressure, using the value of the temperature and pressure at the pseudocritical point for calculating the reduced quantities. In these figures the deviations from the perfect gas law are plotted against the reduced pressure for different reduced temperatures. The smoothed experimental data are shown as points, and the corresponding data for the pure hydrocarbon are represented by the curves. Figure 3 shows the results on three refinery gases. The curves for  $T_r = 1.0, 1.1$ , and  $1.2$  are for pure isopentane (10); those for  $T_r = 1.3, 1.4$ , and  $1.5$  are for pure ethylene (5). In Figure 4 a comparison is made between isopentane and stocks containing large quantities of gas (up to 10 per cent by weight). In Figure 5 narrow-boiling stocks and in Figure 6 stocks of somewhat greater boiling range are compared with isopentane. In Figure 6 previously published data on a straight-run naphtha from Midcontinent crude (1) have been included. The agreement between the data on mixtures and pure compounds is, in general, excellent and is independent of the boiling range of the mixture.

A similar comparison of the data on methane-propane mixtures (7) with data on pure methane is shown in Figure 7. The pseudocritical temperatures and pressures calculated from the mole fractions and actual critical constants of the pure compounds are given in Table III. Here again the agreement between mixtures and compounds may be considered good.

TABLE III. PSEUDOCRITICAL POINTS OF METHANE-PROPANE MIXTURES<sup>a</sup>

Sample No.	CH <sub>4</sub> Mol. %	Mol. Wt. <sup>b</sup>	Pseudocritical Point <sup>b</sup> Temp. ° F.	Pressure Lb./sq. in.
1	90	18.8	-84	667
2	80	21.6	-52	662
3	70	24.4	-20	657
4	60	27.3	13	651
5	40	32.9	77	639

<sup>a</sup> Data of Sage, Lacey, and Schaafsma (7)

<sup>b</sup> Calculated from analysis.

### Correlation of Pseudocritical Point with Other Properties

A study of the relations between the critical point and other physical properties of a homologous series of hydrocarbons indicates that the critical point is directly related to the molecular weight and chemical nature as well as molecular structure of the compound. Thus, if the critical temperature and pressure of the hydrocarbons are plotted against their molecular weight, it is found that compounds in the same homologous series and of the same molecular structure form separate and individual curves; compounds of the straight-chain paraffin series having the lowest critical temperature and pressure for a given molecular weight, compounds of

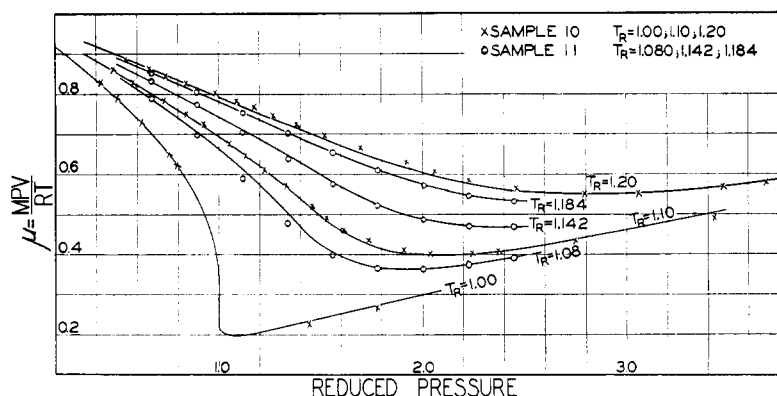


FIGURE 4. COMPARISON OF LIQUID-GAS MIXTURES WITH ISOPENTANE

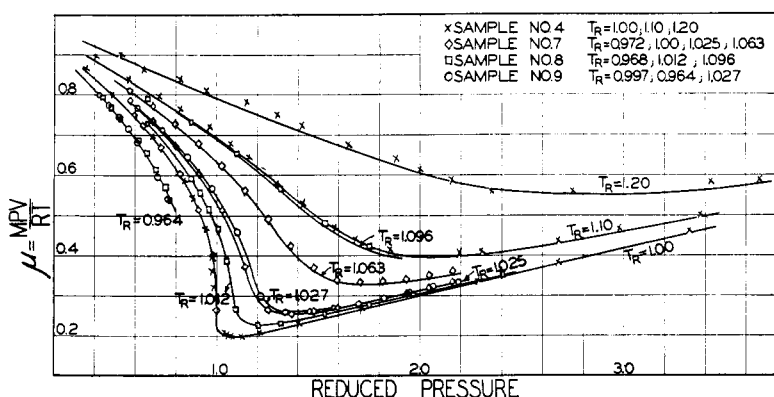


FIGURE 5. COMPARISON OF NARROW-BOILING-RANGE DISTILLATES WITH ISOPENTANE

the aromatic series have the highest, and other homologous series occupy a position between these two extremes. Similar relations may be expected to hold for the pseudocritical point of a mixture, since the pseudocritical point is analogous to the critical point of a pure substance. It might be expected, therefore, that, if the chemical composition of the mixture were known, the pseudocritical temperature and pressure could be calculated by the mixture rule from the composition expressed in mole fractions and the critical constants of the constituents of the mixture. To test this assumption, these quantities were calculated for the three refinery gases (samples 1, 2, and 3) and for ethane-heptane mixture (sample 11) as well as for the methane-propane mixtures of Sage, Lacey, and Schaafsma (7). The calculated values for the former are given in Table II (columns 3 and 7) and for the latter in Table III. As shown in Table II, the agreement with the values estimated from the P-V-T data is very good for samples 1 and 2. For sample 3 the pressure is about 3 per cent low;

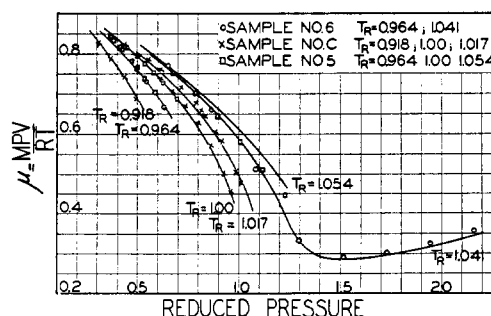


FIGURE 6. COMPARISON OF WIDE-BOILING-RANGE DISTILLATES WITH ISOPENTANE

for the heptane-ethane mixture (sample 11) the temperature is lower by 13° F. and pressure higher by 6.7 per cent than what were found. For the methane-propane mixtures the good agreement in the deviations from the perfect gas law for the mixture and pure methane (Figure 7) indicates a satisfactory agreement between the calculated values given in Table III and what would be estimated from the  $P$ - $V$ - $T$  data. These results lead to the conclusion that values of the pseudocritical constants can be estimated in this manner for the light hydrocarbon gases with sufficient accuracy for most engineering calculations. However, for mixtures whose constituents differ greatly in molecular weight as well as chemical nature, values of the pseudocritical constants calculated in similar manner are likely to be in error by an amount greater than that allowable.

In mixtures whose chemical composition cannot be determined, such as petroleum distillates, the need for information concerning the molecular structure and chemical nature of the material may be met by characterizing the mixture by a factor calculated from certain properties of the mixture, such as boiling point and specific gravity, which gives a quantitative measure of its paraffinicity. If this factor is used, it is to be expected that the pseudocritical temperature and pressure can be correlated with the critical temperature and pressure *vs.* molecular weight relations of pure hydrocarbons. Recently Watson and Nelson (9) proposed the quantity

$$\frac{(T_B)^{1/3}}{S}$$

where  $T_B$  = molal av. boiling point, ° Rankine  
 $S$  = sp. gr. at 60°/60° F.

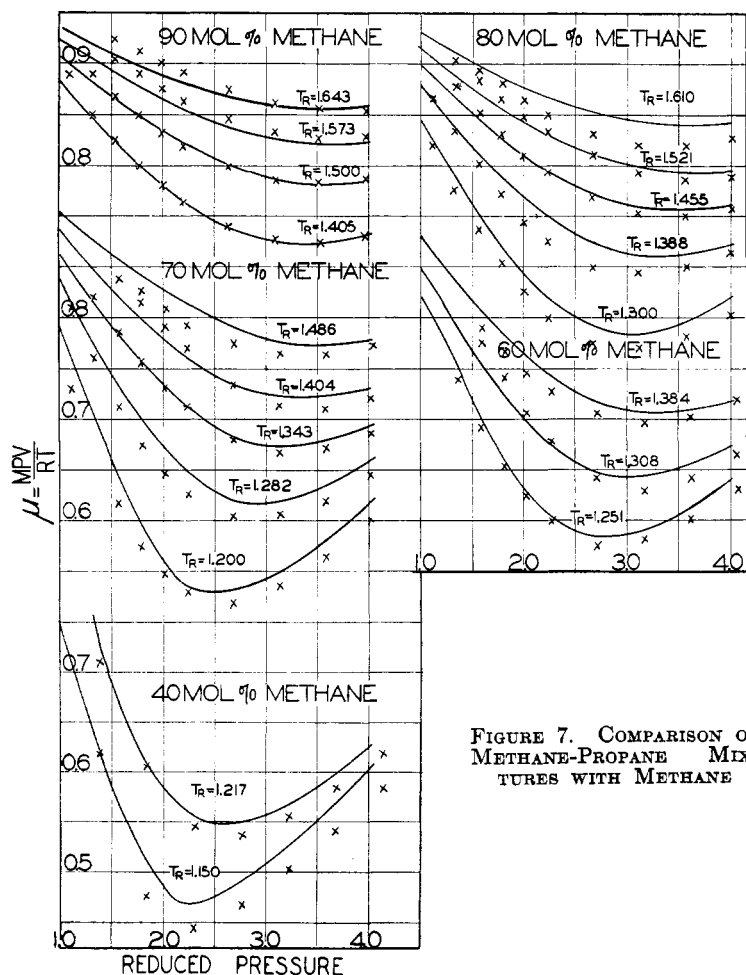


FIGURE 7. COMPARISON OF METHANE-PROPANE MIXTURES WITH METHANE

as a characterization factor indicative of the chemical nature of hydrocarbon mixtures. This factor has a value of about 12.7 for paraffinic compounds, 10.0 for aromatics, and intermediate values for other homologous series. Its values for the mixtures that were studied are given in Table II. Application of this factor to the correlation of the pseudocritical data has been made, and Figure 8 gives curves showing the relation between the pseudocritical temperature and pressure and the molecular weight for mixtures of the same characterization factor. In drawing these curves, the pseudocritical as well as the critical data on pure hydrocarbons were plotted against the molecular weight and smooth curves of constant characterization factor drawn. The data read from these curves were then plotted in such a way as to give straight lines which were extrapolated into the region of high molecular weight. The extent to which the values of the pseudocritical temperature and pressure, estimated by means of these curves, agree with those found is shown in Table II. The agreement is considered to be within the accuracy of the data.

The correlation of the pseudocritical temperature and pressure of mixtures which exist as liquid and gas at room temperature and atmospheric pressure is somewhat more difficult because, on account of the physical nature of the mixture, the inspection data regularly obtained on gases and liquids separately, such as the A. S. T. M. distillation, specific gravity, etc., cannot be determined and, therefore, the characterization factor cannot be calculated in the usual way. Data obtained on blends of light and heavy naphtha indicate that the characterization factor of the blend can be calculated, approximately, from the weight fractions and characteriza-

tion factors of the components. Assuming these relations to hold for gas-liquid mixtures, the characterization factor of the mixture can be calculated and the pseudocritical temperature and pressure correlated with the average molecular weight as in the case of liquids. In calculating the characterization factors for samples 10 and 11, however, it was found necessary to use smaller values of the characterization factor for the light hydrocarbon gases than those calculated from the boiling point in degrees Rankine and the specific gravity of the liquid at 60°/60° F., in order to obtain a value for the mixture which would be in line with the pseudocritical point-molecular weight relations shown in Figure 8. Characterization factors for the gas in these samples were obtained by extrapolating the molecular weight-characterization factor curve for the paraffin compounds from pentane to ethane as a straight line. The equation of the curve between ethane and hexane is as follows:

$$K = 14.3 - (M - 30) 0.0268$$

where  $K$  = characterization factor

$M$  = av. mol. weight of the gas

The characterization factors and the pseudocritical temperatures and pressures estimated from Figure 8 for samples 10 and 11 are given in Table II. The agreement between the pseudocritical quantities and those obtained from the  $P$ - $V$ - $T$  data on the mixtures is comparable with that obtained for liquids without gas.

### Discussion

In the preparation of a general plot showing the deviations from the perfect gas law *vs.* the reduced pressure for various reduced temperatures, the  $P$ - $V$ - $T$  data on isopentane (10) are recom-

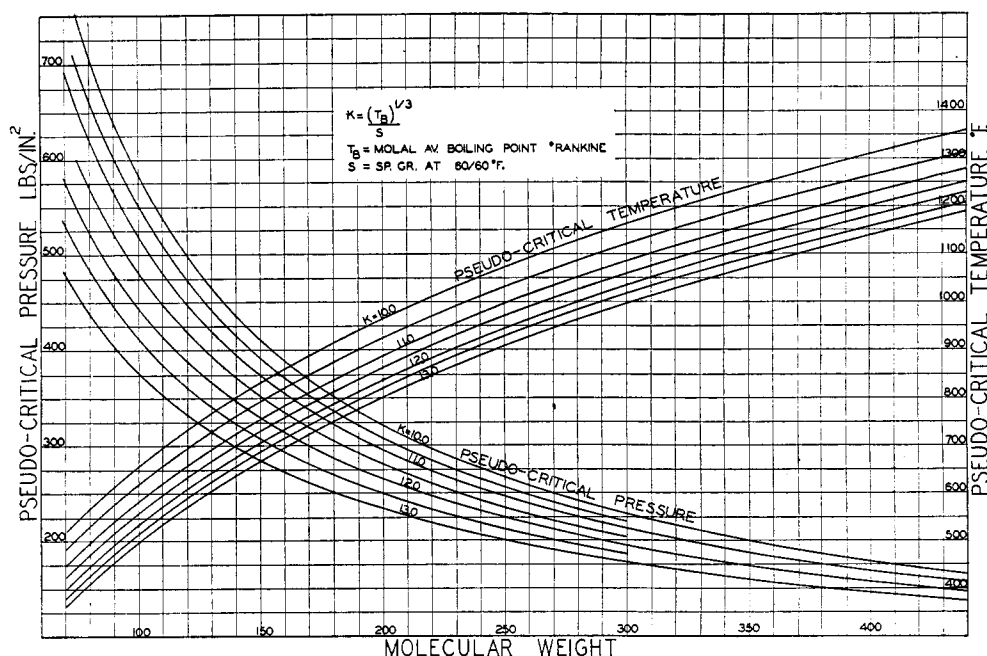


FIGURE 8. PSEUDOCRITICAL TEMPERATURES AND PRESSURES OF HYDROCARBON MIXTURES

mended. These data, however, are given only for reduced temperatures up to about 1.2. For higher reduced temperatures, data on lighter hydrocarbons, such as ethylene, must necessarily be used. Lewis (6) recently presented a large-scale plot of these curves; therefore it does not seem necessary to reproduce the plot here.

The accuracy of the method presented here for calculating the  $P$ - $V$ - $T$  data of a mixture is comparable to that with which the theorem of corresponding states has been found to hold for pure hydrocarbons. A comparison of the reduced  $P$ - $V$ - $T$  relations of pure hydrocarbons (3) shows that, although the relations are not exactly the same for different hydrocarbons, the differences, in general, are insignificant except at high, reduced temperatures. In the latter region these differences are definitely a function of the molecular weight. The data, however, are so meager that it is only possible to say that the deviation from the perfect gas law will be less at the same reduced temperature and pressure, the higher the molecular weight. The use of the "ethylene" curves for estimating the deviation from the perfect gas law at reduced temperatures around 1.5, for example, of a mixture whose average molecular weight corresponds to octane may, therefore, lead to a small error. Fortunately, since the pseudocritical temperature increases with molecular weight, the reduced temperatures at which  $P$ - $V$ - $T$  relations of heavy stocks are desired are small, and the difficulty mentioned should not give serious trouble.

The most important factor affecting the accuracy of the calculated results is the pseudocritical temperature and pressure. Values of these quantities can be estimated for mixtures of low molecular weight with an error of 2 to 3 per cent or less, but for the mixtures of high molecular weight the

error is probably larger. This is due to the fact that, because of the great experimental difficulties encountered in the determination of the critical constants of the high molecular weight compounds, no critical data on such compounds are available and the data must necessarily be obtained by extrapolation, as in Figure 8. It must be remembered, however, that the numerical accuracy of the pseudocritical constants is not directly comparable with the accuracy of the deviations calculated by the use of the constants and the deviation-reduced pressure chart. Thus, for example, at low reduced temperatures and at pressures near the pseudocritical point a small error in the pseudocritical temperature or pressure or both may lead to a relatively large error in the value of the deviation from the perfect gas law, whereas at high reduced temperatures the error may be insignificant.

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RECEIVED June 23, 1936. Presented before the Division of Petroleum Chemistry at the 91st Meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936.

