

Critical Properties of Mixtures of Normal Paraffin Hydrocarbons

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THE P - T PHASE DIAGRAM of a natural gas mixture is of great practical value to the petroleum engineer in recovery operations in high pressure gas fields. Also, in certain refinery and chemical synthesis processes involving the natural gas hydrocarbons under pressure, a knowledge of the phase diagram is important. The P - T diagram can be calculated with moderate accuracy only up to pressures and temperatures near the critical region of the mixture. To establish the curve in the critical region it is essential to know the coordinates of the three unique points on the curve—namely, the critical point, or the convergence point of the quality lines of the mixture, the cricondenbar point, or the point of maximum pressure, and the cricondentherm point, or point of maximum temperature. Heretofore, these data have had to be determined experimentally.

The present study was undertaken to find relations between the composition and the pressure and temperature at these points, which could be used to predict the temperature and pressure values. This involved a study of the P - T - x data in the critical region of systems reported in the literature, as well as the experimental determination of the critical constants of a series of multicomponent mixtures containing from two to six components. Since most of the data available are for mixtures of light hydrocarbons, the study has been limited to mixtures of the low molecular weight, normal paraffin hydrocarbons and is, therefore, of particular interest to those associated with the natural gas industry.

P , T , AND M_{av} RELATIONS FOR BINARY SYSTEMS

Figure 1 shows the critical pressure plotted against the average molecular weight, calculated on a weight basis, for a series of binary hydrocarbon systems containing methane as a common component. The systems considered are the methane-propane (11) methane-*n*-butane (13), and methane-*n*-pentane (14). All are tied together by lines of constant weight fraction of methane which are approximately straight lines and which converge to a common point whose coordinates are the molecular weight and critical pressure of pure methane. For a weight fraction greater than $W_{c1} = 0.024$, the critical pressure of a mixture increases with an increase in the average molecular weight and the concentration of methane. Below $W_{c1} = 0.024$ the critical pressure decreases and approaches the critical pressure of the heavier component. The constant composition line $W_{c1} = 0$ is, therefore, the locus of the critical pressures of methane and heavier normal paraffin hydrocarbons.

Plots of the cricondenbar pressure and cricondentherm pressure vs. the average molecular weight for the same methane systems, yield curves that are similar in all respects, to the critical pressure curves (Figure 1).

Binary systems containing ethane and propane as the common components with higher members of the paraffin series, display relationships similar to those shown by the methane binaries, except that the lines of constant composition are lines of constant mole fraction, and not weight fraction. The curves for ethane-*n*-butane (5) and ethane-*n*-heptane (4) are shown in Figure 2 and propane-*n*-butane (10) and propane-*n*-pentane (12) in Figure 3.

Figure 4 shows a plot of $\log T_c$ vs. $\log M_{av}$ for the methane binary systems. Points of constant weight fraction of

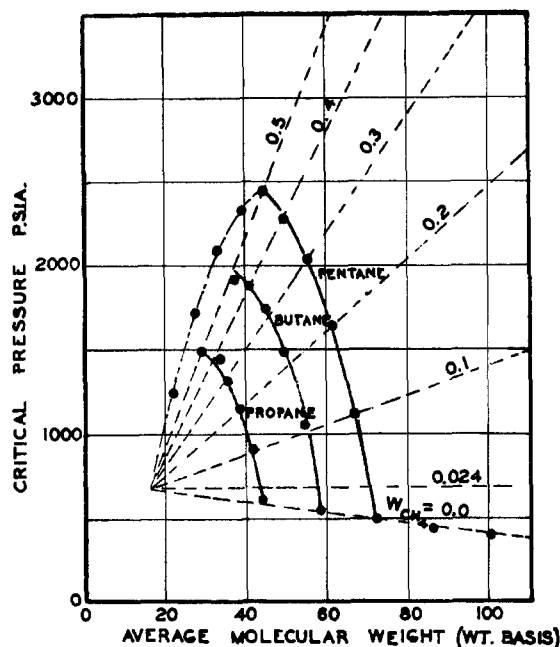


Figure 1. Relation between critical pressure and average molecular weight of methane binaries

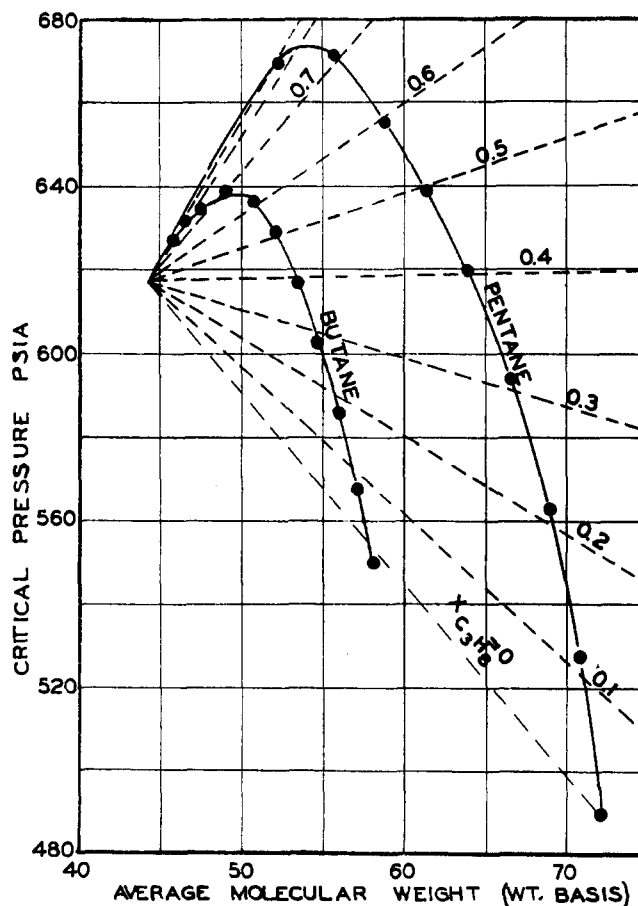


Figure 2. Relation between critical pressure and average molecular weight of ethane binaries

methane in each of the systems lie approximately on a straight line, and these constant composition lines converge to a common point at the molecular weight of methane and a temperature of 420° R. The latter is not the true critical

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temperature of methane, but a fictitious critical temperature obtained by extending the line for $W_{c_1} = 0$ to a molecular weight of 16. For a composition less than $W_{c_1} = 0.7$, the critical temperature increases with the average molecular weight (calculated on a weight basis), and decreases with increasing methane content. The constant composition line $W_{c_1} = 0$ is the locus of the critical temperature of normal paraffin hydrocarbons of molecular weight greater than methane.

Plots of the logarithm of the cricondenbar and cricondenthem temperatures vs. the logarithm of the average molecular weight (on a weight basis), of the same binary systems of methane, are similar in all respects to the critical temperature plot (Figure 4).

Binary systems of ethane-*n*-butane (5), ethane-*n*-heptane (4) and propane-*n*-butane (10), propane-*n*-pentane (12) exhibit relations similar to those exhibited by the methane binaries except that the constant composition lines are in mole fraction instead of weight fraction.

Additional data with which to test the accuracy and degree of similarity of the diagrams presented in Figures 1 to 4 are not available. However, it seems plausible to assume that these diagrams are representative of a general relationship existing in binary systems of the light normal paraffin hydrocarbons which contain a common component. On the basis of this assumption and with a minimum of experimental data on relatively few systems, the pressure and temperature at the critical, cricondenbar, and cricondenthem points have been estimated for systems for which no experimental data exist.

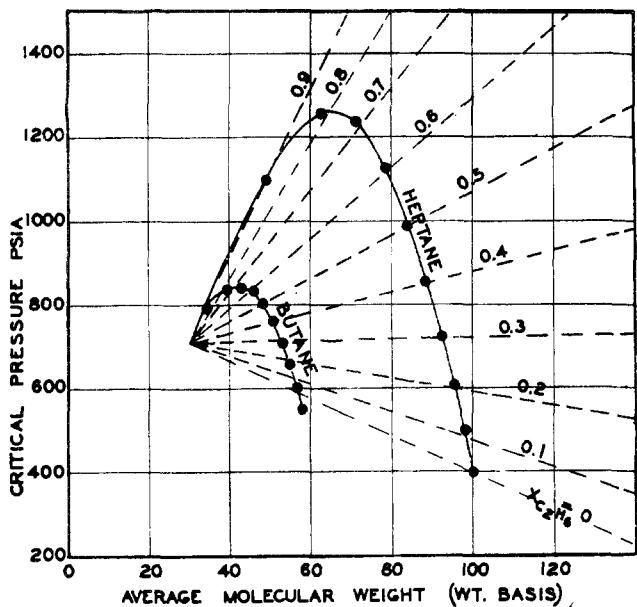


Figure 3. Relation between critical pressure and average molecular weight of propane binaries

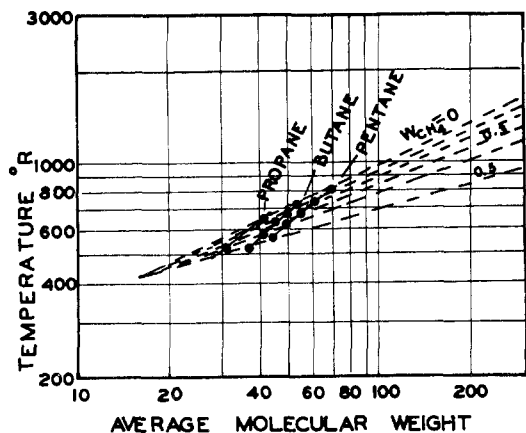
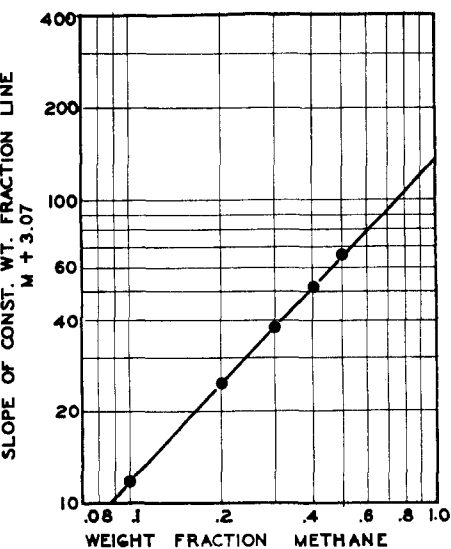


Figure 4. Relation between critical temperature and average molecular weight of methane binaries

Figure 5. Slope of any straight line of constant weight fraction of methane vs. weight fraction of methane for methane binaries



Empirical Equations of Pressure. The relations between the critical pressure, average molecular weight, and composition (Figure 1), may readily be expressed in the form of an empirical equation. Referring to Figure 1, the equation for any straight line of constant composition of methane may be written

$$(P_c)_{mix} = P_{c_1} + m(M_{av} - M_{c_1}) \quad (1)$$

where m is the slope. Plots of the logarithm of m against the logarithm of W (Figure 5) show that m can be expressed as a function of the composition by the equation

$$m = m_0 + aW_{c_1}^b \quad (2)$$

where m_0 = slope of the line $W_{c_1} = 0$; a = the intercept on the $(m - m_0)$ axis at $W_{c_1} = 1.0$; b = the slope of the straight line in Figure 5. Substituting Equation 2 into 1 gives:

$$(P_c)_{mix} = P_{c_1} + (aW_{c_1}^b + m_0)(M_{av} - M_{c_1}) \quad (3)$$

Equations of similar form may be derived for the cricondenbar pressure and for the cricondenthem pressure.

When methane is not present, Equation 3 may be written in the general form:

$$(P)_{mix} = P_{c_L} + (a_L x_L^b + m_0)(M_{av} - M_L) \quad (4)$$

where subscript L refers to the lighter component of the binary and x_L is its mole fraction. Using the P - T - x data for the binary systems of methane, ethane, and propane, previously cited, and for *n*-butane-*n*-heptane (6), values of the constants a , b , and m_0 for methane, ethane, propane, and *n*-butane were evaluated and are listed in Table I.

P - T - x data on *n*-pentane-*n*-paraffin hydrocarbons and other binary systems higher than *n*-pentane were not available for the construction of diagrams similar to Figures 2 and 3. However, the constants in Equation 4 for these systems were estimated (1), thereby making it possible to calculate the pressure at the three unique points in the critical region. These equations are as follows:

$$P_c = P_{c_L} + [9400M_L^{-1.71}x_L^{2.006}M_L^{-1.115} - 557M_L^{-1.265}] (M_{av} - M_L) \quad (5)$$

$$P_{cb} = P_{c_L} + [9400M_L^{-1.71}x_L^{1.96}M_L^{-1.107} - 557M_L^{-1.256}] (M_{av} - M_L) \quad (6)$$

$$P_{ct} = P_{c_L} + [700M_L^{-1.08}x_L^{1.2} - 557M_L^{-1.265}] (M_{av} - M_L) \quad (7)$$

where M_L refers to the molecular weight of *n*-pentane or higher members of the normal paraffin series and M_{av} is the

Table I. Constants for Pressure Equation 4 for Binary Systems of Methane, Ethane, Propane, and *n*-Butane

	Critical Pressure			M_L	P_{cL} , P.S.I.A.
	a	b	m_0		
Methane	137	1.073	-3.07	16.04	673.1
Ethane	28.6	1.595	-4.0	30.07	708.3
Propane	13.6	1.225	-4.3	44.09	617.4
<i>n</i> -Butane	9.24	1.284	-3.5	58.12	550.1

	Cricondenbar Pressure		
	a	b	m_0
Methane ($W_1 < 0.5$)	127.7	0.965	-3.07
($W_1 > 0.5$)	520	2.99	-3.07
Ethane ($x_2 < 0.8$)	28.6	1.503	-4.0
($x_2 > 0.8$)	41.7	3.222	-4.0
Propane	13.6	1.216	-4.3
<i>n</i> -Butane	9.24	1.272	-3.5

	Cricodentherm Pressure		
	a	b	m_0
Methane	33.5	0.76	-2.1
Ethane	14.0	1.175	-4.7
Propane	10.0	1.00	-4.75
<i>n</i> -Butane	7.54	1.585	-3.2

molecular weight of the binary mixture calculated on a weight basis.

Empirical Equations for Temperature. The relations between the critical temperature, average molecular weight, and composition, shown in Figure 4, may also be expressed by an empirical equation.

Referring to the diagram in Figure 4, the equation for any one of the straight lines may be written as:

$$\log(T_c/420) = m \log(M_{av}/M_{c1})$$

or (8)

$$T_c = 420(M_{av}/M_{c1})^m$$

where m is the slope of the line. When the logarithm of the slope is plotted against the logarithm of the weight fraction of methane, a straight line results which may be expressed by the equation:

$$m = -0.597 W_{c1}^{1.86} + 0.447 \quad (9)$$

The value of m is then substituted into Equation 8 to give an equation for the critical temperature.

In a similar manner, empirical equations for the temperature at the critical, cricondenbar and cricodentherm points were derived for the binaries of methane, ethane, propane, and *n*-butane. For binaries of *n*-pentane and heavier members, general equations were derived in a manner entirely analogous to the derivation of the pressure equations. The equations are as follows:

Critical Temperature.

$$(T_c)_{c1} = 420(M_{av}/16.04)^{0.447} - 0.597 W_{c1}^{1.86} \quad (10)$$

$$(T_c)_{c2} = 565(M_{av}/30.07)^{0.454} - 10^{2x_{c2}-2.37} \quad (11)$$

$$(T_c)_{c3} = 677(M_{av}/44.09)^{0.452} - 0.209 x_{c3}^{1.85} \quad (12)$$

$$(T_c)_{c4} = 769(M_{av}/58.12)^{0.447} - 10^{0.842x_{c4}-1.78} \quad (13)$$

For *n*-pentane and higher,

$$(T_c)_{cL} = T_{cL}(M_{av}/M_L)^{0.344} - 290M_L^{-2}x_L^{15}M_L^{-0.556} \quad (14)$$

where the subscripts c_1 , c_2 , c_3 , and c_4 refer, respectively, to methane, ethane, etc. Other symbols have their usual significance.

Cricondenbar Temperature.

$$(T_{cb})_{c1} = 420(M_{av}/16.04)^{0.447} - 0.306 W_{c1}^{0.904} \quad (15)$$

$$(T_{cb})_{c2} = 565(M_{av}/30.07)^{0.45} - 0.14x_{c2}^{1.275} \quad (16)$$

$$(T_{cb})_{c3} = 677(M_{av}/44.09)^{0.451} - 0.198x_{c3}^{1.688} \quad (17)$$

$$(T_{cb})_{c4} = 769(M_{av}/58.12)^{0.427} - 0.083x_{c4}^{1.593} \quad (18)$$

For *n*-pentane and higher,

$$(T_{cb})_{cL} = T_{cL}(M_{av}/M_L)^{0.344} - 290M_L^{-2.05}x_L^{15}M_L^{-0.64} \quad (19)$$

Cricodentherm Temperature.

$$(T_{ct})_{c1} = 380(M_{av}/16.04)^{0.533} + 10^{2.75W_{c1}-2.87} \quad (20)$$

$$(T_{ct})_{c2} = 550(M_{av}/30.07)^{0.473} + 10^{3.88x_{c2}-4.56} \quad (21)$$

$$(T_{ct})_{c3} = 671(M_{av}/44.09)^{0.473} - 0.111x_{c3}^{2.35} \quad (22)$$

$$(T_{ct})_{c4} = 769(M_{av}/58.12)^{0.429} - 0.0262x_{c4}^{2.11} \quad (23)$$

For *n*-pentane and higher,

$$(T_{ct})_{cL} = T_{cL}(M_{av}/M_L)^{0.344} + 74.00M_L^{-3.07}x_L^{10}M_L^{-3.384} \quad (24)$$

EXCESS PRESSURE AND EXCESS TEMPERATURE

The pressure and the temperature at the critical, cricondenbar and cricodentherm points of a multicomponent mixture may be considered as consisting of two parts:

$$G_{mix} = G_{ideal} + G_{excess} \quad (25)$$

G_{ideal} is the critical pressure or temperature calculated as the sum of the products of the critical constants and the compositions; G_{excess} is a molecular interaction quantity equal to the difference between the actual and ideal values. This quantity is called an "excess" property by analogy to the excess thermodynamic functions. Thus, we may speak of the excess pressure and excess temperature at the critical, cricondenbar and cricodentherm points. The excess pressure and excess temperature of a mixture are conceived as being made up of the contributions of each of the components, with the component of lowest molecular weight producing the greatest effect in proportion to the amount present. It is postulated that these contributions can be calculated from a knowledge of the composition of the mixture and the equations previously developed for the pressure and temperature of binary systems. Thus, the excess critical pressure, P_{ct} , of a component of a binary mixture will be

$$(P_{ct})_{cL} = (P_c)_{cLmix} - (P_c)_{cL=0} = P_{cL} + (a_Lx_L^{2L} + m_{0L})(M_{av} - M_L) - P_{cL} - \tilde{m}_{0L}(M_{av} - M_L)$$

or

$$(P_{cl})_L = a_L x_L^{b_L} (M_{av} - M_L) \quad (26)$$

where L refers to the lighter component in the binary. When L refers to methane, x_L is replaced by W_{c1} , the weight fraction of methane.

The equations for the excess cricondenbar pressure and cricondentherm pressure of a component of a binary system are identical in form to Equation 26. The constants are given in Table I for the indicated point.

In like manner the equations for the excess critical temperature T_{cd} , excess cricondenbar temperature T_{cbd} and excess cricondentherm temperature T_{cfd} of a component are derived by subtracting the equation for the respective "zero" line from the equation for the binary mixture using Equations 10 through 24.

MULTICOMPONENT MIXTURES

The approach to the calculation of the total excess pressure and temperature from the excess quantities associated with the various components has been strictly an empirical one. It becomes necessary, therefore, to deal separately with each individual pressure and temperature point.

Critical Pressure. The critical pressure of a multicomponent mixture of hydrocarbons is:

$$(P_c)_{mix} = \sum x_i P_{ci} + \sum \Phi_i (P_{cdi}, x_i) \quad (27)$$

where $\sum x_i P_{ci}$ is the pseudocritical pressure of the mixture and $\sum \Phi_i (P_{cdi}, x_i)$ is the total excess critical pressure and is equal to the sum of the contributions of the excess critical pressure of the components, except the heaviest.

$\sum \Phi_i (P_{cdi}, x_i)$ is calculated as follows: Consider a mixture of three or more of the normal paraffin hydrocarbons from methane through n -octane. Let their molecular weights, weight fractions and mole fractions be $M_1, M_2, M_3, \dots; W_1, W_2, W_3, \dots; x_1, x_2, x_3, \dots;$ respectively, where subscripts 1, 2, and 3... refer to the components in the order of increasing molecular weight. The contribution to the total excess critical pressure for each component, except the heaviest is

Component 1

$$\Phi_1(P_{cd1}, x_1) = a_1 x_1^{b_1} (M_{av} - M_1) \quad (28)$$

If component 1 is methane, x_1 is replaced by W_1 .

Component 2

$$\Phi_2(P_{cd2}, x_2) = a_2 \left(\frac{x_2}{1 - x_1} \right)^{b_2} \left[\frac{M_{av} - M_1 W_1}{1 - W_1} - M_2 \right] (1 - x_1) \quad (29)$$

Component 3

$\Phi_3(P_{cd3}, x_3) =$

$$a_3 \left(\frac{x_3}{1 - x_1 - x_2} \right)^{b_3} \left[\frac{M_{av} - M_1 W_1 - M_2 W_2}{1 - W_1 - W_2} - M_3 \right] (1 - x_1 - x_2) \quad (30)$$

Component 4

$$\Phi_4(P_{cd4}, x_4) = a_4 \left(\frac{x_4}{1 - x_1 - x_2 - x_3} \right)^{b_4} \left[\frac{M_{av} - M_1 W_1 - M_2 W_2 - M_3 W_3}{1 - W_1 - W_2 - W_3} \right] (1 - x_1 - x_2 - x_3) \quad (31)$$

The form of the equations for additional components is obvious. The values of constants a and b are given in Table I. The sum of the contributions of each component,

except the heaviest, is then added to the pseudo-critical pressure of the mixture to give the calculated critical pressure of the mixture.

Cricondenbar Pressure. The cricondenbar pressure of any multicomponent normal paraffin-hydrocarbon mixture is calculated by summing up the contributions to the excess pressure of each component except the heaviest and adding to this sum, the pseudocritical pressure of the mixture

$$(P_{cb})_{mix} = \sum x_i P_{ci} + \sum \Theta_i (P_{cbdi}, x_i) \quad (32)$$

The total excess cricondenbar pressure $\sum \Theta_i (P_{cbdi}, x_i)$ is calculated in the same manner as the excess critical pressure using the same Equations 28 to 31, but with values of the constants a and b for the cricondenbar pressure.

Cricondentherm Pressure. The cricondentherm pressure of a multicomponent mixture of normal paraffin hydrocarbons is given by the equation

$$(P_{ct})_{mix} = \sum x_i P_{ci} + \sum (P_{ctdi}) \quad (33)$$

where $\sum x_i P_{ci}$ is the pseudocritical pressure, and $\sum (P_{ctdi})$ is the excess cricondentherm pressure of the components whose molecular weights are less than the average molecular weight (on a weight basis) of the mixture. The excess cricondentherm pressures are calculated by Equation 26 using the appropriate values of constants a and b listed in Table I.

Since the magnitude of the excess pressure at the three points decreases sharply with increasing molecular weight of the common component, the contributions due to n -pentane and higher are relatively unimportant.

Critical Temperature. The critical temperature of a mixture of normal paraffin hydrocarbons may be expressed as

$$(T_c)_{mix} = \sum W_i T_{ci} + \sum (T_{cxi} - T_{cxi=0}) \quad (34)$$

where

$$\sum W_i T_{ci} = W_{c1} T_{c1} + W_{c2} T_{c2} + W_{c3} T_{c3} + \dots$$

(when $W_{c1} > 0.4$ and/or $(W_{c1} + W_{c2} + W_{c3} + W_{c4}) > 0.8$, $T_{c1} = 420^\circ \text{R.}$; at other concentrations $T_{c1} = 343.2^\circ \text{R.}$, the critical temperature of methane).

$\sum (T_{cxi} - T_{cxi=0})$ is the sum of the excess temperatures of all components whose molecular weight is less than M_{av} for the mixture. The excess critical temperature of these components is calculated using the appropriate Equations 10 to 14.

Cricondenbar Temperature. The cricondenbar temperature of a multicomponent paraffinic hydrocarbon mixture is calculated as follows:

A. When $(W_{c1} + W_{c2} + W_{c3} + W_{c4}) < 0.5$

$$(T_{cb})_{mix} = \sum W_i T_{ci} + \sum (T_{cbdi}) \quad (35)$$

where $\sum (T_{cbdi})$ is the sum of the excess cricondenbar temperatures of all components whose molecular weight is less than M_{av} of the mixture. Since $(T_{cbdi}) = (T_{cb})_{xi} - (T_{cb})_{xi=0}$, Equations 15 to 19 may be used to express the excess cricondenbar temperature of any component i .

B. When $\sum (W_{c1} + W_{c2} + W_{c3} + W_{c4}) > 0.5$ Equation 35 becomes

$$(T_{cb})_{mix} = \sum W_i T_{ci} + (T_{cbL} - T_{cbL=0}) + \sum (T_{cbci} - T_{cbci=0}) \quad (36)$$

where $\sum (T_{cbci} - T_{cbci=0})$ is the sum of the excess cricondenbar temperatures of all components whose molecular weight is less than the average molecular weight of the mixture but excluding the component of lowest molecular weight.

Cricodentherm Temperature.

$$(T_{cd})_{mix.} = \sum_{i=1}^n T_{ci} + (T_{cd})_{xL} + \sum (T_{cd}) \quad (37)$$

where $\sum (T_{cd})_i$ is the sum of the excess cricodentherm temperatures of all components whose molecular weight is less than the average molecular weight of the mixture but excluding the component of lowest molecular weight. The excess cricodentherm temperature for any component i is

$$(T_{cd})_{i_x} = (T_{\alpha_{x_i}} - T_{\alpha_{x_i=0}}) \quad (38)$$

and is calculated using Equations 20 to 24.

EXPERIMENTAL PRESSURE AND TEMPERATURE DATA

To supplement the data available in the literature on the P - T - x relations of normal paraffin hydrocarbon mixtures, the pressure and temperature at the critical, cricodenbar and cricodentherm points were determined for eight mixtures varying from two to six components of the hydrocarbons, methane through n -hexane. The apparatus and

experimental procedures were the same as those used in earlier studies and have been described in detail (7, 8).

Samples of methane through n -hexane of the highest purity (99.90 mole % or better) were furnished by the Phillips Petroleum Co. Each of the hydrocarbons was carefully deaerated by pumping under vacuum. Mixtures of known composition were prepared by mixing together measured amounts of the deaerated compounds. The mixtures were confined over mercury in a thick-walled glass tube which was surrounded by a constant temperature bath. The tube was fastened into a mercury-filled compressor with means for controlling the pressure on the sample. Equilibrium between the liquid and vapor phases was established by means of a magnetic stirrer consisting of a small steel ball confined with the sample and moved by a magnet around the outside of the tube. The critical point was located by the disappearance of the meniscus method; the cricodenbar and cricodentherm point by determining a portion of the P - T border curve in the vicinity of the points and locating the points graphically. Pressures were measured by means of a dead weight gage to within ± 0.1 p.s.i.

Table II. Composition of Multicomponent Mixtures Used to Test Correlation

Ref.	Mixture		Mole Fraction								
	No.	Series	CH ₄	C ₂ H ₆	C ₃ H ₈	n -C ₄ H ₁₀	n -C ₅ H ₁₂	n -C ₆ H ₁₄	C ₇ ⁺	N ₂	CO ₂
	A	II	32.76	33.98	33.26
	B	III	...	34.14	34.21	...	31.65
	C	III	...	25.42	25.47	25.54	23.57
	D	III	20.19	20.29	20.33	20.38	18.81
	E	IV	64.49	23.59	11.92
	F	IV	48.58	33.16	12.13	6.13
	G	IV	...	39.77	29.26	19.97	7.13	3.69
		IV	10.15	35.73	26.29	17.94	6.57	3.32
(8)		IV	78.4	3.55	1.36	1.30	6.31	4.47	3.82	.36	.43
(8)			81.5	3.72	1.41	1.02	5.01	3.54	3.03	.38	.44
(8)			83.0	3.76	1.44	.89	4.36	3.08	2.63	.38	.45
(8)			72.8	5.46	3.02	2.07	6.88	4.38	3.75	.54	...
(8)			65.2	2.98	1.13	30.0030	.35
(8)			66.26	10.93	10.57	...	6.16	6.08

Table III. Synthetic and Natural Gas Mixtures
Comparison of Calculated with Experimental Pressure

Mixture No.	P_c , P.S.I.A.			P_{cb} , P.S.I.A.			P_{cd} , P.S.I.A.		
	Exptl.	Calcd.	% Dev.	Exptl.	Calcd.	% Dev.	Exptl.	Calcd.	% Dev.
A	607.4	627	3.3	609.2	628	3.1	595.7	609	2.2
B	812.5	799	-1.7	816.1	814	-0.2	736.0	740	0.5
C	741.6	730	-1.5	746.6	744	-0.4	700.0	693	-0.9
D	1047.2	1023	-2.3	1106.8	1108	0.1	845.2	846	0.0
E	562.8	569	1.1	564.0	571	1.2	558.6	553	-1.0
F	653.5	666	1.9	654.3	670	2.3	635.0	634	-0.1
G	815.7	815	-0.1	817.4	829	1.4	738.0	738	0
H	948.0	939	-1.0	961.5	999	3.9	804.0	815	1.3
I	2730	2730	0	2825	2747	-2.8
J	2675	2682	0.3
K	2605	2621	0.6
L	2537	2503	-1.3	2574	2559	-0.6
M	1797	1808	0.6
N	1994	2043	2.5	583.7	579	-0.8

Comparison of Calculated with Experimental Temperature

	T_c , ° R.			T_{cb} , ° R.			T_{cd} , ° R.		
	Exptl.	Calcd.	% Dev.	Exptl.	Calcd.	% Dev.	Exptl.	Calcd.	% Dev.
A	771.9	766	-0.8	770.3	773	0.4	774.5	776	0.2
B	714.9	715	0	709.8	717	0.9	728.5	730	0.2
C	730.6	729	-0.2	726.3	730	0.5	737.9	736	-0.3
D	696.7	697	0	672.3	685	1.9	715.0	718	0.4
E	810.4	804	-0.8	809.6	808	-0.2	812.1	812	-0.1
F	752.3	743	-1.2	750.5	751	0.1	757.1	758	1.0
G	693.8	686	-1.1	689.6	694	0.6	707.1	703	-0.7
H	677.6	679	0.1	667.7	668	0	696.9	691	-0.9
I	550	563	2.4	605	593	2.0
J	525	522	-0.6	612	628	2.7
K	514	499	-3.0	557	549	-1.4
L	569	564	-0.9	600	602	0.4
M	576	579	0.5	563	580	3.0
N	559	544	-2.7	584	579	-0.8

Table IV. Summary of Agreement between Calculated and Experimental Critical Data on Hydrocarbon Mixtures

Mixtures			Pressure Deviations				Temperature Deviations		
Type	No.		Av. %	Max. %	Standard, p.s.i.	Mixtures, No.	Av. %	Max. %	Standard, ° F.
Experimental Data									
Critical	(synthetic)	8	1.60	3.3	13.8	8	0.55	1.23	5.4
Cricondenbar	(synthetic)	8	1.57	3.9	16.6	8	0.57	1.87	5.7
Cricondentherm	(synthetic)	8	0.76	2.2	7.0	8	0.35	0.92	2.9
Data for Literature									
Critical	(natural gas)	6	0.9	2.5	22.0	6	1.7	3.0	10.5
Cricondenbar	(natural gas)	3	1.4	2.8	45.9	6	1.7	3.0	10.9
Critical	(methane binaries)	17	2.0	9.2	49.1	17	1.0	3.1	7.2
Cricondenbar	(methane binaries)	16	2.9	8.4	64.7	16	1.7	7.0	16.6
Cricondentherm	(methane binaries)	18	8.4	24.5	122.6	18	0.32	2.4	4.5
Critical	(other binaries)	25	0.85	4.03	12.3	25	0.48	3.22	6.4
Cricondenbar	(other binaries)	20	0.98	3.58	9.6	20	0.32	2.12	4.3
Cricondentherm	(other binaries)	25	1.45	11.80	21.2	25	0.12	0.75	1.7

and the temperature by means of a thermocouple and sensitive potentiometer to within 0.02° C.

The composition of the eight mixtures are given in Table II. The mixtures are identified by letters A through H and are grouped into four series. Each series represents mixtures which were progressively built up from the preceding mixture by the successive addition of a different component. The pressure and temperature at the critical, cricondenbar, and cricondentherm points are listed in Table III.

COMPARISON OF CALCULATED WITH EXPERIMENTAL DATA

To test the accuracy of the correlation, a comparison of calculated with experimental values of the pressure and temperature at the critical, cricondenbar, and cricondentherm points of mixtures of known composition was made. For this purpose, the P - T data on synthetic mixtures of the hydrocarbons which were determined in this laboratory and those for natural gas mixtures reported by Kurata and Katz (9) as well as data on binary mixtures (4, 5, 6, 10, 12, 13, 14) were employed. A total of about 60 mixtures, varying from two to nine components, were studied. The results for mixtures containing more than two components are given in Table III; those for binary mixtures are available from the American Documentation Institute (1). Table IV gives a summary of the results for all mixtures.

In general, the agreement is moderately good; the over-all deviation of the calculated values from the experimental is about 2% for the pressure and about 1% for the temperature. The greatest deviations occur in the pressure at the cricondentherm point in binary mixtures, especially in those containing methane. This could be due to an error in locating the point. In the vicinity of the cricondentherm point the pressure along the phase boundary curve is extremely sensitive to small changes in temperature. If the temperature is not determined with great accuracy, large errors in the pressure will result.

While inaccuracy of the data may explain some of the deviation, there are other factors to be considered. Methane does not conform to the general relations applicable to higher members (2) of the paraffin series. The fact that the lines of constant composition in the diagrams of Figures 1 and 4 are for constant weight fraction and not mole fraction is additional evidence of this nonconformity. Indeed, the great difference in size and shape between the methane molecule and a molecule of a higher member of the series would lead one to suspect nonconformity. The explanation of this behavior in terms of intermolecular forces, shape factors, and structural effects belongs to the realm of statistical mechanics. It would seem that the relations presented here for binary systems containing a common component, yield important clues for such an explanation.

NOMENCLATURE

M = molecular weight
 M_{av} = average molecular weight calculated on weight basis
 P = pressure, p.s.i.
 T = temperature, ° R.
 x = mole fraction
 W = weight fraction
 m, a, b = constants
 ϕ = function of

Subscripts

0 = initial value
 c_1, c_2, c_3, c_4 = methane, ethane, propane, n -butane
 c = critical
 cb = cricondenbar
 ct = cricondentherm
 cd = excess critical
 cbd = excess cricondenbar
 ctd = excess cricondentherm
 L = lighter component
 i = any component

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