range. Sage et al. (*4*) reported equilibrium composition data for this system for temperatures from 100° up to 340°F.

Figure 4 shows their critical pressures for the methane-*n*-pentane system at high temperature match quite well with our critical pressures at low temperatures.

The critical composition loci of this system are shown in Figure 5. The critical compositions of Sage et al. have been converted from weight fraction to mole fraction to make this plot on the same basis. Our data also join smoothly with theirs in this plot.

Generalization

The triple-valued dew points observed in the methane-*n*-butane system (*2*) and the quadruple-valued dew points observed here are a general phenomena not specifically limited to these systems. Similar behavior will be observed for other binary systems of widely different relative volatilities. The pressure for such systems at the cricondenbar point at temperatures immediately above the critical temperature of the more volatile component falls below the critical pressure of that component. The authors have named this phenomenon "double retrograde vaporization" (*1*).

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Vapor-Liquid Equilibria in Three Binary and Ternary Systems Composed of *n*-Butane, Butene-1, and Butadiene-1,3

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Total pressure and PVT data are reported on *n*-butane, butene-1, and butadiene-1,3 and their mixtures over the temperature range 100–150°F and the pressure range 20–500 psia. The data have an estimated precision of 0.1%. The experimental data are correlated, and the vapor-liquid equilibrium behavior of the binary systems is computed by integration of the general coexistence equation by the method of Manley and Swift. Wilson parameters for the binary systems are computed from the experimental data and used to predict the ternary system bubble-point pressures. The predicted pressures are compared with experimental results to test the validity of the predictions, and satisfactory agreement is achieved. No ternary azeotrope is observed over the range of conditions investigated. The precision of the computed results of this work is 0.003, 0.001, 0.007, and 0.005 relative volatility units for the systems butene-1-*n*-butane, butene-1-butadiene-1,3, *n*-butane-butadiene-1,3, and *n*-butane-butene-1-butadiene-1,3, respectively.

The accurate design of distillation units for systems made up of close boiling components requires precise vapor-liquid equilibrium-phase data. The C_4 hydrocarbon systems composed of mixtures of *n*-butane, butene-1, and butadiene-1,3 (butane, butene, and butadiene for brevity) are close boiling systems for which a paucity of vapor-liquid equilibrium data are available.

As shown by Manley and Swift (*11*) and Laurance and Swift (*8*), the direct sampling procedure for obtaining vapor-liquid equilibrium data by measuring the compositions of coexisting vapor and liquid phases at equilibrium is in general an unsatisfactory method for close boiling systems, and the total pressure method is far superior in precision. Since the relative volatility is close to 1 in close boiling systems, errors in measured phase compositions lead to large errors in the computed relative volatilities, and in the subsequent design calculations, the level of imprecision is roughly 10 times the expected error in the measured phase compositions.

Manley (*10*) developed a method for computing vapor-phase compositions from experimental total pressure data by integrating the isothermal general coexistence equation. The method is described by Manley and Swift (*11*) and is completely rigorous and can be applied to a binary system if the following experimental data are available: the pure component and binary mixture bubble-point pressure as a function of liquid composition and temperature, and the vapor and liquid-phase specific volumes as a function of pressure, temperature, and composition.

Correlations of the experimental data are used to numerically integrate the isothermal general coexistence equation, and thermodynamically consistent vapor-phase compositions are computed. The significant advantage of the total pressure method is that the bubble point and PVT data may be used to calculate phase compositions with considerably greater precision than they can be measured in close boiling systems.

Experimental

The experimental apparatus used in this work has been described most recently by Laurance (*7*) and is discussed in earlier articles by Laurance and Swift (*8*), Manley (*10*), and Manley and Swift (*11*).

The materials used in this work are Phillips research-grade chemicals and have a stated purity of not less than 99.97, 99.85, and 99.89 mol % for butane, butene, and butadiene, respectively. The most probable impurities are isobutane in the butane, isobutylene and butadiene in the butene, and butene and tertiary butyl catechol (TBC) in the butadiene.

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The TBC is a polymerization inhibitor for the butadiene. Prior to use, the cylinders containing the pure components are vented on the vapor side to reduce the amount of light impurities, and both butene and butane are withdrawn as liquids from the cylinders to further avoid contamination. Because of the presence of TBC, the butadiene samples are withdrawn as vapors from the cylinders. All materials are stored at 40°F when not in use. The final sample purity is such that the pressure rise across the two-phase region is less than 0.1% of the measured pressure.

The pressure measurements of this work are made with a Ruska dead weight gage which has been calibrated by Ruska Corp. against their reference gage which has been calibrated by the National Bureau of Standards. The precision of the pressure measurement is 0.1%. Temperatures are measured with a platinum resistance thermometer which has been calibrated against a standard platinum resistance thermometer calibrated by the National Bureau of Standards according to the IPTS of 1948. The precision is within 0.01°F.

The volume measurements of this work are based on calibrations made with demineralized water and a Mettler balance with a precision of approximately 0.01% in weighing.

The volume measurements have a precision of approximately 0.01%. Liquid mixtures are made up in the experimental apparatus with a precision of approximately

Table I. Vapor Specific Volume: Redlich-Kwong Constants

	a	b	σ, psia
Butane	0.24425 (10^7)	4.9150	0.25
Butene	0.19213 (10^7)	3.1125	0.39
Butadiene	0.33256 (10^7)	6.9355	0.47

Table II. Liquid Specific Volume: Redlich-Kwong Constants

	a	b	σ, psia
Butane	0.15360 (10^7)	1.2262	44.9
Butene	0.13912 (10^7)	1.1391	27.7
Butadiene	0.13333 (10^7)	1.0578	28.7

Table III. Bubble-Point Correlation Constants of Butene–Butadiene System

	$j = 3$	$j = 2$	$j = 1$
b_{4j}	−10.217	24.219	−13.285
b_{3j}	13.583	−35.860	18.438
b_{2j}	−0.413	9.646	−3.582
b_{1j}	87.131	−95.885	68.629
		$\sigma = 0.04$ psia	

Table IV. Bubble-Point Correlation Constants of Butene–Butane System

	$j = 3$	$j = 2$	$j = 1$
b_{4j}	12.718	−27.906	14.121
b_{3j}	7.236	−16.124	6.742
b_{2j}	11.438	−13.621	16.348
b_{1j}	72.834	−72.167	50.828
		$\sigma = 0.06$ psia	

Table V. Bubble-Point Correlation Constants of Butane–Butadiene System

		$j = 3$	$j = 2$	$j = 1$
$0 \leqslant X_3 < 0.9$	b_{4j}	−4.460	3.604	0.475
	b_{3j}	0.945	−1.188	−8.912
	b_{2j}	18.438	−27.790	27.712
	b_{1j}	72.710	−71.809	50.576
$0.9 \leqslant X_3 \leqslant 1.0$	b_{3j}	−32.328	48.656	−83.455
	b_{2j}	63.024	−95.648	155.765
	b_{1j}	56.424	−48.869	−3.710
			$\sigma = 0.04$ psia	

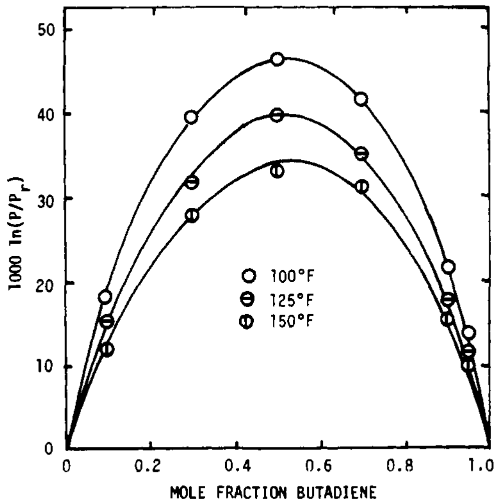

Figure 1. Butane–butadiene bubble points

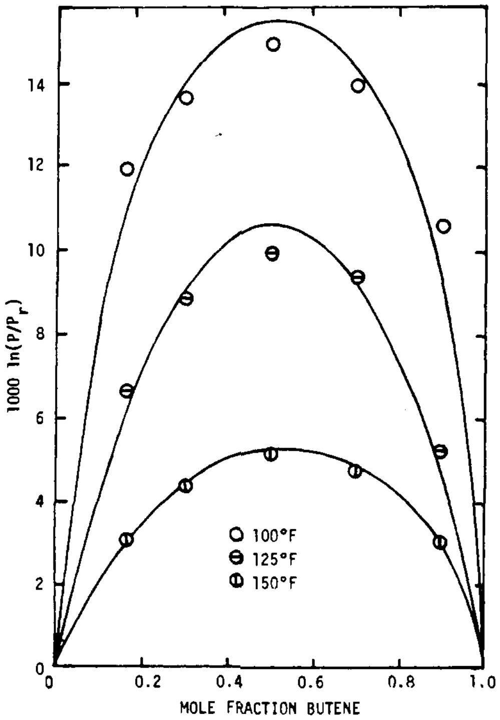

Figure 2. Butene–butane bubble points

0.0002 mole fraction units based on the precision of the volume measurements, the resolution limits of the Mettler balance, and the precision of the pressure measurements. PVT data and bubble-point pressures can be determined with this apparatus with a precision of 0.1% in both the specific volume data and the measured pressures.

Correlations

The following correlations are required to apply the total pressure method to the data of this work. The constants in the equations are determined by least-squares analysis of the data, and the computer programs used in this work are given by Laurance (*7*).

The pure component and binary mixture bubble-point data are correlated by the following empirical relationship:

$$P^\circ = \sum_k ([\sum_i b_{ki}(T/100)^{i-1}]x^{k-1})$$

The PVT data for the liquid and vapor phase are correlated by the Redlich-Kwong (*15*) equation of state.

$$P = \frac{RT_a}{V\text{-}b} - \frac{a}{T_a^{0.5}\, V(V+b)}$$

or

$$Z = 1 + BP - \frac{A^2P(Z - BP)}{Z(Z + BP)}$$

where

$$A^2 = a/(R^2T_a^{2.5})$$

and

$$B = b/(RT_a)$$

The composition dependence of the vapor-phase specific volume data is represented by the mixing rules

$$A = \sum_i y_iA_i \qquad \text{and} \qquad B = \sum_i y_iB_i$$

where the A_i and B_i terms are the pure component Redlich-Kwong constants. The composition dependence of the liquid-phase specific volume data is expressed by the mixing rules

$$a = \sum_i x_ia_i \qquad \text{and} \qquad b = \sum_i x_ib_i$$

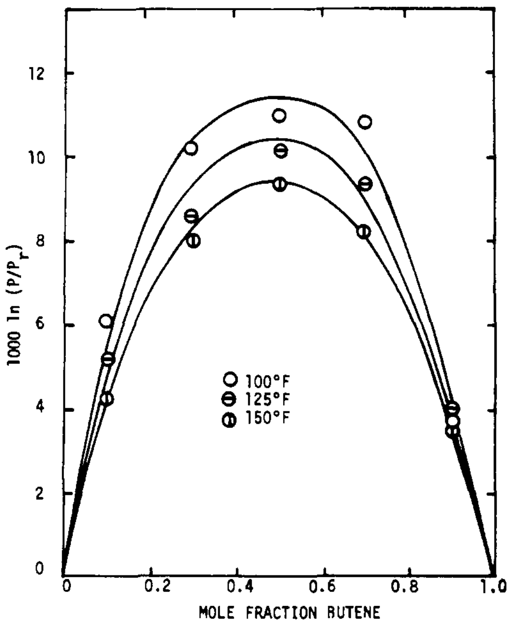

Figure 3. Butene–butadiene bubble points

Wilson parameters (*19*) are computed for the binary systems by fitting the results of the work to the equation

$$P = \sum_i (\gamma_i{}^L x_iP_i{}^\circ F_i)$$

where γ_i is the liquid-phase activity coefficient, $P_i{}^\circ$ is the pure component vapor pressure, F_i is a correction for nonideal behavior, and P is the bubble-point pressure. The activity coefficients are computed from the Wilson equation.

$$\ln \gamma_i = 1 - \ln (\sum_j x_j\Lambda_{ij}) - \sum_k ((x_k\Lambda_{ki})/(\sum_j x_j\Lambda_{kj}))$$

$$\Lambda_{ij} = (V_j{}^L/V_i{}^L) \exp[-(\lambda_{ij} - \lambda_{ii})/RT_a]$$

The vapor-phase nonideality correction terms are computed from the expression

$$F_i = [\phi_i{}^\circ/\hat{\phi}_i] \exp ((RT_a)^{-1} \int_{P_i{}^\circ}^{P} V_i{}^L dP)$$

where the ϕ terms are the vapor-phase fugacity coefficients and are computed from the equations given by Redlich and Kwong (*15*) based on their equation of state.

Data

The experimental results for the pure components and the binary systems are given by Laurance (*7*). Tables I–V give the constants for the correlating equations. The measured bubble-point pressures are plotted as the logarithm of the observed pressure divided by the pressure computed by assuming Raoult's Law (P_r) so that any variations in the data will be clearly evident. One unit on the ordinate of Figures 1–3 represents an error of approximately 0.1% in the observed bubble-point pressure. The bubble-point pressures for the butane–butadiene system are correlated with two equations since the shape of the $P - x$ surface precludes using a single low-order equation to precisely fit the data. The butane–butadiene azeotrope is a maximum pressure azeotrope, and the azeotropic composition is found by locating the maximum in the $P - x$ surface. The azeotrope occurs at 0.9172, 0.9206, and 0.9260 mole fraction butadiene at 100°, 125°, and 150°F, respectively.

Calculated Results

The isothermal general coexistence equation was used to compute the vapor-liquid equilibrium data given for the binary systems in Tables VI–VIII. Wilson parameters for the binary systems are given as a function of temperature in Table IX. The temperature dependence of the Wilson parameters is a necessary consideration when precise calculations are required. The precision of the results of this work on close boiling systems justifies such a procedure. Table X compares the computed vapor-phase compositions, relative volatilities, and bubble-point pressures as computed from the coexistence equation method and the Wilson equation method, giving the average difference between values of P, y, and α computed by the Wilson equation and those computed from the coexistence equation.

Table XI gives the experimental ternary bubble-point pressures used to test the predictions of the Wilson equation along with the predicted results at the experimental points. The estimated levels of precision of the computed

Table VI. Butane–Butene Vapor-Liquid Equilibrium Data

	100°F		125°F		150°F	
X_2	Y_2	P	Y_2	P	Y_2	P
0.0000	0.0000	51.50	0.0000	74.42	0.0000	106.46
0.1000	0.1206	52.89	0.1168	76.12	0.1143	108.61
0.2000	0.2345	54.23	0.2284	77.77	0.2247	110.73
0.3000	0.3425	55.52	0.3354	79.37	0.3313	112.82
0.4000	0.4452	56.75	0.4383	80.91	0.4344	114.87
0.5000	0.5436	57.91	0.5375	82.38	0.5344	116.88
0.6000	0.6383	58.99	0.6336	83.79	0.6315	118.84
0.7000	0.7302	59.99	0.7273	85.12	0.7262	120.74
0.8000	0.8204	60.91	0.8191	86.37	0.8189	122.58
0.9000	0.9099	61.73	0.9097	87.54	0.9100	124.36
1.0000	1.0000	62.45	1.0000	88.62	1.0000	126.07

Table VII. Butane–Butadiene Vapor-Liquid Equilibrium Data

	100°F		125°F		150°F	
X_3	Y_3	P	Y_3	P	Y_3	P
0.0000	0.0000	51.48	0.0000	74.42	0.0000	106.46
0.1000	0.1249	53.22	0.1200	76.51	0.1172	109.12
0.2000	0.2386	54.78	0.2315	78.41	0.2276	111.59
0.3000	0.3435	56.15	0.3360	80.10	0.3321	113.83
0.4000	0.4417	57.33	0.4349	81.58	0.4318	115.83
0.5000	0.5351	58.32	0.5298	82.84	0.5276	117.56
0.6000	0.6257	59.11	0.6220	83.85	0.6210	118.99
0.7000	0.7157	59.71	0.7134	84.62	0.7133	120.10
0.8000	0.8069	60.11	0.8058	85.12	0.8061	120.89
0.9000	0.9012	60.31	0.9008	85.35	0.9011	121.25
1.0000	1.0000	59.86	1.0000	84.90	1.0000	120.83

Table VIII. Butene–Butadiene Vapor-Liquid Equilibrium Data

	100°F		125°F		150°F	
X_2	Y_2	P	Y_2	P	Y_2	P
0.0000	0.0000	59.87	0.0000	84.91	0.0000	120.85
0.1000	0.1061	60.40	0.1057	85.65	0.1051	121.79
0.2000	0.2093	60.86	0.2088	86.28	0.2081	122.65
0.3000	0.3104	61.24	0.3099	86.83	0.3095	123.40
0.4000	0.4099	61.57	0.4096	87.29	0.4094	124.06
0.5000	0.5083	61.83	0.5082	87.67	0.5084	124.63
0.6000	0.6062	62.04	0.6063	87.97	0.6066	125.11
0.7000	0.7039	62.19	0.7042	88.22	0.7045	125.49
0.8000	0.8020	62.30	0.8024	88.40	0.8024	125.77
0.9000	0.9006	62.37	0.9009	88.52	0.9008	125.97
1.0000	1.0000	62.40	1.0000	88.60	1.0000	126.07

Table IX. Wilson Parameters

	100°F	σ, psia	125°F	σ, psia	150°F	σ, psia
$\lambda_{12}-\lambda_{11}$	2036	0.010	1531	0.003	1439	0.003
$\lambda_{12}-\lambda_{22}$	−1311	0.010	−1059	0.003	−1087	0.003
$\lambda_{23}-\lambda_{22}$	560	0.003	472	0.004	−865	0.005
$\lambda_{23}-\lambda_{33}$	−188	0.003	−112	0.004	1161	0.005
$\lambda_{13}-\lambda_{11}$	2097	0.080	1940	0.080	2104	0.081
$\lambda_{13}-\lambda_{33}$	−605	0.080	−631	0.080	−843	0.081

Table X. Wilson Equation Vs. Coexistence Equation

	Av error in:		
System	P	Y	α
Butane-butene	<0.01	0.0001	0.0010
Butene-butadiene	<0.01	0.0001	0.0008
Butane-butadiene	0.08	0.0008	0.0072

results, computed by inserting maximum errors of 1% in the molar volume data and 0.2% in the bubble-point pressure data, are 0.003, 0.001, 0.007, and 0.005 relative volatility units for butane–butene, butene–butadiene, butane–butadiene, and butane–butene–butadiene, respectively.

Comparison with Literature Data

Examples of the agreement of the experimental molar volume data of this study with those of previous investigators are shown in Figures 4–6. Table XII compares the vapor-pressure data of this study with the literature data available at the temperatures of interest. Since no raw experimental literature data are available for comparison, Table XII lists the smoothed and/or correlated results of

Table XI. Ternary System: Experimental Results

T	X_1	X_2	X_3	P_{calcd}	P_{exptl}	ΔP
100.0	0.3505	0.3501	0.2994	59.71	59.81	0.10
125.0	0.3505	0.3501	0.2994	84.67	84.67	0.00
150.0	0.3505	0.3501	0.2994	120.03	120.10	0.07
100.0	0.1998	0.2000	0.6002	60.62	60.58	−0.04
125.0	0.1998	0.2000	0.6002	85.84	85.76	−0.08
150.0	0.1998	0.2000	0.6002	121.75	121.58	−0.17
100.0	0.0499	0.0503	0.8998	60.33	60.43	0.10
125.0	0.0499	0.0503	0.8998	85.48	85.46	−0.02
150.0	0.0499	0.0503	0.8998	121.50	121.54	0.04
100.0	0.3496	0.3501	0.3003	59.72	59.77	0.05
125.0	0.3496	0.3501	0.3003	84.68	84.63	−0.05
150.0	0.3496	0.3501	0.3003	120.04	120.11	0.07
100.0	0.6804	0.1601	0.1595	56.10	56.17	0.07
125.0	0.6804	0.1601	0.1595	80.07	80.12	0.05
150.0	0.6804	0.1601	0.1595	113.76	113.79	0.03

Table XII. Vapor-Pressure Comparison

Component	T	P_{exp}	P_{lit}
Butane	100	51.44	51.50 (*13*)
		51.49	51.62 (*16*)
			51.50 (*18*)
			51.37 (*1*)
			51.57 (*3*)
	150	106.45	106.50 (*18*)
			106.20 (*1*)
			106.20 (*3*)
Butene	100	62.40	61.50 (*1*)
		62.40	62.50 (*14*)
		62.42	62.26 (*3*)
	150	126.06	125.50 (*1*)
			125.80 (*3*)
Butadiene	100	59.76	59.30 (*12*)
		59.86	59.31 (*3*)
	150	120.83	120.90 (*12*)
			121.00 (*3*)

Table XIII. Comparison of Precision of Reported Data

System	True α	N	$\Delta\alpha$-Source	%ΔN
Butane-butene	1.140	70.1	0.003, this study	1.9–2.1
			0.050 (*17*)	24.6–52.1
			0.040 (*9*)	20.8–37.5
Butene-butadiene	1.039	240.2	0.001, this study	2.4–2.6
			0.040 (*9*)	49.7–100.0
Butane-butadiene	1.100	46.2	0.007, this study	6.4–7.0
			0.014 (*4*)	11.9–15.3
			0.040 (*9*)	27.4–63.2

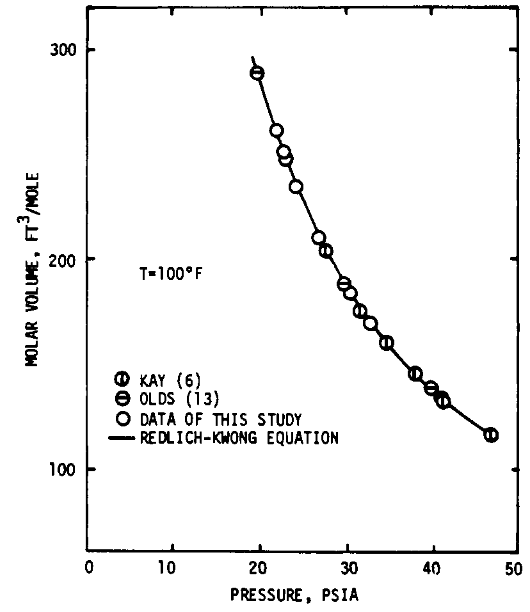

Figure 4. Butane vapor molar volume comparison

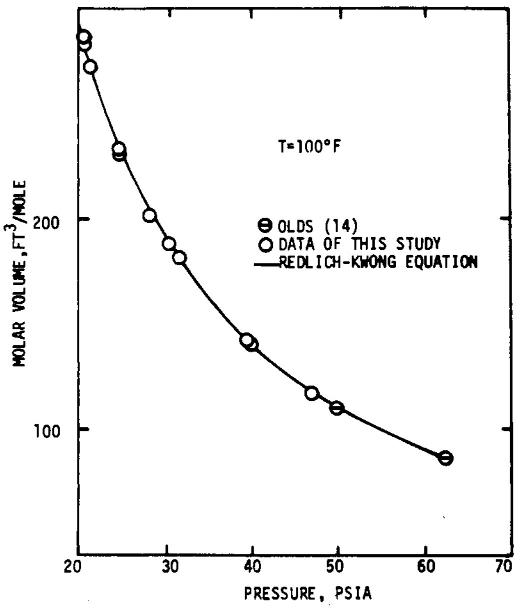

Figure 5. Butene vapor molar volume comparison

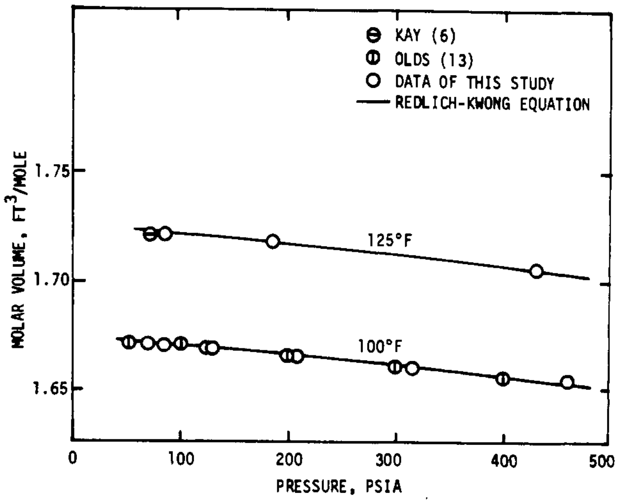

Figure 6. Butane liquid molar volume comparison

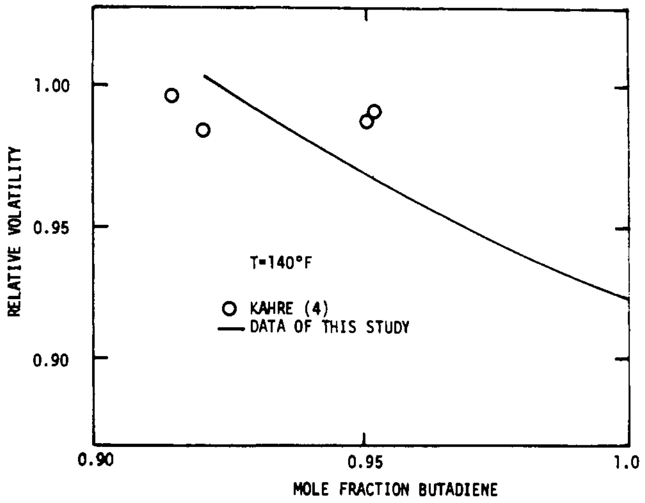

Figure 7. Relative volatility comparison: butane-butadiene

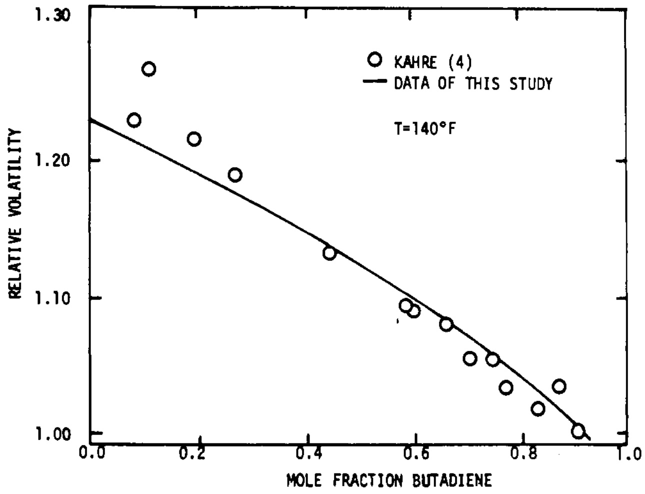

Figure 8. Relative volatility comparison: butane-butadiene

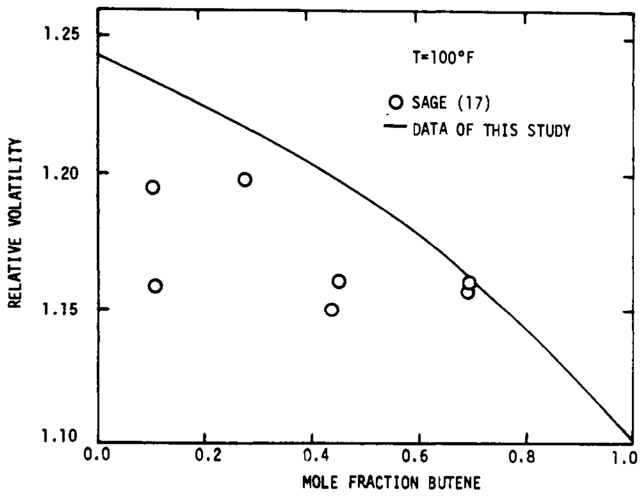

Figure 9. Relative volatility comparison: butene-butane

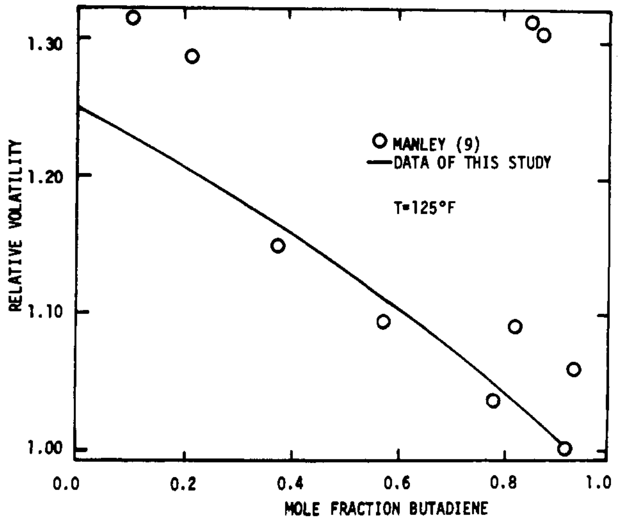

Figure 10. Relative volatility comparison: butane-butadiene

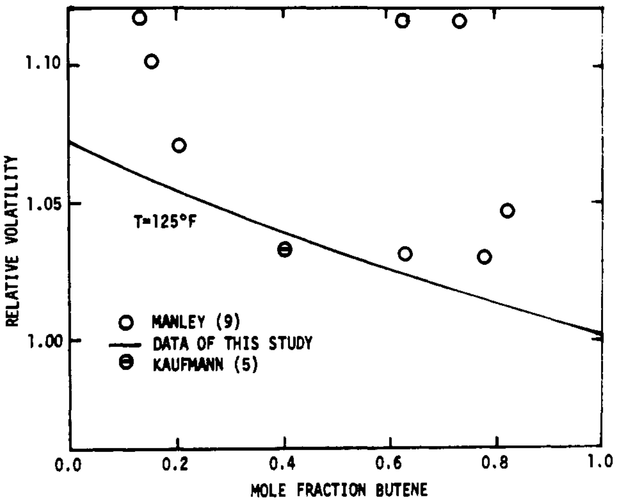

Figure 11. Relative volatility comparison: butene-butadiene

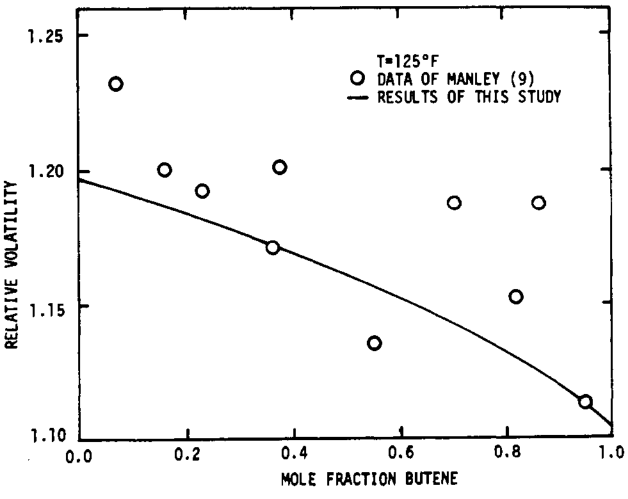

Figure 12. Relative volatility comparison: butene-butane

other investigators. The computed results of this work are compared with the literature data in Figures 7–12. As seen, considerable scatter is evident in the literature data; this may be largely attributed to the direct sampling methods which the previous investigators used.

Table XIII illustrates the effect of this scatter on design calculations. The Fenske equation is used to compute the number (N) of theoretical stages required to separate an equal-molar binary feed stream into 99% butene in the overhead and 1% butene in the bottoms for the butene purification columns and 90% butadiene in the overhead and 10% in the bottoms for the butadiene separation. Total reflux at 150°F is assumed, and the value of "true α" given in Table XIII is the geometric mean of α over the composition range occurring in the column. Errors are inserted into the calculations based on the reported precision of the various investigators, and the resultant error bounds are shown as $\%\Delta N$.

Conclusions

The phase equilibria and PVT data of this work provide precise and useful data for the butane-butene-butadiene systems over the temperature range of greatest industrial interest. The experimental data have a precision of 0.1%, and the computed results have a precision of 0.003, 0.001, 0.007, and 0.005 relative volatility units for the systems butane-butene, butene-butadiene, butane-butadiene, and butane-butene-butadiene, respectively.

The ternary system results are of particular interest. No pressure maxima, minima, or saddle points were found; therefore, no ternary azeotrope is expected to exist in this system over the range of conditions investigated.

Acknowledgment

The authors thank the Phillips Petroleum Co. for donating the research-grade chemicals. The University of Kansas Computation Center provided the computer time.

Nomenclature

P = pressure, psia
Z = compressibility factor
V = specific volume, ft^3/lb mol
T = temperature, °F
T_a = temperature, °R
R = gas constant, (ft^3-psia)/(lb mol-°R)
x = liquid-phase composition
y = vapor-phase composition
ϕ = fugacity coefficient
γ = activity coefficient
α = relative volatility
$\lambda_{ij} - \lambda_{ii}$ = Wilson parameter, lb mol/(ft^3-psia)
Δ = "error in"

Subscripts

i = component identification
1 = n-butane
2 = butene-1
3 = butadiene-1,3

Superscripts

° = saturation conditions
$\hat{}$ = mixture property
L = liquid phase
V = vapor phase

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Low-Temperature *K* Data for Methane-*n*-Butane

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Phase-equilibrium data are presented for the methane-*n*-butane system at low temperatures and high pressures. Eight isotherms from 50° to −160°F and 20-1600 psia were obtained. The data obtained confirmed the unusual shape of the dew-point curve near the methane critical point reported by Chen et al. Observed critical pressures were significantly lower than previous measurements.

Previous low-temperature phase-equilibrium data for this system (*7, 9*) contain considerable "scatter" in the reported phase analyses. With the recent improvement in sampling and analyzing techniques and with the industrial interest in recovering light hydrocarbons from natural gas, a reinvestigation of this system is justified.

Experimental

Equipment. The 50°F isotherm was obtained with the equipment previously described (*5*). Because of pressure limitations of this equipment, a close approach to the critical pressure could not be made.

The 0°F and lower isotherms were obtained with equipment (Figure 1) manufactured by the Rice University Shop. This system is basically the same as that used by Wichterle and Kobayashi (*10*). It consists of a windowed equilibrium cell and magnetic pump, to recirculate the vapors, immersed in a suitable liquid bath. Cooling was obtained with either mechanical refrigeration or liquid nitrogen, depending on the temperature level. The bath temperature was controlled with a Bayley precision temperature controller. The temperature was measured with a platinum resistance thermometer (PRT) located in the body of the windowed cell. The pressure was measured with a calibrated 0-2000 psia Heise gage. Sample analyses were made with a bis(2-methoxyethyl) adipate (BMEA) chromatographic column and thermal conductivity detector. Helium was used as the carrier gas.

Procedure. Phillips research grade *n*-butane was charged to the evacuated cell to a level above the liquid sample point. The vapor was analyzed to assure that no noncondensables were present. If necessary, the vapor phase was evacuated until analysis showed negligible noncondensables (air). Research grade methane was added until the desired pressure was obtained. The vapor was recirculated for at least 30 min at constant temperature and pressure to assure equilibrium.

Initially, an attempt was made to sample the equilibrium phases with the method used by Wichterle (that is, to continuously bleed a small flow to the chromatographic sample valve while maintaining the pressure constant from a reservoir of methane). However, with this system this method of sampling gave unreproducible results. Also, diluting the vapor phase with pure methane during vapor sampling was philosophically unacceptable. Therefore, it was necessary to develop a new sampling technique.

The vapor circulation line was repiped to go outside the cryostat so that small samples could be taken directly into the sample loop of the chromatographic analyzer (valve 1). It was recognized that the change in temperature of the vapor phase might introduce problems if data were taken in the region where retrograde condensation existed, but the ease of sampling outweighed this disadvantage.

After much experimentation with obtaining the right liquid sample, the following procedure was adopted: the vapor circulation was stopped, and the phases were allowed to separate; with valve 3 closed, valve 2 was opened to fill the line with liquid sample; valve 2 was closed, and valve 3 was opened to admit the sample into an evacuated sample cylinder (150-cc volume) containing several glass beads; the sample cylinder was im-

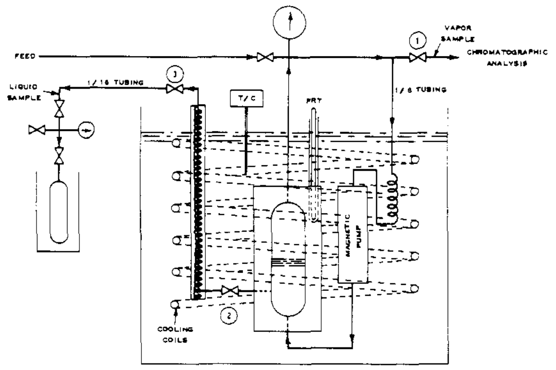

Figure 1. Schematic diagram of experimental equipment