SRRL, New Orleans, La., who performed the nmr and mass spectra.

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Relative Volatility of Propane–Propene System by Integration of General Coexistence Equation

DAVID B. MANLEY[1] and GEORGE W. SWIFT[2]
Department of Chemical and Petroleum Engineering,
The University of Kansas, Lawrence, Kan. 66044

Experimental data on the propane–propene system ranging from –20° to 100° F and from 20 to 1600 psia are reported. They include vapor compressibility factors for pure propane and pure propene; liquid specific volumes for propane, propene, and three mixtures containing 0.25, 0.50, and 0.75 mole fraction propene; and vapor pressures for propane, propene, and mixtures containing approximately 0.17, 0.33, 0.50, 0.67, and 0.83 mole fraction propene. The data have an estimated probable error of ±0.1%. The experimental data are correlated, and relative volatilities are calculated by integration of a rigorous form of the isothermal general coexistence equation at –20°, 10°, 40°, 70°, and 100° F. By incorporating some literature data into the correlations, relative volatilities are also calculated at 130° F. The relative volatilities have an estimated probable error of ±0.005 unit.

Vapor-liquid equilibrium compositions of the propane–propene system under various conditions have been experimentally measured by several investigators (*2-4, 8, 9*); however, due to the physical similarity of these two chemicals, the effect of experimental error on column design is greatly magnified. The purpose of this work was to resolve the experimental differences in the literature data by developing improved relative volatility information on the propane–propene system.

The method chosen to accomplish this purpose was integration of the isothermal general coexistence equation to generate vapor-liquid equilibrium compositions from vapor pressure and pressure-volume-temperature data on the pure components and their mixtures. This method has the advantage of requiring neither vapor-phase compositions nor dew-point pressures, both difficult to determine experimentally. In lieu of these data, the method relies heavily on the requirement that the physical properties of coexisting phases at equilibrium satisfy the general coexistence equation.

THEORY

Previous investigators (*6, 12*) have not applied the general coexistence equation to high-pressure isothermal *P-x* data for the purpose of generating *P-y* information. Consequently, it was necessary to derive a form of the equation for this purpose. Also, to perform the numerical integration, it was necessary to have analytical correlations for the vapor pressure, the liquid specific volume, and the vapor compressibility factor. The computer programs used are given by Manley (*7*).

High-Pressure Isothermal General Coexistence Equation. The starting point for the derivation is taken from Van Ness (*14*). For a single-phase binary system

$$VdP/RT_a = z_1 d(\ln \hat{f}_1) + z_2(\ln \hat{f}_2) \tag{1}$$

at constant temperature. Since the vapor and liquid fugacities are equal at equilibrium, writing Equation 1 for both phases and subtracting gives

$$\Delta' V/(y - x) = d[\ln (\hat{f}_2/\hat{f}_1)]/dP \tag{2}$$

where

$$\Delta' V = (V^V - V^L)/RT_a \tag{3}$$

Expanding the right-hand side of Equation 2 gives

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[1] Present address, University of Missouri-Rolla, Rolla, Mo. 65401.
[2] To whom correspondence should be addressed.

$$\Delta' V/(y-x) = \{\partial[\ln (\hat{f}_2/\hat{f}_1)]/\partial P\}_y + \{\partial[\ln (\hat{f}_2/\hat{f}_1)]/\partial y\}_P(dy/dP) \quad (4)$$

where the ordinary derivative is constrained to saturation, but the partial derivatives are not. Define

$$\hat{f}_i = \hat{\phi}_i y_i P \quad (5)$$

$$\Gamma = \ln (\hat{\phi}_2/\hat{\phi}_1) \quad (6)$$

Then substituting into Equation 4 and rearranging gives the isothermal general coexistence equation:

$$dy/dP = \Delta' V[y(1-y)/(y-x)]\left\{\frac{1-[(y-x)/\Delta' V](\partial\Gamma/\partial P)_y}{1+y(1-y)(\partial\Gamma/\partial y)_P}\right\} \quad (7)$$

Equation 7 is completely rigorous and can be numerically integrated to yield y as a function of P at saturation and constant temperature, once the following functional relationships are provided:

$$x = F_1(T,P) \text{ at saturation} \quad (8)$$

$$z = F_2(T,P,y) \quad (9)$$

$$V^L = F_3(T,P,x) \quad (10)$$

Knowledge of these relationships reduces Equation 7 to the form

$$dy/dP = F(P,y) \quad (11)$$

The numerical integration of Equation 7 was carried out via the fourth-order, Runge-Kutta-Gill single-step integration formula as given by Lapidus (*5*). As shown by Van Ness (*13*), it was necessary to start the integration with the component of lowest vapor pressure (propane) since the integration is numerically unstable in the reverse direction.

Correlations. The functional relationships given by Equations 8–10 were implicitly given by correlations of the experimental data measured in this work.

The vapor pressures of the pure components were correlated as functions of temperature using the Antoine equation

$$\ln (P) = A + B/(C+T) \quad (12)$$

From the vapor pressures of the two components at a given temperature, the vapor pressure of a mixture can be estimated by Raoult's law which assumes ideal mixing in the liquid phase

$$P_r = x_1P_1 + x_2P_2 \quad (13)$$

To account for the effect of mixing, the deviations from Raoult's law were correlated as functions of temperature and composition by

$$463 \log (P/P_r) = [A + Bx + C/(T+430) + Dx/(T+430)]x(1-x) \quad (14)$$

This is strictly an empirical correlation chosen because it appears to fit the experimental data within experimental error.

The vapor compressibility factor of the pure components was correlated with the Redlich-Kwong equation of state (*11*)

$$Z = 1 + BP - [A^2P(Z-BP)/Z(Z+BP)] \quad (15)$$

where

$$A^2 = a/R^2(T_a)^{2.5} \quad (16)$$

and

$$B = b/RT_a \quad (17)$$

The constants for mixtures of the two components were determined by use of the original mixing rules developed by Redlich and Kwong

$$A = A_1y_1 + A_2y_2 \quad (18)$$

$$B = B_1y_1 + B_2y_2 \quad (19)$$

$(\partial\Gamma/\partial y)_P$ and $(\partial\Gamma/\partial P)_y$ were also evaluated by application of the standard thermodynamic relationships to Equation 15.

The liquid specific volume was correlated using the Redlich-Kwong equation in the form

$$P = RT_a/(V-b) - a/[T_a^{0.5}V(V+b)] \quad (20)$$

Since experimental data for both the pure components and three mixtures of these components were determined, it was possible to calculate the effect of composition on the constants a and b without resorting to theoretical mixing rules. The constants were correlated by the equations

$$a = a_1x_1 + a_2x_2 + a_{12}x_1x_2 \quad (21)$$

$$b = b_1x_1 + b_2x_2 + b_{12}x_1x_2 \quad (22)$$

Limits at $x = 0$ and $x = 1$. For the pure components, Equation 7 becomes indeterminate and must be evaluated from L'Hospital's rule

$$\lim_{\substack{x\to 0\\ y\to 0\\ P\to P_1}} (dy/dP) = \Delta' V[(dy/dP)/(dy/dP - dx/dP)] \quad (23)$$

and therefore at $x = 0$

$$dy/dP = \Delta' V + dx/dP \quad (24)$$

and at $x = 1$

$$dy/dP = -\Delta' V + dx/dP \quad (25)$$

with these, the limiting relative volatility can be calculated as

$$\lim_{x\to 0} \alpha = 1 + \Delta Zd(\ln P)/dx \quad (26)$$

$$\lim_{x\to 1} \alpha = 1/[1 - \Delta Zd(\ln P)/dx] \quad (27)$$

EXPERIMENTAL EQUIPMENT

The experimental equipment used in this work was designed to measure the specific volumes of mixtures of light hydrocarbons and their common impurities with an accuracy of ±0.5% over a pressure range of 20 to 2000 psia and a temperature range of −200° to 100° F.

It consisted of three interconnected systems; the volumetric metering system, the low temperature system, and the weighing bomb. A more complete description is given by Manley (*7*).

Volumetric Metering System. The volumetric metering system was used for making up mixtures of the materials to be studied, and for volumetrically metering these materials under conditions of constant pressure and temperature to either the weighing bomb or the low-temperature cell. A detailed description of the volumetric metering system is given in Figure 1.

The bath consisted of a liquid (A) contained in a stainless steel Dewar (B) which could be controlled at a constant temperature between 100° and 160° F by a Bayley proportional band temperature controller (C). The temperature of the bath was measured with a U. S. Bureau of Standards calibrated Meyers platinum resistance thermometer (D) connected to a Honeywell Mueller resistance bridge (E). The bath liquid was agitated by a centrally located series of stirring blades (F) which were driven by a Gast air motor (G) mounted in the bottom of the bath. The air flow (H) to and from the air motor provided cooling for the heater (I) from the temperature controller to work against.

Four high pressure stainless steel cells (1–4) with cal-

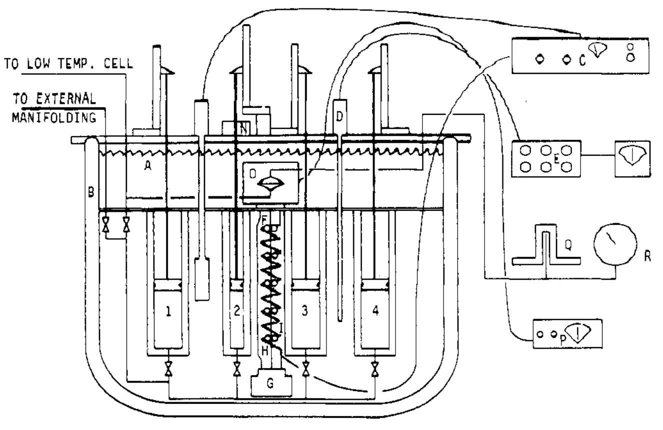

Figure 1. Volumetric metering system

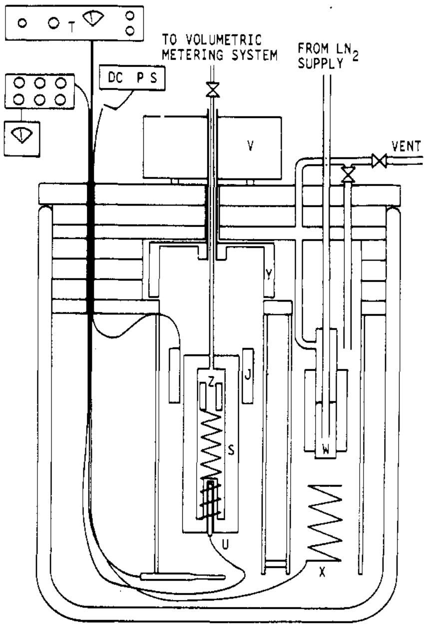

Figure 2. Low-temperature system

ibrated areas were mounted in the bath. These cells had movable pistons attached to rods protruding from the bath so that the volume of the cell could be varied (by moving the piston) and the position of the piston could be precisely known (by measuring the height of the rods with a Vernier height gauge). Three of these cells (1, 3, 4) had a diameter of approximately 1.25 in. and their pistons were driven by high pressure oil from a Sprague oil pump (not shown). The fourth cell (2) had a diameter of approximately 0.312 in. and its piston was driven by a mechanical screw drive (N). The cells were all made of stainless steel with highly polished interior surfaces, and the pistons were made of brass and sealed with O-rings.

System pressure was measured through a Ruska differential pressure transducer (O) which was also mounted in the bath. This consisted of a stainless steel diaphragm with an attached magnetic core whose position was sensed by a coil mounted in the transducer body. When the pressure on both sides of the diaphragm was the same, the position indicator (P) gave a null reading. On the nonsystem side of the diaphragm, oil was used which was connected to a Ruska dead weight gauge (Q) capable of measuring pressures from 20 to 1600 psia. The approximate oil pressure could be read from an attached Heise gauge (R).

Low-Temperature System. The low-temperature system shown in Figure 2 was used to measure the volume of the material at various temperatures. It consisted of a stainless steel cell (S) of calibrated volume in a constant temperature air bath capable of operating from −200° to 100° F. The cell contents could be agitated by means of a 416 stainless steel slider and attached spring (Z) which was moved by energizing an electromagnet surrounding the cell.

The bath temperature was controlled with a Bayley proportional band temperature controller (T), and the temperature was measured with a Rosemount platinum resistance thermometer (U) calibrated against the Meyers standard thermometer used in the high-temperature system. To measure true system temperature, the Rosemount thermometer was embedded in the cell.

The air was circulated by a squirrel cage blower (Y) powered with a Gast air motor (V) mounted outside the bath, and was cooled by a copper heat exchanger (W) with boiling nitrogen on the inside. The vaporized nitrogen could either be directly injected into the bath for fast cooldown or vented to the atmosphere to enhance the temperature control. To decrease temperature gradients, the bath was fitted with a downcomer, housing the heat exchanger and the control heater (X), and with an upcomer containing the cell.

Weighing Bomb. The weighing bomb consisted of a high-pressure stainless steel cylinder and valve with a total weight of approximately 150 grams and a volume of about 12 cm^3. It would hold pressures of up to 2000 psia and was weighed with a Mettler balance with a capacity of 160 grams. This bomb provided a means of measuring the mass of materials metered from the volumetric metering system.

EXPERIMENTAL RESULTS

Assuming that the experimental data are distributed about the true values in a Gaussian distribution, approximately 50% of the data will fall within 0.6745 SD of the true values. This distance is labeled the probable error and has been calculated for all the data and also the correlation constants.

Vapor Pressures. The experimental vapor pressures for propane, propene, and several mixtures are given in Table I and are estimated to have a probable error of 0.1% of the pressure. The pure component data were correlated with Equation 12 and the resulting constants with their estimated probable errors are given in Table II. The mixture data were then correlated via Equation 14 and the resulting constants with their estimated probable errors are given in Table III.

Figure 3 shows the deviation of the vapor pressure from

Table I. Vapor Pressure Data

X	$T = -20$, P	$T = 10$, P	$T = 40$, P	$T = 70$, P	$T = 100$, P
0.0000	25.50	46.50	78.66	124.63	187.89
0.0000	25.42	46.45	78.61	124.68	
0.1671	27.01	49.07	82.65	130.58	196.04
0.3334	28.34	51.28	86.12	135.73	203.28
0.4948	29.44	53.18	89.07	140.53	209.45
0.4995	29.53	53.19	89.28	140.36	209.94
0.5018	29.59	53.35	89.17	140.62	209.90
0.6668	30.43	55.00	91.88	144.65	216.24
0.6668	30.54	54.94	91.96	144.61	216.18
0.6677	30.57	55.16	91.93	144.54	216.15
0.8331	31.41	56.51	94.38	148.44	221.67
0.8332	31.30	56.51	94.38	148.47	221.79
1.0000	32.07	57.76	96.46	151.58	226.30
1.0000	32.04	57.73	96.42	151.69	226.34

Raoult's law. In Figure 3 the scale is chosen so that one unit on the ordinate is equivalent to 0.5% of the vapor pressure.

Vapor Compressibility Factor. The experimental vapor compressibility factors for pure propane and pure propene are given in Table IV and are estimated to have a probable error of 0.1% of the compressibility factor. These data were correlated with Equation 15, and the resulting constants with their estimated probable errors are given in Table V.

Liquid Specific Volumes. The experimental liquid specific volumes for pure propane, pure propene, and three mixtures of propane and propene are given in Table VI and are estimated to have a probable error of 0.1% of the specific volume. The data were correlated for each composition with Equation 20, and the resulting constants with their estimated probable errors are given in Table VII. The constants for Equations 21 and 22 are given in Table VIII.

RESULTS OF NUMERICAL INTEGRATION

By use of the correlation constants determined from the experimental data, Equation 7 was numerically integrated. The results are given in Table IX and in Figure 4.

Effect of Correlation Errors on Relative Volatility. To see what effect systematic errors in the correlations might have on the integration results, artificial errors were introduced into the correlations in three ways (see Table X):

(1) A systematic error of 0.5% was added to the vapor compressibility factor calculated by the correlation.

(2) A systematic error of 0.1% was added to the vapor pressure of pure propene calculated from the Antoine equation.

(3) A systematic error was added to the deviation from Raoult's law which amounted to 0.1% of the total pressure at $x = 0.5$ and which was proportionally less for mixtures richer in one or the other component. These were the only errors considered to be worth reporting since an error in the propane vapor pressure has the same effect as error 2, and an error in the liquid specific volume is overshadowed by error 1.

As Table X indicates, the calculated relative volatility is most sensitive to errors in the deviation from Raoult's law. Since the correlation used for this effect is strictly empirical and since the error introduced into the correlation is fairly small, it is estimated that the probable error in relative volatility is ±0.005 unit.

Relative Volatility at 130° F. Since industrial fractionators of propane and propene are often operated at temperatures greater than 100° F, the correlations developed from the data of this study were extrapolated to 130° F. However, comparison of the calculated vapor compressibility factors with the literature values for propane (*10*) and propene (*1*) indicated errors of as much as 5%. Consequently, new Redlich-Kwong constants were determined to fit the literature data between 100° and 160° F with an estimated probable error of 0.3%. These new constants for higher temperatures are given in Table XI and the corresponding results of the numerical integration are given in Table IX and Figure 4, where, for comparison, both the extrapolated results and the results after recorrelating the vapor compressibilities are shown. By comparing the two sets of results, it can be seen that they differ by no more than 0.005 unit at 130° F. There was no significant change at 100° F.

At temperatures greater than 130° F, errors in the extrapolation of the liquid specific volume and in the pure component vapor pressures become significant. Thus, no attempt was made to extend the results to higher temperatures.

Table II. Antoine Constants for Pure Components

Propane	Propene
$A1 = 12.040$, $\%\Delta A1 = 0.47$	$A2 = 12.116$, $\%\Delta A2 = 0.17$
$B1 = -3597.1$, $\%\Delta B1 = 1.43$	$B2 = -3554.1$, $\%\Delta B2 = 0.55$
$C1 = 428.61$, $\%\Delta C1 = 0.76$	$C2 = 430.96$, $\%\Delta C2 = 0.29$

Table III. Constants for Deviation from Raoult's Law

$A = -32.353$	$\%\Delta A = 16.6$
$B = 20.566$	$\%\Delta B = 45.8$
$C = 23574.0$	$\%\Delta C = 10.6$
$D = -11881.0$	$\%\Delta D = 36.8$

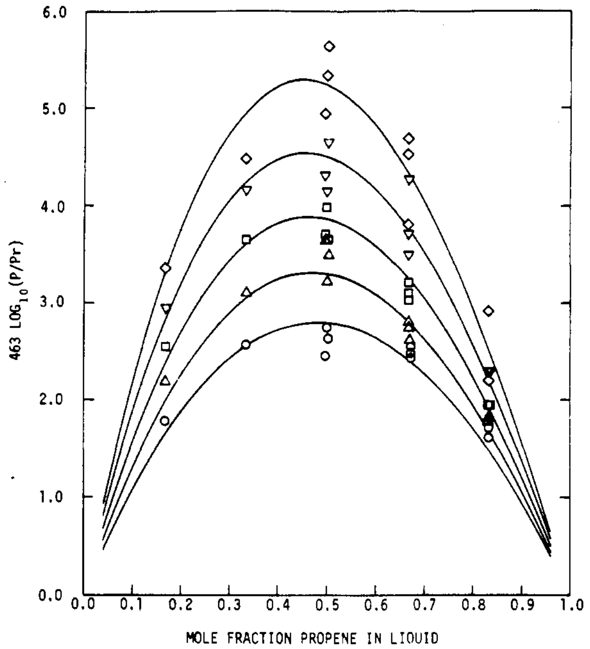

Figure 3. Deviation of vapor pressures from Raoult's law

—Correlation

Experimental data

◇ −20° F

▽ 10° F

□ 40° F

△ 70° F

○ 100° F

Table IV. Vapor Compressibility Factors

Propane			Propene		
T	*P*	*Z*	*T*	*P*	*Z*
100	27.45	0.9702	100	25.64	0.9746
100	88.67	0.9059	100	99.11	0.9069
100	127.40	0.8603	100	177.96	0.8208
100	161.09	0.8160	100	217.99	0.7678
100	184.33	0.7768	100	223.65	0.7587
70	27.66	0.9657	70	23.84	0.9750
70	54.37	0.9320	70	93.00	0.8950
70	88.58	0.8865	70	136.89	0.8372
70	112.99	0.8498	70	149.64	0.8163
70	119.89	0.8372	40	21.77	0.9729
40	21.98	0.9670	40	45.15	0.9406
40	36.64	0.9449	40	86.78	0.8793
40	65.28	0.8991	40	94.41	0.8650
40	76.58	0.8720	10	21.71	0.9670
10	22.24	0.9586	10	40.33	0.9350
10	33.57	0.9372	10	57.37	0.8891
10	44.21	0.9124	−20	21.53	0.9568
−20	21.02	0.9494	−20	29.78	0.9316

Table V. Vapor Compressibility Factor Redlich-Kwong Constants

	$a(10^{-3})$	$\%\Delta a$	$b(10)$	$\%\Delta b$
Propane	11.644	3.16	19.123	9.92
Propene	10.497	3.41	17.663	9.73

Table VI. Liquid Specific Volume

		$x = 0$,	$x = 0.25$		$x = 0.50$		$x =$ 0.75,	$x =$ 1.00,
T	P	V	V	V^a	V	V^a	V	V
140	600	1.596^b						1.551^b
130	600	1.557^b						1.462^b
100	300	1.486	1.465		1.441		1.414	1.387
70	300	1.409	1.388		1.362		1.337	1.307
70	600	1.394	1.372		1.347		1.321	1.292
70	1000	1.377	1.355		1.329		1.303	1.275
70	1600	1.354	1.332		1.307		1.282	1.254
40	300	1.344	1.323	1.323	1.297	1.301	1.273	1.244
40	600	1.335	1.312	1.312	1.286	1.290	1.261	1.233
40	1000	1.322	1.300	1.299	1.274	1.278	1.248	1.221
40	1600	1.305	1.283	1.282	1.257	1.260	1.232	1.205
10	300	1.292	1.270		1.244	1.248	1.220	1.191
10	600	1.284	1.262		1.237	1.240	1.212	1.184
10	1000	1.275	1.252		1.227	1.231	1.203	1.175
10	1600	1.262	1.239		1.215	1.214	1.190	1.163
−20	300	1.245	1.223		1.199		1.174	1.146
−20	600	1.240	1.217		1.193		1.167	1.141
−20	1000	1.232	1.210		1.186		1.160	1.134
−20	1600	1.222	1.199		1.176		1.151	1.124

[a] Replication. [b] Not used in correlation.

Table VII. Liquid Specific Volume Redlich-Kwong Constants for Individual Fits

X	$a \times 10^{-5}$	$\%\Delta a$	$b \times 10$	$\%\Delta b$
0.00	9.9176	0.81	9.7681	0.24
0.25	9.6390	0.74	9.5694	0.23
0.50	9.3865	0.60	9.3663	0.19
0.75	9.0609	0.67	9.1296	0.21
1.00	8.7836	0.67	8.8994	0.22

Table VIII. Liquid Specific Volume Redlich-Kwong Constants for Combined Fit

$a_1 = 9.9176(10^5)$ $a_2 = 8.7836(10^5)$ $a_{12} = 0.0600(10^5)$

$b_1 = 9.7681(10^{-1})$ $b_2 = 8.8994(10^{-1})$ $b_{12} = 0.1200(10^{-1})$

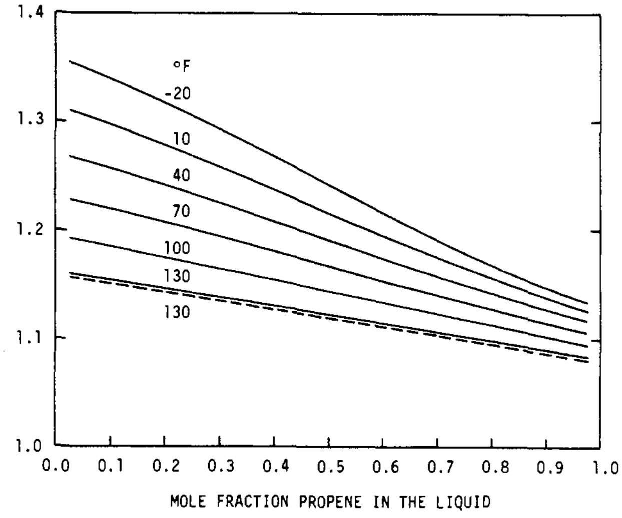

Figure 4. Relative volatility of propene to propane

— *Calculated from data of this study*

— *Calculated from correlation using literature vapor compressibility factors*

Table IX. Results of Integration of General Coexistence Equation

x	y	P	V^L	Z	α
T = −20° F					
0	0	25.45	1.2562	0.9446	1.3609
0.1000	0.1296	26.40	1.2478	0.9432	1.3401
0.2000	0.2478	27.28	1.2389	0.9420	1.3175
0.3000	0.3566	28.09	1.2298	0.9409	1.2933
0.4000	0.4581	28.84	1.2203	0.9400	1.2680
0.5000	0.5540	29.52	1.2104	0.9392	1.2419
0.6000	0.6458	30.13	1.2002	0.9385	1.2158
0.7000	0.7353	30.69	1.1896	0.9379	1.1904
0.8000	0.8235	31.19	1.1787	0.9375	1.1668
0.9000	0.9116	31.65	1.1674	0.9372	1.1461
1.0000	1.0000	32.06	1.1558	0.9370	1.1291
T = 10° F					
0	0	46.47	1.3030	0.9142	1.3141
0.1000	0.1259	48.04	1.2945	0.9124	1.2964
0.2000	0.2421	49.51	1.2856	0.9107	1.2775
0.3000	0.3502	50.87	1.2764	0.9092	1.2576
0.4000	0.4519	52.13	1.2667	0.9079	1.2369
0.5000	0.5487	53.29	1.2567	0.9068	1.2156
0.6000	0.6418	54.35	1.2464	0.9059	1.1944
0.7000	0.7325	55.32	1.2356	0.9051	1.1736
0.8000	0.8220	56.21	1.2245	0.9045	1.1541
0.9000	0.9109	57.01	1.2131	0.9040	1.1366
1.0000	1.0000	57.75	1.2012	0.9038	1.1215
T = 40° F					
0	0	78.56	1.3578	0.8755	1.2711
0.1000	0.1225	80.98	1.3492	0.8732	1.2564
0.2000	0.2368	83.26	1.3403	0.8711	1.2409
0.3000	0.3442	85.39	1.3310	0.8691	1.2247
0.4000	0.4461	87.38	1.3213	0.8674	1.2079
0.5000	0.5435	89.23	1.3112	0.8660	1.1908
0.6000	0.6378	90.93	1.3007	0.8647	1.1737
0.7000	0.7297	92.51	1.2898	0.8637	1.1569
0.8000	0.8203	93.95	1.2785	0.8629	1.1409
0.9000	0.9102	95.28	1.2668	0.8623	1.1260
1.0000	1.0000	96.50	1.2548	0.8620	1.1128
T = 70° F					
0	0	124.68	1.4227	0.8292	1.2312
0.1000	0.1193	128.20	1.4142	0.8263	1.2192
0.2000	0.2318	131.54	1.4052	0.8237	1.2068
0.3000	0.3385	134.70	1.3959	0.8214	1.1938
0.4000	0.4404	137.66	1.3861	0.8193	1.1805
0.5000	0.5385	140.44	1.3760	0.8175	1.1669
0.6000	0.6337	143.03	1.3654	0.8159	1.1533
0.7000	0.7268	145.44	1.3544	0.8147	1.1399
0.8000	0.8184	147.67	1.3429	0.8137	1.1268
0.9000	0.9093	149.73	1.3311	0.8130	1.1144
1.0000	1.0000	151.63	1.3188	0.8126	1.1029
T = 100° F					
0	0	187.76	1.5008	0.7773	1.1943
0.1000	0.1163	192.65	1.4924	0.7741	1.1849
0.2000	0.2271	197.33	1.4835	0.7712	1.1751
0.3000	0.3330	201.77	1.4742	0.7685	1.1650
0.4000	0.4350	206.00	1.4645	0.7662	1.1547
0.5000	0.5336	209.98	1.4543	0.7641	1.1441
0.6000	0.6297	213.73	1.4437	0.7624	1.1335
0.7000	0.7237	217.25	1.4326	0.7610	1.1228
0.8000	0.8165	220.53	1.4211	0.7600	1.1123
0.9000	0.9084	223.57	1.4091	0.7592	1.1020
1.0000	1.0000	226.39	1.3967	0.7588	1.0922
T = 130° F					
0	0	270.60	1.5965	0.7257	1.1612
0.1000	0.1137	277.12	1.5882	0.7227	1.1541
0.2000	0.2228	283.40	1.5795	0.7198	1.1467
0.3000	0.3280	289.44	1.5703	0.7173	1.1391
0.4000	0.4299	295.22	1.5607	0.7151	1.1312
0.5000	0.5290	300.72	1.5507	0.7132	1.1232

(Continued on next page)

Table IX. (*Continued*)

x	y	P	V^L	Z	α
		$T = 130°$ F			
0.6000	0.6258	305.94	1.5401	0.7115	1.1150
0.7000	0.7208	310.87	1.5291	0.7103	1.1066
0.8000	0.8146	315.50	1.5177	0.7094	1.0982
0.9000	0.9075	319.83	1.5058	0.7089	1.0898
1.0000	1.0000	323.84	1.4934	0.7087	1.0815
		$T = 130°$ F^a			
0	0	270.60	1.5965	0.7078	1.1568
0.1000	0.1133	277.12	1.5882	0.7040	1.1496
0.2000	0.2221	283.40	1.5795	0.7005	1.1422
0.3000	0.3272	289.44	1.5703	0.6974	1.1346^d
0.4000	0.4290	295.22	1.5607	0.6945	1.1268
0.5000	0.5280	300.72	1.5507	0.6921	1.1188
0.6000	0.6249	305.94	1.5401	0.6900	1.1108
0.7000	0.7201	310.87	1.5291	0.6884	1.1026
0.8000	0.8141	315.50	1.5177	0.6873	1.0945
0.9000	0.9072	319.83	1.5058	0.6866	1.0864
1.0000	1.0000	323.84	1.4934	0.6865	1.0784

[a] Including vapor compressibility factor data from the literature.

Table X. Errors in Relative Volatility Generated by Errors in Correlations at 100° F

	$X = 0.90$		$x = 0.99$	
	α	$\Delta\alpha$	α	$\Delta\alpha$
No error	1.1020		1.0932	
Error 1	1.1026	0.0006	1.0938	0.0006
Error 2	1.1027	0.0007	1.0939	0.0007
Error 3	1.1047	0.0027	1.0965	0.0033

Table XI. High Temperature Redlich-Kwong Constants for Vapor Compressibility Factor

	$a(10^{-5})$	$\%\Delta a$	$b(10)$	$\%\Delta b$
Propane	10.316	2.20	12.845	6.13
Propene	8.924	1.39	10.762	3.87

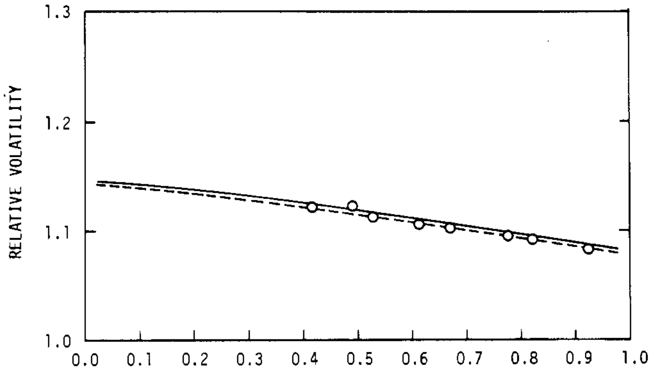

Figure 5. Relative volatility propane–propene system 320 psia
○ Data of Mann et al. (*8*)
— Calculated from data of this study
-- Calculated from correlation using literature vapor compressibility factors

Comparison with Literature Data. A comparison of the relative volatilities calculated from the data of this study with some of those obtained from the literature is given in Figures 5–7. Additional comparisons are presented by Manley (*7*). The agreement with the data of Mann et al. (*8*), taken in an equilibrium still, is excellent. The data of the other investigators (*2, 9*), which was acquired by sampling vapor and liquid at equilibrium, show a great deal of scatter but generally follow the trend of results obtained in this study.

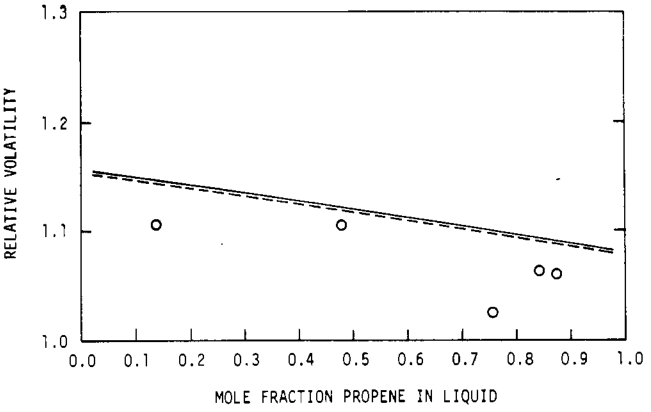

Figure 6. Relative volatility propane–propene system 134.9° F
○ Data of Hanson et al. (2)
— Calculated from data of this study
-- Calculated from correlation using literature vapor compressibility factors

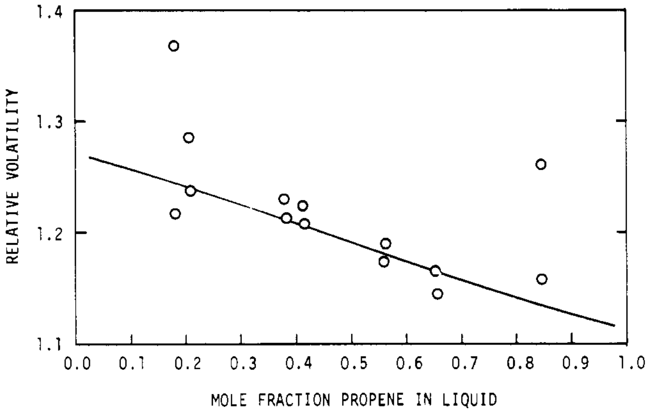

Figure 7. Relative volatility propane–propene system 40° F
○ Data of Reamer and Sage (9)
— Calculated from data of this study

CONCLUSIONS

A significant amount of new data on the propane–propene system has been determined. Mostly, the vapor and liquid density data obtained corroborates existing literature data; the relatively accurate data describing the deviation of the vapor pressure from Raoult's law are of particular importance in establishing more precise relative volatility information.

By integrating the isothermal general coexistence equation with the data obtained to establish the necessary functional relationships for densities and vapor pressure, relative volatilities for the propane–propene system have been determined from −20° to 130° F with an estimated probable error of ±0.005 relative volatility unit.

NOMENCLATURE

A, B = temperature dependent Redlich-Kwong constants
A, B, C = Antoine constants
A, B, C, D = vapor-pressure deviation constants
a, b = temperature independent Redlich-Kwong constants
a_{12}, b_{12} = Redlich-Kwong mixing effect constants
F, F_1, F_2, F_3 = functions representing physical properties
$\hat{f}_i$ = fugacity of component i in solution, psia
P = total pressure, psia
P_r = total pressure as calculated from Raoult's law, psia

P_i = vapor pressure of component i, psia
R = ideal gas constant, ft^3 (psia)/(lb-mol)° R
T = temperature, ° F
T_a = temperature, ° R
V = specific volume, ft^3/lb-mol
V^V = specific volume of vapor, ft^3/lb-mol
V^L = specific volume of liquid, ft^3/lb-mol
$\Delta' V$ = $(V^V - V^L)/RT_a$
x = mole fraction propene in liquid
x_i = mole fraction component i in liquid
y = mole fraction propene in vapor
y_i = mole fraction component i in vapor
z_i = mole fraction component i
Z = compressibility factor, PV/RT_a
ΔZ = $Z^V - Z^L$
α = relative volatility, $y(1 - x)/x(1 - y)$
$\hat{\phi}_i$ = fugacity coefficient of component i in solution
Γ = $\ln (\hat{\phi}_2/\hat{\phi}_1)$
%Δ = percent probable error

Subscripts

1 = propane
2 = propene

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