Relative Volatility of Propane–Propene System from 100–160°F

DALE R. LAURANCE and GEORGE W. SWIFT[1]
Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, KS 66044

Vapor pressure data on propane, propene, and their mixtures are reported in the temperature range 100–160°F. The data have an estimated probable error of ±0.1%. The experimental data are correlated and by incorporating literature data for vapor compressibility factors and liquid specific volumes, relative volatilities are computed. Using the method described by Manley and Swift, the authors computed the relative volatilities by integration of the isothermal general coexistence equation.

The design of commercial distillation units to separate close-boiling components to a high degree of purity requires extremely accurate vapor-liquid equilibrium phase data. Manley (*7*) summarizes the data in the literature for the propane–propene system and illustrates that differences of 35% in the design number of trays can be obtained by using different sources for the design data. This difference can be largely attributed to the difficulty in obtaining representative phase samples in extremely close-boiling systems with conventional methods and equipment. To circumvent this difficulty, Manley (*7*) developed a method to compute binary vapor-liquid equilibrium constants by integrating the isothermal general coexistence equation. The method is described by Manley and Swift (*8*). The method requires neither vapor-phase compositions nor dew-point pressures, both of which are difficult to determine experimentally. To use Manley's method, analytical expressions are required for four conditions: the pure component vapor pressures as a function of temperature, the mixture bubble point pressures as a function of liquid composition and temperature, the vapor compressibility factors for the pure components as a function of pressure and temperature, and the liquid specific volume of the mixtures as a function of temperature, pressure, and composition. The analytical expressions are then used to integrate numerically the isothermal coexistence equation and compute relative volatilities.

Manley and Swift (*8*) report experimental data on vapor pressures, liquid specific volumes, and vapor compressibility factors for mixtures of propane and propene in the temperature range −20–100°F. The experimental data were correlated and used to compute relative volatilities. That study revealed that the application of the general coexistence equation is most sensitive to the accuracy of the vapor pressure data. In addition, the experimental apparatus used in that study was limited to 100°F maximum temperature and the reported vapor pressure data at 100°F were lower than those reported by other investigators (*12*).

EXPERIMENTAL

Laurance (*6*) describes modifications carried out on the apparatus used by Manley and Swift which extend the temperature range of the equipment to 200°F. A new pressure measurement system was devised to circumvent the limitations faced by the previous investigators. Manley and Swift measured vapor pressures by connecting a tube from the top of the cell containing the propane–propene mixture to a differential pressure indicator mounted in a 100°F bath. At conditions close to saturation, the possibility existed for two phases to occur in either the tube connecting the test cell to the pressure transducer or in the transducer itself. Should two phases exist in that portion of the apparatus, an artificially low vapor pressure for the temperature and composition of the test cell would be measured. This condition limited the experimental apparatus to temperatures less than 100°F.

A small (2-in. diam) differential pressure indicator was designed and constructed such that it could be mounted directly to the cell containing the propane–propene mixtures and operate at the temperature of the cell. The indicator diaphragm is a sheet of 0.002-in. stainless steel and the housing for the diaphragm is also stainless steel. The position of the diaphragm is sensed by a connecting rod. The rod passes out of the variable temperature bath housing the test cell and differential pressure indicator to a linear differential transformer which drives an ammeter for visual null detection. A pressure null is obtained by varying the pressure in an *n*-heptane reservoir connected to the nonsystem side of the diaphragm. The pressure of the *n*-heptane is then measured using a Ruska dead weight gauge and a Ruska differential pressure indicator at the interface of the Ruska oil and the *n*-heptane. The *n*-heptane is used so that a change of state of the fluid will not occur over the −200° to +200°F operating range of the modified apparatus. The null point of the pressure indicator can be reproducibly read within 0.02 lb/in.^{2} over the entire pressure range of this study.

This modification was shown to improve the accuracy of the data at 100°F. The modified experimental apparatus was used to measure the vapor pressures for propane, propene, and their mixtures across the temperature range 100–160°F.

CORRELATIONS

To use the method described by Manley and Swift (*8*), analytical correlations of the experimental data are required. The computer programs used in this work are given by Manley (*7*) and Laurance (*6*).

For pure component vapor pressures, the data were correlated as a function of temperature with the Antoine equation:

$$\ln P_i = A_i + B_i/(C_i + T)$$

To correlate the vapor pressure data of the mixtures, the empirical correlation developed by Manley (*7*) was used to account for the effects of composition and temperature:

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

In the preceding equation, P_r is the vapor pressure of the mixture at the prevailing temperature and composition as predicted by Raoult's Law.

The numerical integration of the isothermal general co-

---

[1] To whom correspondence should be addressed.

Table I. Vapor Pressure Data

X	T = 100°F	T = 110°F	T = 120°F	T = 130°F	T = 140°F	T = 150°F	T = 160°F
0.0000	188.61	214.03	242.26	273.11	306.99	343.08	382.64
0.0000	188.59	...	...	...	...	...	...
0.0000	188.67	...	...	...	...	...	...
0.1616	197.63	...	...	283.86	...	...	396.95
0.2806	202.85	...	...	291.88	...	...	407.08
0.5187	212.48	...	...	305.28	...	...	424.30
0.6780	218.17	...	...	313.93	...	...	436.34
0.8563	223.90	...	...	321.68	...	...	447.53
1.0000	227.61	...	...	...	...	...	...
1.0000	227.62	258.20	291.81	327.74	367.14	409.41	454.70

existence equation also requires correlations for liquid specific volumes and vapor compressibility factors. Manley and Swift (*8*) have correlated literature data (*4*, *13*) to provide Redlich-Kwong constants in the 100–160°F range for the vapor compressibility factors. Those constants and the liquid specific volume constants reported in that study are used in the calculation of the relative volatilities presented in this article.

EXPERIMENTAL RESULTS

The experimental results are given in Table I and the correlation constants in Tables II and III. The estimated error in the measured vapor pressure is ±0.1%.

Figure 1 presents the pure component vapor pressure and Figure 2 the mixture vapor pressure data.

Figures 3–5 show the deviation from ideality exhibited by the mixtures at 100°, 130°, and 160°F. These plots represent a severe test of the data as one unit on the ordinate represents 0.1% of the measured vapor pressure.

Table II. Antoine Constants for Pure Components

Propene		Propane	
$A2 = 12.059$	$\%\Delta A1 = 0.86$	$A1 = 13.226$	$\%\Delta A2 = 1.80$
$B2 = -3414.5$	$\%\Delta B1 = 3.29$	$B1 = -4928.3$	$\%\Delta B2 = 0.62$
$C2 = 414.91$	$\%\Delta C1 = 2.15$	$C1 = 517.07$	$\%\Delta B3 = 3.87$

Table III. Constants for Deviation from Raoult's Law

$A = -0.414$	$\%\Delta A = 20.8$
$B = 0.453$	$\%\Delta B = 35.3$
$C = 268.86$	$\%\Delta C = 17.8$
$D = -262.20$	$\%\Delta D = 34.0$

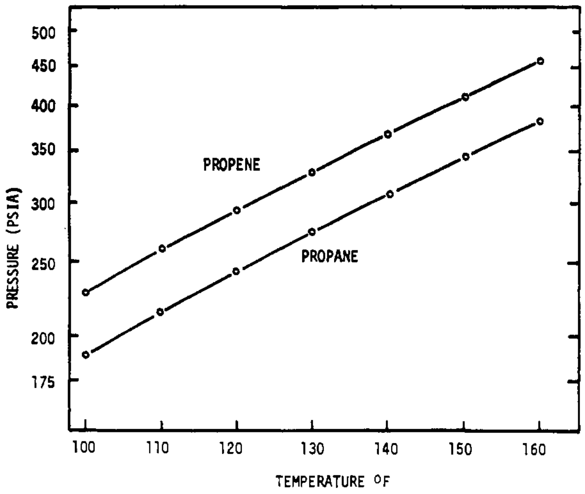

Figure 1. Pure component vapor pressures

CALCULATIONS

The computation method of Manley and Swift (*8*) was used to calculate the Table IV relative volatilities from the vapor

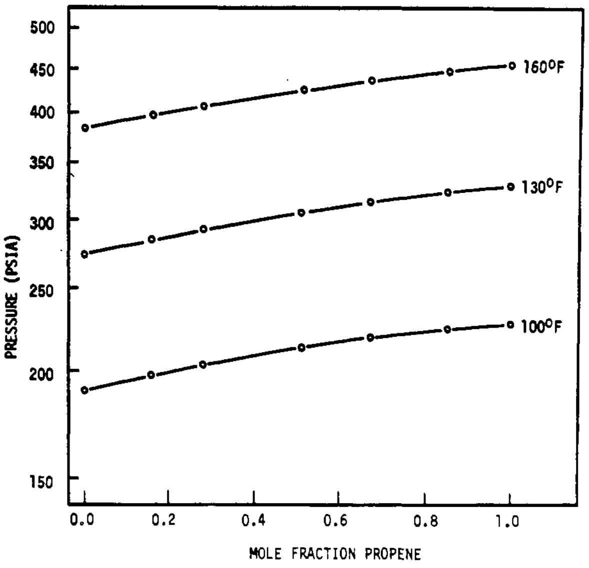

Figure 2. Mixture vapor pressures

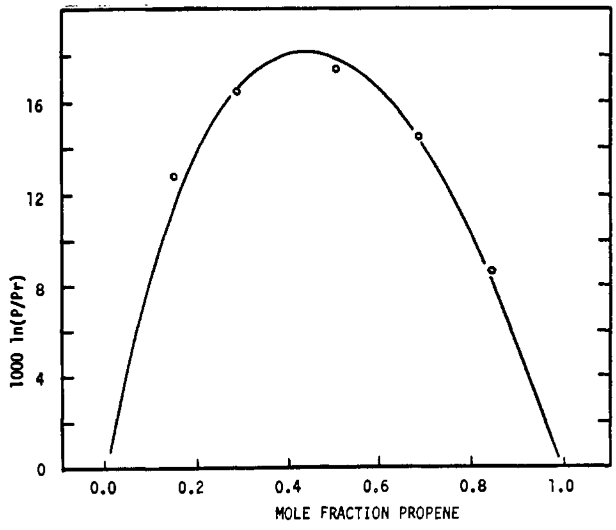

Figure 3. Deviation from Raoult's law, 100°F

Table IV. Results of Calculations

X	Y	P	V^L	Z	α
T = 100°F					
0	0	188.55	1.5007	0.7755	1.2186
0.1000	0.1178	194.01	1.4922	0.7718	1.2022
0.2000	0.2286	199.06	1.4833	0.7685	1.1855
0.3000	0.3338	203.70	1.4740	0.7658	1.1692
0.4000	0.4347	207.97	1.4643	0.7636	1.1536
0.5000	0.5325	211.90	1.4541	0.7619	1.1390
0.6000	0.6281	215.50	1.4435	0.7607	1.1257
0.7000	0.7222	218.84	1.4324	0.7598	1.1143
0.8000	0.8155	221.94	1.4209	0.7594	1.1048
0.9000	0.9081	224.85	1.4090	0.7592	1.0976
1.0000	1.0000	227.64	1.3966	0.7592	1.0925
T = 110°F					
0	0	214.17	1.5304	0.7533	1.2032
0.1000	0.1166	220.17	1.5319	0.7593	1.1884
0.2000	0.2259	225.77	1.5130	0.7458	1.1739
0.3000	0.3320	230.97	1.5037	0.7428	1.1598
0.4000	0.4331	235.79	1.4940	0.7403	1.1461
0.5000	0.5312	240.25	1.4838	0.7383	1.1331
0.6000	0.6271	244.38	1.4732	0.7368	1.1211
0.7000	0.7215	248.22	1.4622	0.7357	1.1104
0.8000	0.8150	251.78	1.4507	0.7351	1.1012
0.9000	0.9078	255.13	1.4387	0.7348	1.0936
1.0000	1.0000	258.29	1.4263	0.7348	1.0879
T = 120°F					
0	0	242.29	1.5621	0.7295	1.1868
0.1000	0.1154	248.84	1.5537	0.7252	1.1740
0.2000	0.2251	255.01	1.5448	0.7214	1.1617
0.3000	0.3300	260.79	1.5356	0.7181	1.1495
0.4000	0.4313	166.19	1.5259	0.7153	1.1376
0.5000	0.5297	271.22	1.5157	0.7130	1.1262
0.6000	0.6259	275.91	1.5052	0.7112	1.1154
0.7000	0.7206	280.27	1.4941	0.7099	1.1054
0.8000	0.8143	284.34	1.4826	0.7090	1.0965
0.9000	0.9074	288.13	1.4707	0.7087	1.0886
1.0000	1.0000	291.69	1.4583	0.7086	1.0822
T = 130°F					
0	0	273.05	1.5961	0.7040	1.1690
0.1000	0.1141	280.17	1.5877	0.6995	1.1593
0.2000	0.2231	286.91	1.5789	0.6953	1.1489
0.3000	0.3279	293.29	1.5697	0.6916	1.1385
0.4000	0.4293	299.29	1.5601	0.6885	1.1282
0.5000	0.5279	304.92	1.5500	0.6858	1.1182
T = 130°F (*contd*)					
0.6000	0.6245	310.20	1.5394	0.6837	1.1086
0.7000	0.7195	315.12	1.5285	0.6821	1.0994
0.8000	0.8135	319.71	1.5170	0.6811	1.0908
0.9000	0.9069	323.98	1.5051	0.6806	1.0828
1.0000	1.0000	327.94	1.4927	0.6805	1.0751
T = 140°F					
0	0	306.61	1.6326	0.6768	1.1518
0.1000	0.1128	314.27	1.6243	0.6719	1.1443
0.2000	0.2211	321.60	1.6156	0.6675	1.1357
0.3000	0.3257	328.58	1.6065	0.6634	1.1269
0.4000	0.4271	335.21	1.5969	0.6598	1.1182
0.5000	0.5259	341.47	1.5868	0.6567	1.1095
0.6000	0.6228	347.36	1.5764	0.6542	1.1009
0.7000	0.7182	352.87	1.5654	0.6523	1.0924
0.8000	0.8126	358.01	1.5540	0.6510	1.0842
0.9000	0.9064	362.76	1.5422	0.6504	1.0763
1.0000	1.0000	367.14	1.5299	0.6503	1.0681
T = 150°F					
0	0	343.10	1.6718	0.6479	1.1361
0.1000	0.1115	351.29	1.6636	0.6427	1.1292
0.2000	0.2191	359.21	1.6550	0.6378	1.1222
0.3000	0.3233	366.81	1.6460	0.6333	1.1149
0.4000	0.4247	374.07	1.6365	0.6292	1.1075
0.5000	0.5238	380.98	1.6265	0.6257	1.1000
0.6000	0.6210	387.51	1.6161	0.6227	1.0923
0.7000	0.7168	393.63	1.6053	0.6204	1.0846
0.8000	0.8116	399.33	1.5940	0.6188	1.0769
0.9000	0.9059	404.59	1.5823	0.6179	1.0691
1.0000	1.0000	409.39	1.5701	0.6178	1.0615
T = 160°F					
0	0	382.66	1.7139	0.6172	1.1193
0.1000	0.1102	391.36	1.7059	0.6117	1.1141
0.2000	0.2170	399.85	1.6974	0.6064	1.1085
0.3000	0.3209	408.07	1.6885	0.6014	1.1026
0.4000	0.4223	415.99	1.6791	0.5968	1.0964
0.5000	0.5215	423.56	1.6693	0.5927	1.0899
0.6000	0.6190	430.75	1.6590	0.5891	1.0831
0.7000	0.7152	437.50	1.6483	0.5863	1.0761
0.8000	0.8104	443.79	1.6371	0.5842	1.0689
0.9000	0.9052	449.56	1.6256	0.5831	1.0615
1.0000	1.0000	454.78	1.6136	0.5830	1.0539

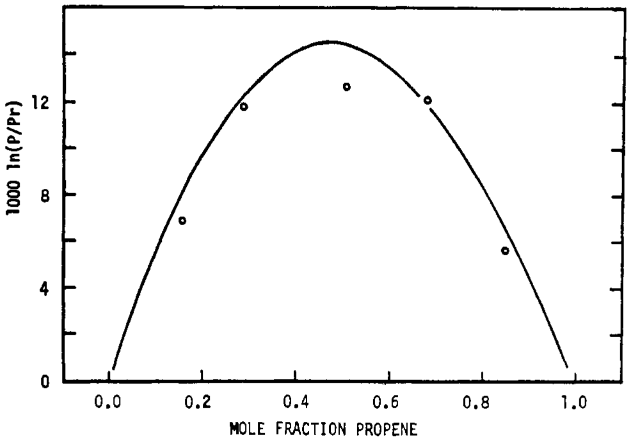

Figure 4. Deviation from Raoult's law, 130°F

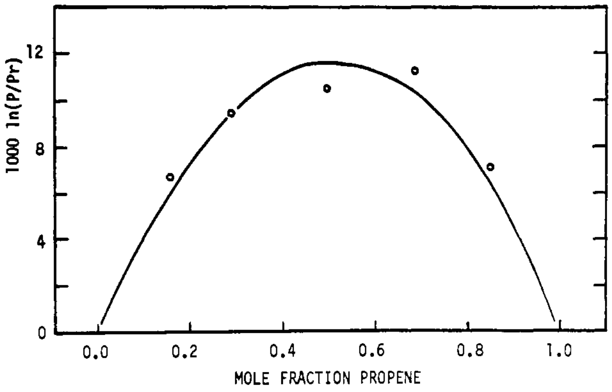

Figure 5. Deviation from Raoult's law, 160°F

pressure data of this study and from correlations of literature data for liquid and vapor densities.

The computed relative volatilities have an estimated error of ±0.005 unit.

The relative volatilities of this study differ from those reported by Manley and Swift by an average of 0.008 unit at 100°F.

COMPARISON WITH LITERATURE DATA

The excellent agreement of the data of this study with those of previous investigators is shown in Figures 6–8. In no case

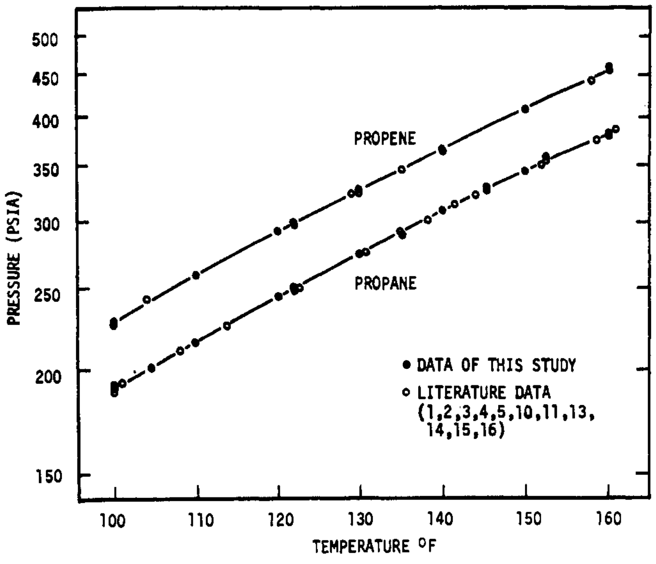

Figure 6. Pure component vapor pressures

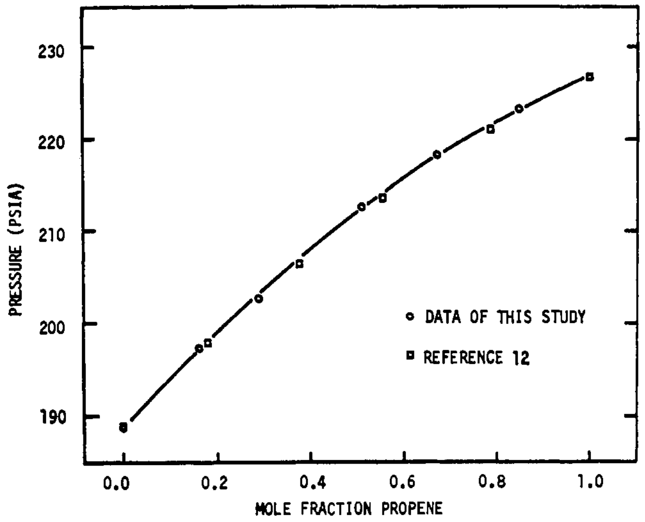

Figure 7. Mixture vapor pressure, 100°F

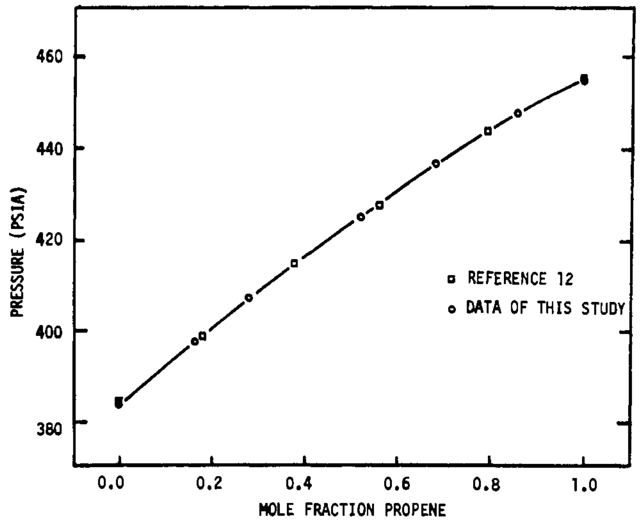

Figure 8. Mixture vapor pressures, 160°F

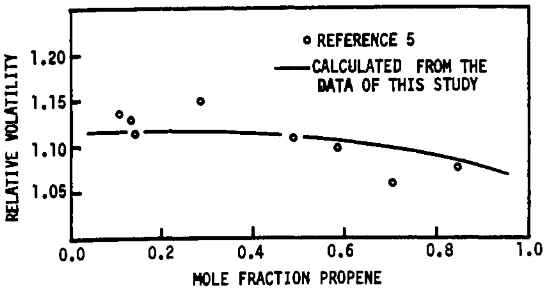

Figure 9. Relative volatility, 322.5 psia

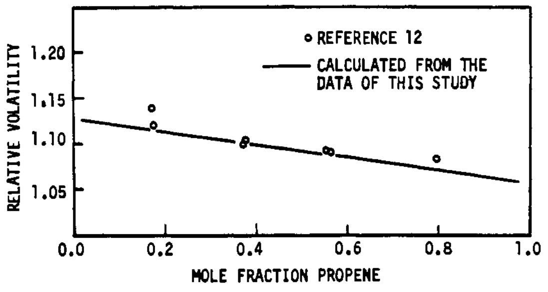

Figure 10. Relative volatility, 160°F

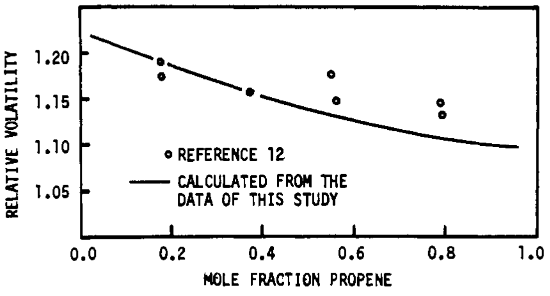

Figure 11. Relative volatility, 100°F

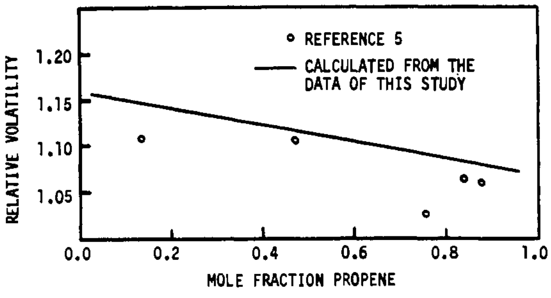

Figure 12. Relative volatility, 134.9°F

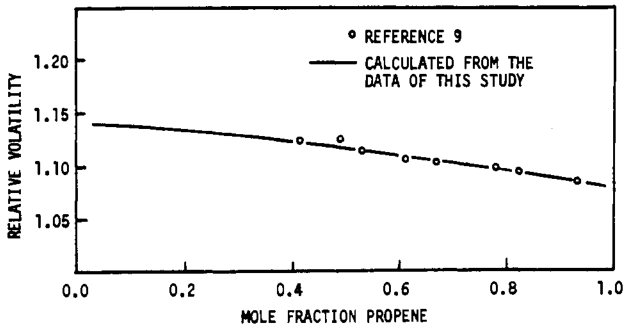

Figure 13. Relative volatility, 320.0 psia

is the difference between the literature values and the experimental correlations greater than 1%.

The mixture vapor pressure data of this study are approximately 1% greater than those reported by Manley and Swift at the 100°F isotherm. This difference is attributed to the difference in the method of pressure measurement employed with the modified equipment.

The computed relative volatilities are compared with the literature data in Figures 9–13. The data of the previous investigators were acquired by sampling liquid and vapor at equilibrium in all but Figure 13. The data of Mann et al. in Figure 13 were taken in an equilibrium still and exhibit less scatter than other data previously reported and show excellent agreement with the computed values of this study.

CONCLUSIONS

The relative volatilities reported in this article extend the range of information on the propane–propene system to the temperatures of greatest industrial interest. Since most industrial separations of propane and propene are carried out at temperatures in excess of 100°F, the data of this study should provide a useful extension of the data reported by Manley and Swift (*8*). The combined data provide relative volatilities for the propane–propene system from $-20°$ to $+160°$F.

NOMENCLATURE

ABCD = vapor pressure correlation constants
P = pressure, psia
T = temperature, °F
T_a = temperature, °R
V = specific volume, ft^3/lb-mol
Z = compressibility factor, PV/RT_a
x = mole fraction propene in liquid
y = mole fraction propene in vapor

Greek Letters

α = relative volatility $[y(1-x)]/[x(1-y)]$
Δ = difference

Superscripts

L = liquid phase
V = vapor phase

Subscripts

1 = propane
2 = propene
i = component i
r = pressure subscript, P computed using Raoult's law

LITERATURE CITED

(1) Beattie, J. A., Poffenberger, N., Cenfield, H., *J. Chem. Phys.*, **3**, 96 (1935).
(2) Cherney, B. J., Marchman, H., York, Robert, *Ind. Eng. Chem.*, **41**, 2653 (1941).
(3) Deschner, W. W., Brown, G. G., *ibid.*, **32**, 836 (1940).
(4) Farrington, P. S., Sage, B. G., *ibid.*, **41**, 1734 (1949).
(5) Hanson, G. H., Hogan, R. J., Melson, W. T., Cings, M. R., *ibid.*, **44**, 604 (1952).
(6) Laurance, D. R., MS thesis, University of Kansas, Lawrence, KS, 1971.
(7) Manley, D. B., PhD thesis, *ibid.*, 1970.
(8) Manley, D. B., Swift, G. W., *J. Chem. Eng. Data*, **16**, 301–7, (1971).
(9) Mann, A. N., Pardee, W. A., Smyth, R. W., *ibid.*, **8**, 499–502 (1963).
(10) Marchman, H., Prengle, H. W., Motard, R. L., *Ind. Eng. Chem.*, **41**, 2658 (1949).
(11) Powell, T. M., Giauque, W. F., *J. Amer. Chem. Soc.*, **61**, 2366 (1939).
(12) Reamer, H. H., Sage, B. H., *Ind. Eng. Chem.*, **43**, 1628 (1951).
(13) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **41**, 482 (1949).
(14) Sage, B. H., Schaafsma, J. G., Lacey, W. N., *ibid.*, **26**, 1218 (1934).
(15) Seibert, F. M., Currell, G. A., *J. Amer. Chem. Soc.*, **37**, 2683 (1915).
(16) Vaughn, W. E., Graves, N. R., *Ind. Eng. Chem.*, **32**, 1252 (1940).

Received for review November 15, 1971. Accepted February 28, 1972.

Temperature Dependence in Determination of Solubilities in System Methylvinylketone in Water

JAN VOJTKO[1] **and MILINA CIHOVA**
Faculty of Chemical Technology, Slovak Technical University, Bratislava, Czechoslovakia

The dependence of solubility in the system methylvinylketone–water on temperature was measured using two mutually independent methods. These two substances form a partially miscible system. The immiscibility range is limited by the lower (27.9°C) and upper (83.0°C) critical temperatures of solubility and by the concentrations 34.7 and 73.7 wt % of methylvinylketone in water.

Methylvinylketone (MVK), a technologically important intermediate, may be prepared by various methods. The most usual methods of preparation are based on the hydrolysis of *cis*- or *trans*-1,3-dichloro-2-butene with Na_2CO_3 and H_2SO_4 (*4*), or catalytically with $CuCl_2$ (*3*) or with HCl (*8*). It is also possible to prepare it by condensation from acetone and formaldehyde (*1, 5, 6, 10*), by dehydrogenation of methylethylketone (*7*), or from vinyl magnesium chloride and acetylchloride (*9*).

One of the oldest methods is its preparation by hydration of vinylacetylene (*2*). It is necessary to know the mutual solubility of methylvinylketone and water for this procedure. This paper presents data as to this solubility.

---

[1] To whom correspondence should be addressed.