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Volumetric Properties of Liquid Propylene

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The available *PVT* data for liquid propylene were critically evaluated. From the resulting data, correlations were obtained which can accurately reproduce the vapor-pressure curve, the saturated liquid densities, and densities of the compressed liquid. The equations were applicable from 40° to 160°F and from saturation pressures to 1600 psia. The derived relationships were used to obtain factors for correcting a measured volume of liquid propylene to standard conditions, here chosen to be 60°F and saturation pressure.

Numerous investigations have resulted in experimental vapor-pressure data for propylene (*6, 9, 10, 12–14, 19, 21*). The experimental data were plotted both on a P vs. T basis and on an Ln P vs. $1/T$ basis to allow visual screening of the data. Only the data of Maass and Wright (*10*) appeared to be inconsistent with the remainder of the data. The thermometer which they used was calibrated incorrectly, and unfortunately, they do not give sufficient detail to allow their results to be corrected to the proper temperature scale. As a result, none of their data (*10*) was used in the evaluation of the coefficients in the vapor-pressure equation. The remaining data sets (*6, 9, 12–14, 19, 21*) appeared consistent.

On the Ln P vs. $1/T$ plot, the data fell about a straight line covering the range −20° to 160°F. Both the Antoine equation

$$\text{Log}\, P = A + \frac{B}{C + T} \qquad (1)$$

and the Kelvin equation

$$\text{Ln}\, P = A + \frac{B}{T} \qquad (2)$$

were used to correlate the data by standard regression analysis techniques. The Kelvin equation performed much better than the Antoine equation in that it was not necessary to alter the temperature scale to account for any deviation from linearity over the temperature range of interest. Table I gives the experimental data used and the fit of the Kelvin equation. The Kelvin equation reproduces the entire input data set of 28 points with an average deviation of 0.55 psi (0.33%). By removal of the most widely scattered points from the data set, the equation reproduces 23 points with an average deviation of 0.37 psi (0.24%).

Two widely cited compilations (*2, 8*) also tabulate vapor-pressure data for propylene. Canjar et al. (*2*) correlated vapor pressure using an analytical function with a graphical residual. As such, their method could not be adopted here. Hanson (*8*) does not state his method of correlation. Since both reports (*2, 8*) tabulate correlated values, they were not used as input data for this work.

Manley and Swift (*12*) give ±0.1% as the precision in their determinations. None of the other investigations cites tolerance limits. As a result, the uncertainty in all data cited has been assumed as ±0.25%.

Table II gives values of the vapor pressure calculated from the Kelvin equation used here. Table III includes the coefficients for the Kelvin equation, as derived in this work.

Table I. Propylene Vapor-Pressure Data

T, °F	P_s (exptl), psia	P_s (calc),[a] psia
−20 (*12*)[b]	32.04	32.03
10	57.73	57.44
40	96.42	96.03
70	151.69	151.46
100	226.34	227.50
76.61 (*14*)	166.56	166.31
111.44	262.56	262.71
151.40	416.76	416.27
166.56	489.58	488.14
25.5 (*9*)	76.30	75.51
82.7	180.80	180.92
128.7	322.50	322.96
134.9	346.50	346.81
10 (*19*)	58.00	57.44
40	96.90	96.03
100	227.30	227.50
160	455.30	456.07
86 (*13*)	189.43	189.21
122	298.18	298.52
167	492.02	490.34
40 (*6*)	97.50	96.03
70	152.10	151.46
100	227.30	227.50
130	327.10	327.86
160	456.60	456.07
32 (*21*)	84.50	84.24
77	167.24	167.22
122	298.03	298.52
167	492.32	490.34

[a] Calculated using Equation 2. See Table III for coefficients.
[b] Numbers in parentheses are literature references.

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Density of Saturated Liquid

Experimental data for the density of saturated liquid propylene have been reported (*6, 10, 15–17, 21*). A plot of density vs. temperature was constructed to aid in preliminary screening of the data. The data given by Vaughan and Graves (*21*) deviated widely from those of the remaining investigations. The data presented (*21*) are not internally consistent and were removed from further consideration. Also, the data of Maass and Wright (*10*) were not used because of the inaccuracies of their temperature measurements, as discussed earlier in the section on the vapor pressure of propylene. The NGPA data (*16*) were determined by a technique (*4*) known to give erroneous results (*3*). Data used in this work (*6, 15, 17*) were correlated as described below.

Several equations were used in attempts to correlate the density data. A simple power series in temperature was found inadequate. Likewise an equation by Francis, as recommended by the "API Technical Data Book" (*1*), was not sufficient. Another equation proposed by Rackett (*18*) was used, and it too did not correlate the data with the necessary accuracy. Optimization of the coefficients of these various equations with the input data set led to an uncertainty of ±0.25%.

Because a correlation with 0.1% uncertainty was desired, another equation proposed by Guggenheim (*7*) was evaluated. By analyzing numerous data for a series of light, nonpo-

Table II. Saturation Properties of Propylene

T, °F	P_s, psia	D_s, g/cc	V_s, ft^3/lb-mol
40	96.03	0.5400	1.2481
41	97.58	0.5392	1.2501
42	99.16	0.5383	1.2522
43	100.75	0.5374	1.2542
44	102.36	0.5366	1.2562
45	104.00	0.5357	1.2583
46	105.65	0.5348	1.2603
47	107.32	0.5339	1.2624
48	109.01	0.5331	1.2645
49	110.72	0.5322	1.2666
50	112.45	0.5313	1.2687
51	114.20	0.5304	1.2708
52	115.97	0.5295	1.2730
53	117.76	0.5286	1.2751
54	119.57	0.5277	1.2773
55	121.40	0.5268	1.2795
56	123.26	0.5259	1.2817
57	125.13	0.5250	1.2839
58	127.03	0.5241	1.2861
59	128.94	0.5232	1.2884
60	130.88	0.5223	1.2906
61	132.84	0.5214	1.2929
62	134.82	0.5204	1.2952
63	136.82	0.5195	1.2975
64	138.85	0.5186	1.2998
65	140.89	0.5177	1.3021
66	142.96	0.5167	1.3045
67	145.05	0.5158	1.3069
68	147.17	0.5148	1.3092
69	149.30	0.5139	1.3116
70	151.46	0.5130	1.3141
71	153.64	0.5120	1.3165
72	155.85	0.5110	1.3190
73	158.08	0.5101	1.3214
74	160.33	0.5091	1.3239
75	162.60	0.5082	1.3264
76	164.90	0.5072	1.3290
77	167.22	0.5062	1.3315
78	169.57	0.5053	1.3341
79	171.94	0.5043	1.3367
80	174.33	0.5033	1.3393
81	176.75	0.5023	1.3419
82	179.19	0.5013	1.3446
83	181.66	0.5003	1.3472
84	184.15	0.4993	1.3499
85	186.67	0.4983	1.3526
86	189.21	0.4973	1.3554
87	191.78	0.4963	1.3581
88	194.37	0.4953	1.3609
89	196.99	0.4943	1.3637
90	199.63	0.4932	1.3666
91	202.30	0.4922	1.3694
92	205.00	0.4912	1.3723
93	207.72	0.4901	1.3752
94	210.46	0.4891	1.3781
95	213.24	0.4881	1.3811
96	216.04	0.4870	1.3841
97	218.86	0.4859	1.3871
98	221.72	0.4849	1.3901
99	224.59	0.4838	1.3932
100	227.50	0.4827	1.3963
101	230.43	0.4817	1.3994
102	233.39	0.4806	1.4026
103	236.38	0.4795	1.4058
104	239.40	0.4748	1.4090
105	242.44	0.4773	1.4122
106	245.51	0.4762	1.4155
107	248.61	0.4751	1.4188
108	251.74	0.4740	1.4222
109	254.89	0.4728	1.4256
110	258.07	0.4717	1.4290
111	261.28	0.4706	1.4324
112	264.32	0.4694	1.4359
113	267.79	0.4683	1.4394
114	271.09	0.4671	1.4430
115	274.41	0.4650	1.4466
116	277.77	0.4648	1.4503
117	281.15	0.4636	1.4539
118	284.57	0.4624	1.4577
119	288.01	0.4612	1.4614
120	291.48	0.4600	1.4653
121	294.98	0.4588	1.4691
122	298.52	0.4576	1.4730
123	302.08	0.4564	1.4770
124	305.67	0.4551	1.4810
125	309.29	0.4539	1.4850
126	312.94	0.4526	1.4891
127	316.63	0.4514	1.4933
128	320.34	0.4501	1.4975
129	324.08	0.4488	1.5018
130	327.86	0.4476	1.5061
131	331.67	0.4463	1.5104
132	335.50	0.4450	1.5149
133	339.37	0.4436	1.5194
134	343.27	0.4423	1.5239
135	347.20	0.4410	1.5286
136	351.16	0.4396	1.5333
137	355.16	0.4383	1.5380
138	359.19	0.4369	1.5429
139	363.24	0.4355	1.5478
140	367.33	0.4341	1.5528

lar molecules, Guggenheim derived the following expression for the saturated liquid density:

$$D_{S,T} = D_C\ (1 + 1.75\,\theta + 0.75\,\theta^3) \qquad (3)$$

Tomlinson (*20*) has modified this expression for heavier molecules, with pronounced nonspherical symmetry, by replacing D_C with function of θ. The function

$$D_{S,T} = (A_1 + A_2\,\theta)\ (1 + 1.75\,\theta + 0.75\,\theta^3) \qquad (4)$$

correlated the data very well.

Table IV gives the experimental data and comparisons with values calculated from Equation 4. Table II gives calculated values of the density and of the molar volume of the saturated liquid over the range 30° to 160°F. Table III gives the values of the coefficients used in Equation 4. This correlation leads to a value of 0.5223 g/cc for the density at saturation pressure and 60°F. The corresponding specific gravity at 60/60 is 0.5228.

Compressed Liquid Density

The compressed liquid density of propylene has been the object of three investigations (*5, 6, 12*), all of which agree to within 0.25% over the normal metering range. This agreement is excellent in view of the widely different methods of investigations used.

A plot of the isothermal P vs. D data was made. Several equations were used in attempts to correlate the data. The isotherm expression

$$D_T = \Sigma\, a_i P_T{}^i \qquad (5)$$

with i ranging from 2 to 4 proved unsatisfactory. Attempts to derive an expression for the isothermal bulk modulus of the form

$$\beta_T = \Sigma\, b_i P_T{}^i \qquad (6)$$

with i ranging from 2 to 3 did not give sufficient sensitivity. Finally, the Tait equation was tested and found to be satisfactory. This equation was used in the form

$$v_{P,T} = v_{S,T}\ \left[1 - C\,\mathrm{Ln}\left\{\frac{B + P}{B + P_S}\right\}\right] \qquad (7)$$

The $v_{P,T}$ data (*5, 6, 12*) and the $v_{S,T}$ values from Equation 4 were subjected to standard nonlinear regression analysis to optimize the values of C and B for each isotherm. For the range from 32° to 140°F, there were 13 experimental isotherms. The parameter B is strongly temperature dependent, whereas C is essentially temperature independent.

The results of the nonlinear regression analysis showed that C could be treated as a true constant. Undoubtedly, this is true because the temperature range under consideration is quite small, on an absolute basis, and occurs well below the critical temperature of propylene.

The parameter B, however, was quite temperature dependent. By treating C as a true constant, it was possible to derive a rather simple expression for the temperature dependence of B. The equation

$$B = \frac{A_3}{T} + \frac{A_4}{T^2} \qquad (8)$$

correlated the behavior very well.

The *PVT* surface of propylene, as determined by Farrington and Sage (*6*), contains a constant bias of nearly 0.20% when compared to that surface as determined by Dittmar et al. (*5*). The data of Manley and Swift (*12*) cover a much narrower range and generally agree with Farrington and Sage (*6*) to within 0.15%.

Farrington and Sage (*6*) claim an accuracy in their data of ±0.3%. Dittmar et al. (*5*) claim a precision in their data of ±0.1% but do not give a figure for accuracy. An analysis of the individual uncertainties for each of their instruments indicates that their accuracy should be approximately ±0.3% also. Manley (*11*) cites a precision of ±0.1% and accuracy of ±0.4% for the *PVT* data reported (*12*).

Since within the accuracies given all three investigations (*5, 6, 12*) are identical, there is no reason to weight one study more heavily than the others. As a result, the *PVT* surface described by the correlation presented here lies between the *PVT* surface of Farrington and Sage (*6*) and the *PVT* surface of Dittmar et al. (*5*). Combining the data from all three sources (*5, 6, 12*), there are 13 isotherms containing 56 *PVT*

Table III. Equations and Conversion Factors

Vapor pressure

$\mathrm{Ln}\, P_S = A + \frac{B}{T}$ (Equation 1)

$A = 12.60996$ $\quad P_S$, psia

$B = -4020.0$ $\quad T$, °R

Saturated liquid density

$D_{S,T} = (A_1 + A_2\theta)(1 + 1.75\,\theta + 0.75\,\theta^3)$ (Equation 4)

$A_1 = 14.358$ $\quad \theta = (1 - T/T_C)^{1/3}$

$A_2 = 0.8459$ $\quad D_{S,T}$ in lb/ft³

Compressed liquid molar volumes

$v_{P,T} = v_{S,T}\left[1 - C\,\mathrm{Ln}\left\{\frac{B + P}{B + P_S}\right\}\right]$(Equation 7)

$B = \frac{A_3}{T} + \frac{A_4}{T^2}$

$C = 0.10$ $\quad P, P_S$, psia

$A_3 = -689.0234 \times 10^4$ $\quad T$, °R

$A_4 = 426.972427 \times 10^7$ $\quad v_{P,T}, v_{S,T}$ in ft³/lb-mol

Molecular weight $= 42.081\ \frac{\text{lb}}{\text{lb-mol}} = 42.081\ \frac{\text{g}}{\text{g-mol}}$

$T_C = 656.57$ °R (from ref. *1*)

v (ft³/lb-mol) $= 0.674053/D$ (g/cc)

1 atm = 14.696 psia

1 kg/cm² = 14.223 psia

D (lb/ft³) $= 62.428\ D$ (g/cc)

Table IV. Saturated Liquid Densities for Propylene

T, °F	D_s (exptl), lb/ft³	D_s (calc),[a] lb/ft³
32 (*15*)	34.21	34.14
77	31.61	31.60
104	29.87	29.86
122	28.67	28.57
140	27.07	27.10
40 (*6*)	33.68	33.71
70	32.04	32.02
100	30.14	30.13
130	27.99	27.94
160	25.11	25.14
68.18 (*17*)	32.25	32.13
80.96	31.40	31.36
90.50	30.74	31.04
100.22	30.16	30.12
110.30	29.47	29.43
121.73	28.60	28.58
131.72	27.82	27.80
139.37	27.16	27.16
147.92	26.36	26.37

[a] Calculated using Equation 4. See Table III for coefficients.
[b] Numbers in parentheses are literature references.

points. These data cover the range from 32° to 140°F, from over 1600 psia to saturation pressure. When Equations 2, 4, 6, and 7 are combined to calculate $v_{P,T}$ values, it is possible to reproduce the 56 input data points with an average deviation of ±0.09%.

Comparisons of the $v_{P,T}$ data used as input and those values calculated using Equation 7 are given in Table V. Values of the parameters A_3 and A_4 are included in Table III.

A recent Russian publication (*22*) received after this work was completed also contains a review of the volumetric properties of liquid propylene. Where the same data sets are evaluated, their conclusions as to their quality are similar to those presented here. However, the Russian monograph does include details of some experimental data not used in this work. Their results, presented in tabular form, were, for the most part, obtained by graphical methods. No analytical correlations are presented.

Volume Correction Factors

In correcting a metered volume of a liquid hydrocarbon to standard conditions, it is necessary to make two types of corrections. One is for specific gravity, and the other is for compressibility. Mathematically, this can be expressed as:

$$V_{P_o,T_o} = V_{P,T} \cdot f_g \cdot (1 + f_b \cdot \Delta P) \qquad (9)$$

The use of this expression implies the use of at least three separate factors; one for f_g, another for f_b, and still another for the vapor pressure, P_s, so that ΔP can be calculated.

An alternative approach is to use a composite volume correction factor which combines both the gravity and compressibility corrections into a single factor. Mathematically, this is expressed as:

$$V_{P_o,T_o} = f_c \cdot V_{P,T} \qquad (10)$$

To complete the calculations, only one table for f_c values is necessary. In terms of molar volume,

$$f_c = \frac{v_{P_o,T_o}}{v_{P,T}} \qquad (11)$$

where $v(P_o,T_o)$ is the molar volume at the reference conditions. Since the reference conditions usually chosen are saturation pressure and 60°F, $v(P_o,T_o)$ can be determined from data for the density of the saturated liquid using Equation 4.

Table V. Propylene Compressed Liquid Molar Volumes

P, psia	$v_{P,T}$ (exptl), ft³/lb-mol	$v_{P,T}$ (calc),[a] ft³/lb-mol
140°F (*5*)[b]	$B = 381.0429$[c]	
469.4	1.5319	1.5330
910.3	1.4653	1.4683
1564.5	1.4043	1.4047
130°F (*6*)	$B = 608.8151$	
400	1.4951	1.4946
500	1.4817	1.4801
600	1.4690	1.4670
1000	1.4270	1.4235
1250	1.4042	1.4015
1500	1.3849	1.3824
122°F (*5*)	$B = 771.0558$	
341.4	1.4653	1.4672
924.5	1.4043	1.4053
104°F (*5*)	$B = 1215.2501$	
284.5	1.4043	1.4047
1009.8	1.3481	1.3491
1465.0	1.3217	1.3229
100°F (*6*)	$B = 1320.0000$	
300	1.3899	1.3899
400	1.3819	1.3815
500	1.3739	1.3736
600	1.3668	1.3662
1000	1.3407	1.3398
1250	1.3268	1.3255
1500	1.3138	1.3125
86°F (*5*)	$B = 1713.4898$	
284.5	1.3481	1.3488
696.9	1.3217	1.3233
1209.0	1.2963	1.2973
70°F (*6*)	$B = 2223.0823$	
200	1.3108	1.3114
300	1.3054	1.3061
400	1.3003	1.3010
500	1.2953	1.2960
600	1.2906	1.2913
1000	1.2734	1.2738
70°F (*6*)	$B = 2223.0823$	
1250	1.2629	1.2639
1500	1.2540	1.2547
70°F (*12*)	$B = 2230.9173$	
300	1.3070	1.3061
600	1.2920	1.2913
1000	1.2750	1.2738
1600	1.2540	1.2513
68°F (*5*)	$B = 2279.8340$	
384.0	1.2963	1.2970
896.0	1.2718	1.2740
1550.3	1.2482	1.2495
50°F (*5*)	$B = 2917.5741$	
597.4	1.2482	1.2499
1308.5	1.2256	1.2265
40°F (*6*)	$B = 3316.1887$	
200	1.2456	1.2444
300	1.2422	1.2409
400	1.2389	1.2375
500	1.2355	1.2342
600	1.2321	1.2309
1000	1.2203	1.2188
1250	1.2128	1.2118
1500	1.2060	1.2051
40°F (*12*)	$B = 3320.0109$	
300	1.2440	1.2409
600	1.2330	1.2309
1000	1.2210	1.2188
1600	1.2050	1.2025
32°F (*5*)	$B = 3645.7380$	
284.5	1.2256	1.2261
1066.7	1.2037	1.2038
1948.6	1.1826	1.1826

[a] Value calculated using smoothed values of B. See Equation 7 and Table III for coefficients. [b] Numbers in parentheses are literature references. [c] B determined by nonlinear regression analysis on data listed.

Table VI. Liquid Propylene Molar Volumes (ft^3/lb-mol)

	Pressure, psia							
T, °F	400	600	800	1000	1200	1400	1600	*T*, °F
40	1.2375	1.2309	1.2247	1.2188	1.2131	1.2077	1.2025	40
45	1.2472	1.2402	1.2336	1.2273	1.2214	1.2157	1.2102	45
50	1.2572	1.2498	1.2428	1.2361	1.2298	1.2238	1.2180	50
55	1.2676	1.2596	1.2522	1.2451	1.2385	1.2321	1.2261	55
60	1.2783	1.2698	1.2619	1.2544	1.2473	1.2406	1.2342	60
65	1.2894	1.2803	1.2719	1.2639	1.2564	1.2494	1.2426	65
70	1.3009	1.2912	1.2822	1.2737	1.2658	1.2583	1.2512	70
75	1.3129	1.3025	1.2928	1.2838	1.2754	1.2675	1.2600	75
80	1.3254	1.3142	1.3039	1.2943	1.2853	1.2769	1.2690	80
85	1.3385	1.3264	1.3153	1.3051	1.2955	1.2866	1.2783	85
90	1.3521	1.3391	1.3272	1.3162	1.3061	1.2966	1.2878	90
95	1.3665	1.3523	1.3395	1.3278	1.3170	1.3069	1.2976	95
100	1.3815	1.3662	1.3524	1.3398	1.3282	1.3176	1.3076	100
105	1.3975	1.3807	1.3658	1.3522	1.3399	1 3285	1.3180	105
110	1.4144	1.3961	1.3798	1.3652	1.3520	1.3399	1.3287	110
115	1.4324	1.4122	1.3946	1.3788	1.3646	1.3517	1.3398	115
120	1.4516	1.4294	1.4101	1.3930	1.3777	1.3639	1.3513	120
125	1.4723	1.4476	1.4265	1.4079	1.3915	1.3766	1.3632	125
130	1.4947	1.4671	1.4438	1.4236	1.4058	1.3899	1.3755	130
135	1.5192	1.4881	1.4623	1.4402	1.4210	1.4038	1.3884	135
140	1.5462	1.5108	1.4821	1.4579	1.4369	1.4184	1.4019	140

The compressed liquid molar volume, $v_{P,T}$, is then determined from the Tait equation (Equation 7) with the values of $V_{S,T}$ and P_s obtained from the saturated liquid density (Equation 4) and the vapor-pressure data (Equation 2), respectively. Values of $v_{P,T}$ calculated at evenly spaced temperature and pressure intervals within the range of the correlation are given in Table VI. These values along with the value for $\dot{v}(P_o,T_o)$ can then be used to obtain the factor, f_c, necessary to correct a measured volume of liquid propylene to standard conditions.

Nomenclature

f_b = isothermal compressibility correction factor, $-1/v_{S,T}\cdot(\Delta v/\Delta P)$
f_c = composite volume correction factor, $[v(P_o,T_o)]/(v_{P,T})$
f_g = specific gravity reduction factor, $[v(S,T_o)]/(v_{S,T})$
P = pressure, psia
T = temperature, °R ($T = 459.67 +$ °F)
$V_{P,T}$ = volume at conditions P,T
$v_{P,T}$ = molar volume at conditions P,T
θ = temperature function $(1 - T/T_C)^{1/3}$

Subscripts

C = critical property
o = standard reference state
P = pressure
T = temperature
S = saturation property

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