Calculating Surface Tension of Light Hydrocarbons and Their Mixtures

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Experimental surface tensions of 15 light hydrocarbons were individually correlated using two different equations. The first had reduced temperature as an independent variable, and the second was a parachor relation. Two different weighting procedures were used to fit the data. Experimental surface tensions of several methane mixtures were fit to a modification of the usual parachor mixing rule. Standard deviation was less than 1.0 dyn/cm. The modified mixing rule had the advantage of being self-consistent for pure components.

The hazards of LNG have gained prominence recently because of its increased usage. Surface tension data are of particular importance to hazard analysis.

For pure methane, the primary component of LNG, data are available, but for most of the other components, there are no data at the temperatures of interest. Because LNG is a mixture, the accuracy of any LNG surface tension calculation is based not only on the accuracy of the pure component data, but also on that of the mixing rule used. There is some question as to the accuracy of mixing rules at temperatures above the critical of any particular component.

Pure Component

Background. In 1894 Van der Waals (*45*) proposed the following equation to correlate surface tension:

$$\sigma = \sigma_0 (1 - T_R)^{\beta} \qquad (1)$$

where σ is the surface tension, σ_0, β are arbitrary parameters, and T_R is the reduced temperature. He suggested that β was a universal constant. However, Ferguson (*16*) showed that surface tensions were better represented with β as a specific parameter. Where only limited data were available, he suggested a β of 1.21. A value of 1.22 was later recommended by Guggenheim (*21*) based on theoretical considerations. Wright (*48*) experimentally determined β for 14 different compounds and found variations from 0.994 to 1.230. Most of his measurements involved ketones and nitriles. Brock and Bird (*6*) presented two formulas for calculating σ_0. One formula was based on critical properties, and the other on the reduced boiling point. Both relationships were strictly empirical and based on a β of 1.22.

Theoretical considerations have given a β of 1.22, but experimental evidence indicates that the value varies depending on the compound. Since there is no theory to predict β and σ simultaneously, Equation 1 is essentially empirical.

Another equation which correlates surface tension was presented by Macleod (*31*) in 1923:

$$\sigma^{\alpha} = [P] (\rho_L - \rho_G) \qquad (2)$$

where ρ_L, ρ_G are the molar densities of saturated liquid and gas, respectively, $[P]$ is the parachor (arbitrary parameter), and α is 0.25 or an arbitrary parameter. This relation is also entirely empirical with $\alpha = 0.25$. In 1953 Quale (*34*) outlined another empirical procedure for calculating the parachor based on molecular structure. However, Wright (*48*) found in 1961 that experimental results could be better correlated with an arbitrary α which varied from 0.241 to 0.284.

Data analysis. Twenty-three sets of surface tension data were chosen for analysis (Table I). All data were reported at saturation pressure except some for *cis*-2-butene. No other data were available for this compound.

All techniques used in these studies to measure surface tension involved a balance between gravitational forces which are proportional to the density difference between the liquid and gas phases and surface forces. Where more accurate density measurements were reported, they were used to modify the value of the experimental surface tensions. If a set of data were modified, the corresponding density reference is given in Table I. The modified surface tension values were used with both Equations 1 and 2.

The densities used in Equation 2 were the same as those of the experimentalists unless referenced otherwise in Table I. [The source for the Chirkin (*7*) density data was undetermined; therefore, the Berry and Sage (*5*) data were used.] The critical temperatures used in Equation 1 are given in Table I. The best fit was determined by minimizing the sum of the squares of the residuals for a particular set of data (*13*). Two different types of residuals were used. Type I residual was the difference between the experimental and the calculated values of the surface tension. This is a standard least-squares technique which minimizes the standard deviation (SD). Type II residual was the difference between the experimental and calculated values of the logarithms of the surface tensions. This fit reduced the error between the experimental and calculated values at low surface tensions but increased it at high surface tensions. The parameters obtained with this fit are referred to as high-temperature weighted.

With Type II residual, the faithfulness of the fit can be characterized by the pseudo-standard percent deviation

$$\text{PSPD} = 100\% \frac{\sqrt{\sum_{i=1}^{n} \left[\ln\left(\frac{\sigma_{\text{exptl}}}{\sigma_{\text{calcd}}}\right) \right]^2}}{n}$$

where σ_{exptl} is the experimental surface tension, σ_{calcd} is the calculated surface tension, and n is the number of data points. For all practical purposes, it is a standard percent deviation.

A general indication of which type of fit is giving the best results for a particular temperature and composition can be made by comparing the PSPD with the standard deviation obtained with a Type I fit multiplied by (100%/surface tension). The lower the percentage, the better the fit.

Results for pure components. Surface tension data for 17 pure hydrocarbons (Table I) were fit to Equations 1 and 2. The parameters obtained sometimes differ slightly from those presented by the experimentalists owing to differences in weighting or to the use of different critical temperatures or densities.

Parameters obtained in the fit of Equation 1 are given in Tables II and III. All β's are close to 1.22, but they are not constant. The variation of σ_0 is from 36.8 for methane to 56.1 for butane. No general trend in β or σ_0 was noted with respect to molecular configurations or temperature region of

Table I. Temperature Range of Surface Tension References and Critical Temperatures

Compound	Temp, K	Surface tension ref	Density ref	Crit temp	Crit temp ref
		Alkanes			
Methane	91–115	(17)	(19)	190.55	(18)
	159–190	(18)	(19, 20)		
Ethane	129–180	(29)	...	305.43	(28)
	165–199	(30)	(29)	...	...
	274–300	(27)	(2)	...	...
Propane	202–234	(30)	...	369.82	(28)
	308–367	(41, 24)	(40)	...	...
2-Methylpropane	237–250	(9)	(11)	408.13	(28)
n-Butane	237–302	(9)	(10)	425.16	(28)
	303–417	(41, 43)	(10)	...	...
n-Pentane	294–424	(26)	(5)	469.65	(28)
	309–460	(7)	(5)	...	...
n-Nonane	273–333	(25)	...	594.56	(28)
n-Decane	273–333	(25)	...	617.55	(1)
		Alkenes			
Ethene	161–185	(30)	...	283.05	(49)
Propene	211–250	(30)	...	364.91	(32)
2-Methylpropene	218–293	(8)	...	417.85	(3)
1-Butene	218–293	(9)	...	419.55	(46)
cis-2-Butene	263–293	(1)	...	435.55	(28)
trans-2-Butene	223–293	(9)	...	428.61	(28)
		Alkynes			
Ethyne	191–217	(30)	...	308.33	(28)
Propyne	235–262	(33)	...	402.38	(28)
1-Butyne	242–282	(33)	...	463.65	(33)

Table II. Temperature Parameters for Surface Tension of Alkanes

Compound, ref	σ_0, dyn/cm	β	SD, dyn/cm	σ_0, dyn/cm	β	PSPD, %
		No weights			High-temperature weighted	
Methane (17)	36.841	1.1794	0.025	36.806	1.1782	0.18
(18)	39.434	1.2822	0.006	40.506	1.2927	1.55
Ethane (29)	48.110	1.1821	0.074	48.279	1.1871	0.34
(30)	47.008	1.1575	0.073	47.249	1.1633	0.43
(27)	55.967	1.2660	0.033	68.766	1.3422	5.39
Propane (30)	56.291	1.3297	0.056	56.116	1.3262	0.34
(41)	48.442	1.1905	0.055	52.966	1.2276	5.45
2-Methylpropane (9)	54.148	1.3123	0.188	54.081	1.3111	1.50
n-Butane (9)	52.729	1.2346	0.059	53.101	1.2416	0.39
(41)	56.091	1.2658	0.107	51.716	1.2201	5.10
Pentane (26)	50.252	1.1917	0.156	47.000	1.1418	1.99
(7)	54.519	1.2407	0.143	51.304	1.2103	9.4
n-Nonane (25)	53.565	1.2480	0.013	53.614	1.2493	0.06
n-Decane (25)	53.634	1.2567	0.014	53.681	1.2580	0.06

Table III. Temperature Parameters for Surface Tension of Alkenes and Alkynes

Compound, ref	σ_0, dyn/cm	β	SD, dyn/cm	σ_0, dyn/cm	β	PSPD, %
		No weights			High-temperature weighted	
			Alkenes			
Ethene (30)	53.948	1.2991	0.038	53.897	1.2980	0.23
Propene (30)	54.909	1.2320	0.041	54.895	1.2317	0.26
2-Methylpropene (8)	54.075	1.2207	0.047	54.315	1.2255	0.27
1-Butene (9)	56.310	1.2467	0.037	56.492	1.2502	0.19
cis-2-Butene (1)	47.983	1.0400	0.001	47.990	1.0401	0.01
trans-2-Butene (9)	55.263	1.2167	0.050	55.539	1.2222	0.30
			Alkynes			
Ethyne (30)	61.328	1.1955	0.044	61.320	1.1954	0.26
Propyne (33)	62.494	1.1379	0.007	62.478	1.1377	0.03
1-Butyne (33)	59.875	1.2689	0.333	59.789	1.2672	0.51

each compound. Standard deviations and percent deviations were generally within 0.1 dyn/cm or 1%, respectively.

Tables IV and V give the parameters obtained in the fit of Equation 2. The value of α was far from a constant 0.25. It varied from 0.228 to 0.282. The value of the pseudo-parachor showed a definite increase with increasing molecular weight. However, the increase would not have been nearly as large if densities had been based on mass rather than moles.

The standard deviation or percent error was larger with Equation 2 than with Equation 1. This is not surprising as densities were often given in tables as a function of temperature and therefore had to be obtained by interpolation. Also, because the density difference was taken to approximately the fourth power, a small error in density estimation was magnified fourfold in the surface tension; hence, Equation 1 is preferred over Equation 2.

Mixtures

Background. Weinaug and Katz (*47*) presented the following empirical formula to calculate the surface tension of mixtures:

$$\sigma^{\alpha_m} = \rho_L \Sigma [P_i] x_i - \rho_G \Sigma [P_i] y_i \qquad (3)$$

where α_m is 0.25, $[P_i]$ is the parachor of component i, x_i is the mole fraction of i in liquid, and y_i is the mole fraction of i in gas. This is a revised form of the equation presented by Hammick and Andrew (*22*) in which gas density was not taken into account. Weinaug and Katz correlated their methane–propane data within 0.1 dyn/cm. In their work a methane parachor of 77 was chosen to give a good fit to the data.

In 1943 Reno and Katz (*36*) measured the surface tension of *n*-heptane and *n*-butane containing dissolved nitrogen. Although the butane mixture data could be correlated with Equation 3, the heptane mixture data required adjustment of the nitrogen parachor. They suggested that the nitrogen parachor may not be a constant for all hydrocarbon mixtures, but because parachors are supposed to be functions solely of the pure component, it would be more precise to say that the parachor mixing rule is not applicable to all mixtures.

Stegemeier (*41*) measured the surface tension of methane–decane and methane–pentane mixtures. He found he could better correlate his data via a pseudo-parachor relationship. He used a value of 3/11 for all α_i's and α_m's. A pseudo-parachor of 77.9 was used for methane. This is equivalent to a parachor of 73.2 with an α of 0.25.

Deam and Maddox (*13*) measured the surface tension of methane–nonane mixtures. They were able to predict their experimental results by using Equation 3 with a methane parachor of 81.

All investigators used a parachor or parachor-type relation to correlate methane–hydrocarbon mixture results but used different values for the parachor of methane. None of the values agrees with the presently available data for methane as given in Table IV. Furthermore, the value of α is not 0.25 for methane, and there is considerable variation in α between compounds.

In addition to parachor-type relationships, other mixing rules have been proposed. Eckert and Prausnitz (*15*) presented a rule based on a statistical model. Sprow and Prausnitz (*39*) used a thermodynamic description of a mixture surface

Table IV. Density Difference Parameters for Surface Tension of Alkanes

Compound, ref	$[P]$ (cm^3/mol)(dyn/cm)$^\alpha$	α	SD, dyn/cm	$[P]$ (cm^3/mol)(dyn/cm)$^\alpha$	α	PSPD, %
	No weights			High-temperature weighted		
Methane (*17*)	72.674	0.25138	0.033	72.723	0.25163	0.18
(*18*)	73.700	0.26973	0.012	74.030	0.27940	2.88
Ethane (*29*)	109.25	0.24436	0.113	108.62	0.24246	0.57
(*30*)	105.24	0.23206	0.066	105.00	0.23127	0.38
(*27*)	112.05	0.26397	0.080	111.30	0.25266	3.97
Propane (*30*)	142.53	0.23032	0.055	142.64	0.23059	0.32
(*41*)	158.12	0.27602	0.081	158.31	0.27472	6.50
2-Methylpropane (*9*)	179.73	0.22769	0.210	180.04	0.22837	1.62
n-Butane (*9*)	184.84	0.23867	0.057	184.54	0.23807	0.38
(*41*)	192.14	0.25269	0.148	199.69	0.27346	6.17
Pentane (*26*)	236.16	0.26024	0.159	242.77	0.27214	2.06
(*7*)	232.08	0.24928	0.271	246.86	0.28160	15.4
n-Nonane (*25*)	401.31	0.25827	0.031	400.72	0.25780	0.14
n-Decane (*25*)	445.10	0.26027	0.026	444.40	0.25977	0.11

Table V. Density Difference Parameters for Surface Tension of Alkenes and Alkynes

Compound, ref	$[P]$ (cm^3/mol)(dyn/cm)$^\alpha$	α	SD, dyn/cm	$[P]$ (cm^3/mol)(dyn/cm)$^\alpha$	α	PSPD, %
	No weights			High-temperature weighted		
			Alkenes			
Ethene (*30*)	96.341	0.23821	0.065	96.421	0.23850	0.39
Propene (*30*)	139.67	0.24918	0.051	139.31	0.24827	0.31
2-Methylpropene (*8*)	178.12	0.24834	0.110	177.15	0.24644	0.64
1-Butene (*9*)	177.78	0.24542	0.061	177.10	0.24409	0.33
cis-2-Butene (*1*)	194.00	0.28087	0.041	193.57	0.28007	0.24
trans-2-Butene (*9*)	175.22	0.24264	0.103	175.08	0.24236	0.62
			Alkynes			
Ethyne (*30*)	89.042	0.25176	0.074	88.801	0.25081	0.44
Propyne (*33*)	127.79	0.24981	0.031	127.58	0.24927	0.15
1-Butyne (*33*)	172.86	0.26023	0.387	172.72	0.26996	0.57

to obtain a mixing rule. Both studies were able to predict the surface tension of mixtures of methane with nonhydrocarbons at low temperatures. However, both of these rules require knowledge of the surface tensions of the pure components at the relevant temperature. Thus, neither rule can be used at temperatures in excess of the critical of any one component. This problem is also encountered with most other mixing rules. Unfortunately, the only methane–hydrocarbon mixture surface tension data available were taken at temperatures in excess of the critical temperature of methane (Table VI).

Mixture results. To use the pure component α's and pseudo-parachors in calculating mixture surface tensions, the following modification of Equation 3 was proposed:

$$\sigma^{\alpha_m} = \sum \epsilon_i \{[P_i]|x_i\rho_L - y_i\rho_G|\}^{\frac{\alpha_m}{\alpha_i}} \qquad (4)$$

where $\epsilon_i = +1$ if $(x_i\rho_L - y_i\rho_G) > 0$, $\epsilon_i = -1$ if $(x_i\rho_L - y_i\rho_G) < 0$, and α_m is an arbitrary parameter.

The data of the methane mixtures (Table VII) were fit to Equation 4 using a Type I residual. All of the data of Deam and Maddox were fit, but only selected representative data of the other investigators were fit because of the much larger amount of data available in these studies. The results are given in Table VII. The parameters used for the pure components were chosen using the recommended procedure given below.

Two different sets of high-temperature weighted parameters were used for methane, and the results of both are given in Table VII. With one exception, the results based on parameters of the Gielen (*18*) data had smaller standard deviations than those based on parameters of the Fuks and Bellemans (*17*) data. This may be attributed to the Gielen data being taken at temperatures close to the critical, and the mixture data were all taken at temperatures in excess of the critical of methane.

The standard deviation for the mixture fits was reduced twofold when a variable α_m was used instead of a value of 0.25, but there was no way to calculate a priori the best α_m. Therefore, a constant α_m of 0.25 is suggested because those obtained from the best fits were clustered around 0.25. Also, available surface tension vs. density correlations for many compounds are often based on an α of 0.25.

Table VI. Methane Mixture References

Methane mix	Temp, K	Surface tension ref	Density and compn ref
Propane	258–363	(*47*)	(*37*)
Pentane	311–367	(*41*, *42*)	(*5*)
n-Nonane	238–298	(*13*)	(*38*)
n-Decane	311–361	(*41*, *44*)	(*35*)

Table VII. Mixture α's

Methane mix, ref	SD, dyn/cm	α_m	$\pm\Delta\alpha_m$	SD with $\alpha_m = 0.25$, dyn/cm
Propane (*18*)	0.185	0.511	0.183	0.737
(*17*)	0.185	0.474	0.174	0.551
Pentane (*18*)	0.179	0.255	0.026	0.180
(*17*)	0.179	0.235	0.024	0.180
Nonane (*18*)	0.810	0.238	0.005	0.918
(*17*)	0.842	0.224	0.004	1.255
Decane (*18*)	0.683	0.240	0.005	0.761
(*17*)	0.704	0.228	0.004	1.05

Recommended Procedure for Calculating Surface Tensions

Pure components. For pure components the reduced temperature correlation, Equation 1, is recommended over the parachor-type relation, Equation 2. Parameters for use with Equation 1 are presented in Tables I–III. Where more than one investigator has measured surface tensions of a particular compound, use the parameters based on data taken at the temperature of interest (Table I). In the cases of ethane and pentane where surface tension measurements by two investigators overlap at a particular temperature region, the parameters from Leadbetter et al. (*29*) and Jeffries et al. (*26*) are recommended.

If the temperature of interest is at the upper limit or above the region of that where data were taken, the "high-temperature weighted" parameters should be used. The "no weights" parameters should be used in all other cases. The temperature of the transition from the lower to the upper end is arbitrary. No temperature is specified here because the surface tensions calculated from either set of parameters are nearly equal in the middle region.

Mixtures. For mixtures the modified parachor mixing rule, Equation 4, is recommended over the previous parachor correlation, Equation 3. A value of 0.25 is suggested for α_m. Parameters for use with Equation 4 are presented in Tables IV and V. The procedure for selecting the parameters is the same as for pure components; however, one uses the parameters for Equation 2 instead of Equation 1.

Literature Cited

(1) API Research Project 44 Data, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Thermodynamics Research Center, Texas A&M University, College Station, Tex. (loose-leaf data sheets, extant 1974).

(2) Barkelew, C. H., Valentine, J. L., Hurd, C. O., *Trans. AIChE*, **43** (1), 25 (1947).

(3) Beattie, J. A., Ingersoll, H. G., Stockmayer, W. A., *J. Am. Chem. Soc.*, **64**, 546 (1942).

(4) Beattie, J. A., Ingersoll, H. G., Stockmayer, W. A., *ibid.*, p 548.

(5) Berry, V. M., Sage, B. H., *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **32** (1970).

(6) Brock, J. R., Bird, R. B., *AIChE J.*, **1**, 174 (1955).

(7) Chirkin, V. S., "Teplofizicheskie Svoistva Materialov," Moscow, USSR, 1959.

(8) Coffin, C. C., Maass, O., *Trans. Roy. Soc. (Can.)*, **21** (3), 33 (1927).

(9) Coffin, C. C., Maass, O., *J. Am. Chem. Soc.*, **50**, 1427 (1928).

(10) Das, T. R., Reed, C. O., Eubank, P. T., *J. Chem. Eng. Data*, **18** (3), 244 (1973).

(11) Das, T. R., Reed, C. O., Eubank, P. T., *ibid.*, p 253.

(12) Deam, J. R., Bennett, S., Maddox, R. N., *Proc. Ann. Conv., Nat. Gas Proc. Assoc.*, Tech. Paper No. 46, 26 (1967).

(13) Deam, J. R., Maddox, R. N., *ibid.*, Tech. Paper No. 47, 30 (1968).

(14) Dye, J. L., Nicely, V. A., *J. Chem. Educ.*, **48**, 443 (1971).

(15) Eckert, C. A., Prausnitz, J. M., *AIChE J.*, **10** (5), 677 (1964).

(16) Ferguson, A., *Phil. Mag.* (*vi*), **31**, 37 (1916).

(17) Fuks, S., Bellemans, A., *Physica*, **32** (3), 594 (1966).

(18) Gielen, H., PhD thesis, Katholieke Universiteit te Leuven, Leuven, Belgium, 1973.

(19) Goodwin, R. D., *J. Res. Nat. Bur. Stand.*, **75A** (1), 15 (1971).

(20) Goodwin, R. D., "Thermophysical Properties of Methane," Third LNG Conference, Washington, D.C., September 1972.

(21) Guggenheim, E. A., *J. Chem. Phys.*, **13** (7), 253 (1945).

(22) Hammick, D. L., Andrew, L. W., *J. Chem. Soc., London*, **1929**, p 754.

(23) Hough, E. W., Stegemeier, G. L., *Trans. AIME*, **222** (2), *Petrol. Eng. J.*, 259 (1961).

(24) Hough, E. W., Stegemeier, G. L., *Prod. Mon.*, **26** (6), 20 (1962).

(25) Jasper, J. J., Kerry, E. R., Gregorich, F., *J. Am. Chem. Soc.*, **75**, 5252 (1953).

(26) Jeffries, T. O., Derrick, M., Musgrave, B., *J. Chem. Phys.*, **23**, 1730 (1955).

(27) Katz, D. L., Saltman, W., *Ind. Eng. Chem.*, **31**, 91 (1939).

(28) Kudchadker, A. P., Alani, G. H., Zwolinski, B. J., *Chem. Rev.*, **68**, 659 (1968).

(29) Leadbetter, A. J., Taylor, D. J., Vincent, B., *Can. J. Chem.*, **42** (12), 2930 (1964).

(30) Maass, O., Wright, C. H., *J. Am. Chem. Soc.*, **43**, 1098 (1921).

(31) Macleod, D. B., *Trans. Faraday Soc.*, **19**, 43 (1923).

(32) Marchman, H., Prengle, H., Motard, R., *Ind. Eng. Chem.*, **41**, 2658 (1949).

(33) Morehouse, F. R., Maass, O., *Can. J. Res.*, **5**, 306 (1941).

(34) Quale, O. R., *Chem. Rev.*, **53**, 439 (1953).

(35) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **34** (12), 1526 (1942).

(36) Reno, G. J., Katz, D. L., *ibid.*, **35**, 1091 (1943).

(37) Sage, B. H., Lacey, W. N., Schaafsma, J. G., *ibid.*, **26** (2), 214 (1934).

(38) Shipman, L. M., Kohn, J. P., *J. Chem. Eng. Data*, **11** (2), 176 (1966).
(39) Sprow, F. B., Prausnitz, J. M., *Trans. Faraday Soc.*, **62** (521), 1097 (1966).
(40) Stearns, W. V., George, E. J., *Ind. Eng. Chem.*, **35** (5), 602 (1943).
(41) Stegemeier, G. L., PhD thesis, University of Texas, Austin, Tex., 1959.
(42) Stegemeier, G. L., Hough, E. W., *Prod. Mon.*, **25** (11), 6 (1961).
(43) Stegemeier, G. L., Hough, E. W., *ibid.*, **26** (6), 20 (1962).
(44) Stegemeier, G. L., Pennington, B. E., Bauer, E. B., Hough, E. W., *Am. Chem. Soc. Div. Petrol. Chem.*, Preprints 5 (2), A27–A32 (1960).
(45) Van Der Waals, J. D., *Z. Phys. Chem.*, **13**, 716 (1894).
(46) Weber, J., *AIChE J.*, **1**, 210 (1955).
(47) Weinaug, C. F., Katz, D. L., *Ind. Eng. Chem.*, **35**, 239 (1943).
(48) Wright, F. J., *J. Appl. Chem.*, **11**, 193 (1961).
(49) York, R., White, E. F., *Trans. Am. Inst. Chem. Eng.*, **40**, 227 (1944).

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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

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

and the Kelvin equation

$$\text{Ln}\, P = A + \frac{B}{T} \tag{2}$$

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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