clusively the superiority of the dilatometric technique. The value of dV^E/dT given by Duff and Everett, −0.0060 cc. mole^{-1} degree^{-1} for an equimolar solution, is in quite reasonable agreement with the present value of −0.0038 cc. per mole degree. A previous anomaly has been resolved in that both V^E and dV^E/dT for the system benzene-diphenylmethane have now been shown to be comparable in sign, magnitude, and composition dependence to the experimental values for other binary systems in which the ratio of the molar volumes of the two pure components is approximately two—e.g., benzene-diphenyl (*7*), cyclohexane-dicyclohexyl, cyclohexane-dicylohexylmethane (*12*). The experimental free energy, enthalpy, and volume of mixing for benzene-diphenylmethane will be used to test various statistical theories of monomer-dimer mixtures in a subsequent publication.

LITERATURE CITED

(1) Danusso, F., *Rend. Accad. Lincei* **13**, 131 (1952).
(2) Diaz-Pena, M., Cavero, B., *Estos Anales* **60B**, 429 (1964).
(3) Duff, G. M., Everett, D. H., *Trans. Faraday Soc.* **52**, 753 (1956).
(4) Duncan, W. A., Sheridan, J. P., Swinton, F. L., *Ibid.*, **62**, 1090 (1966).
(5) Everett, D. H., Penney, M. F., *Proc. Roy. Soc.* **A**, **212**, 164 (1955).
(6) Everett, D. H., Swinton, F. L., *Trans. Faraday Soc.* **59**, 2476 (1963).
(7) Holleman, T., *Z. Electrochem.* **62**, 1119 (1958).
(8) Klapproth, H., *Nova Acta Leap. Carol* **9**, 305 (1940).
(9) Kortüm, G., Schreiber, H., *Z. Naturforschg.* **20a**, 1030 (1965).
(10) Lal, M., Swinton, F. L., *Trans. Faraday Soc.* **63**, 1596 (1967).
(11) Mathieson, A. R., Thynne, J. C., *J. Chem. Soc.* **1956**, p. 3708.
(12) McLure, I. A., Swinton, F. L., *Trans. Faraday Soc.* **61**, 421 (1965).
(13) Reddy, K. C., Subrahmanyam, S. V., Bhimasenachar, J., *J. Phys. Soc. Japan* **19**, 559 (1964).
(14) Watson, A. E. P., McLure, I. A., Bennett, J. E., Benson, G. C., *J. Phys. Chem.* **69**, 2753 (1965).
(15) Wood, S. E., Austin, A. E., *J. Am. Chem. Soc.* **67**, 480 (1945).

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Vapor Pressures of Liquid Oxygen between the Triple Point and Critical Point

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Vapor pressure measurements reported in the literature for liquid oxygen have been subjected to a rigorous analysis to establish the constants of the Frost-Kalfwarf vapor pressure equation. This investigation has considered all pertinent measurements reported since 1884 and includes in excess of 423 values. A screening procedure reduced this number to 259 reliable points which have served to define the constants of this vapor pressure equation as follows:

$$\log P = 13.4275 - \frac{469.150}{T} - 2.7391 \log T + 0.1155 \frac{P}{T^2}$$

where P is millimeters of mercury and T is the temperature in ° K. This relationship covers the range included between the triple point and critical point and has the capability to reproduce the more accurate experimental measurements with an average deviation of 0.43%. The triple point, T_t = 54.363° K., P_t = 1.125 mm. of Hg and the critical point, T_c = 154.33° K., P_c = 49.713 atm. were deduced from the analysis of these data.

VAPOR PRESSURE measurements on oxygen have appeared in the literature since the early studies of Wroblewski (*13*). Since then, additional measurements have appeared until the last studies reported by Hoge (*8*). Virtually no attempts have been made to obtain further vapor pressure measurements since 1950.

Altogether, 12 sources of information were consulted to obtain vapor measurements for liquid oxygen. Of particular interest is the work reported by Kamerlingh Onnes, Dorsman, and Holst (*9*) and that of Hoge (*8*). Both of these studies present vapor pressure measurements in the critical region, which have enabled the independent establishment of the critical constants of oxygen. The critical values, corrected to the National Bureau of Standards 1955 temperature scale of 273.15° K. reported by these two references, are as follows:

Reference	T_c, ° K.	P_c, Atm.	d_c, G./Cc.
(*9*)	154.33	49.713	0.4295
(*8*)	154.77	50.14	0.38

The critical value reported by Hoge was estimated by comparing the isotherms for oxygen in the vicinity of the critical point with those for carbon dioxide reported by Michels, Blaisse, and Michels (*10*). In this investigation, the critical values reported by Kamerlingh Onnes, Dorsman, and Holst (*9*) have been accepted. However, the low pressure measurements of Hoge (*8*) have enabled the establishment of the triple point as T_t = 54.363° K. and P_t = 1.125 mm. of Hg.

TREATMENT OF VAPOR PRESSURE MEASUREMENTS

The Frost-Kalkwarf vapor pressure equation has received considerable attention because of its ability to account for the accurate representation of the vapor pressure function included between the triple point and critical point (*6*). This semitheoretical relationship,

$$\log P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \qquad (1)$$

is a transcendental function in which $D = a/2.303R^2$ and a is the van der Waals constant, $a = 27R^2T_c^2/64P_c$. Thus, for the general case applicable to Equation 1, $D = 0.1832T_c^2/P_c$. For oxygen, $D = 0.1832\ (154.33)^2/(49.713 \times 760) = 0.1155\ (°\mathrm{K.})^2$ per mm.

The evaluation of constants A, B, and C has been carried out by utilizing a reference point (P_1, T_1) included in a set of vapor pressure measurements, to obtain the normalized expression:

$$\log \frac{P}{P_1} - D\left[\frac{P}{T^2} - \frac{P_1}{T_1^2}\right] = B\left[\frac{1}{T} - \frac{1}{T_1}\right] + C \log \frac{T}{T_1} \qquad (2)$$

When Equation 2 is rearranged, the following linear relationship results:

$$\frac{\log \frac{P}{P_1} - D\left[\frac{P}{T^2} - \frac{P_1}{T_1^2}\right]}{\log \frac{T}{T_1}} = B\,\frac{\frac{1}{T} - \frac{1}{T_1}}{\log \frac{T}{T_1}} + C \qquad (3)$$

Equation 3 can be conveniently expressed in the following form:

$$Y = BX + C \qquad (4)$$

where the vapor pressure modulus,

$$Y = \left\{\log \frac{P}{P_1} - D\left[\frac{P}{T^2} - \frac{P_1}{T_1^2}\right]\right\} / \log \frac{T}{T_1}$$

and the temperature modulus,

$$X = \left[\frac{1}{T} - \frac{1}{T_1}\right] / \log \frac{T}{T_1}$$

Within each set of vapor pressure measurements, a reference value, (P_1, T_1) was arbitrarily selected and values of Y and X were calculated for the other measurements in the set. The resulting values of Y and X were plotted to produce the linear relationship of Figure 1. The slope of the straight line of this figure is $B = -469.150$ and its intercept is $C = -2.7391$. Using these constants, B, C, and D and the normal boiling point $T_b = 90.180°\mathrm{K.}$, a value of $A = 13.4276$ resulted. For each vapor pressure measurement included in this study, values of A were calculated and those ranging from $A = 13.4266$ to $A = 13.4286$ were averaged to produce the final value of $A = 13.4275$ from 133 points. Therefore, the final form of the Frost-Kalkwarf vapor pressure equation for oxygen becomes:

$$\log P = 13.4275 - \frac{469.150}{T} - 2.7391 \log T + 0.1155 \frac{P}{T^2} \qquad (5)$$

ACCURACY OF VAPOR PRESSURE EQUATION

Equation 5 has been used to calculate vapor pressures for the temperature corresponding to each of the experimental measurements. For a total of 259 values, covering the range included between the triple point and the critical point, the average deviation was 0.43%. The average deviation corresponding to each investigator is presented in Table I which shows the early work of Wroblewski (*14*) to be considerably in error. The results of Olszewski (*11*), Estreicher (*5*), and Baly (*1*), although considerably

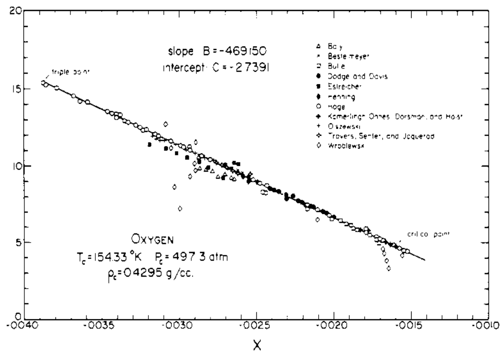

Figure 1. Linear relationship between Y and X resulting from the vapor pressure measurements of oxygen

Table I. Average Deviations Resulting from a Comparison between Experimental and Calculated Vapor Pressures Using Equation 5

Reference	No. of Points	Average Deviation, %
(*1*)	28	4.42
(*2*)	17	3.05
(*3*)	12	2.82
(*4*)	52	0.56
(*5*)	43	4.63
(*7*)	17	0.13
(*8*)	158	0.42
(*9*)	12	0.66
(*11*)	43	4.33
(*12*)	20	0.26
(*13*)	6	11.00
(*14*)	15	172.73

Table II. Experimental Vapor Pressures and Values Calculated with Equation 5

	P, Mm. of Hg		
T, °K.[a]	Exptl.	Calcd.	Reference
54.363*t*	1.125	1.11	(*8*)
56.788	2.28	2.30	(*8*)
60.070	5.53	5.57	(*8*)
65.002	17.60	17.57	(*8*)
67.956	31.90	32.06	(*8*)
71.860	65.20	65.34	(*8*)
75.030	109.20	109.77	(*8*)
80.009	225.60	226.46	(*8*)
85.460	450.00	450.44	(*12*)
90.160	759.92	758.18	(*4*)
90.180*b*	760.00	759.77	(*7*)
94.472	1164.10	1164.12	(*8*)
97.596	1549.10	1548.73	(*8*)
100.163	1931.40	1930.80	(*8*)
102.52	2340.0	2340.2	(*4*)
105.51	2945.8	2948.5	(*4*)
107.172	3333.0	3333.5	(*8*)
110.142	4113.5	4112.0	(*8*)
115.654	5898.6	5898.8	(*8*)
120.996	8110.4	8113.8	(*8*)
124.687	9951.3	9959.7	(*8*)
129.635	12,866	12,887	(*8*)
135.592	17,133	17,182	(*8*)
139.403	20,351	20,425	(*8*)
147.87	29,314	29,221	(*9*)
150.163	31,834	32,030	(*8*)
151.82	34,308	34,185	(*9*)
153.13	35,916	35,969	(*9*)
154.27	37,726	37,580	(*9*)
154.33*c*	37,782	37,666	(*9*)

[a] *t*, triple point; *b*, normal boiling point; *c*, critical point.

Table III. Vapor Pressures of Oxygen between the Triple Point and the Critical Point Calculated at Convenient Temperatures Using Equation 5

T, ° K.^{a}	P, Mm. of Hg	T, ° K.	P, Mm. of Hg.
54.363*t*	1.11	107.000	3,292.0
55.000	1.35	108.000	3,538.6
56.000	1.83	109.000	3,798.4
57.000	2.44	110.000	4,072.0
58.000	3.23	111.000	4,359.8
59.000	4.22	112.000	4,662.3
60.000	5.47	113.000	4,979.8
61.000	7.02	114.000	5,312.8
62.000	8.94	115.000	5,661.7
63.000	11.28	116.000	6,027.1
64.000	14.13	117.000	6,409.3
65.000	17.56	118.000	6,808.8
66.000	21.67	119.000	7,226.0
67.000	26.55	120.000	7,661.5
68.000	32.33	121.000	8,115.7
69.000	39.12	122.000	8,589.1
70.000	47.05	123.000	9,082.1
71.000	56.27	124.000	9,595.2
72.000	66.93	125.000	10,129
73.000	79.19	126.000	10,684
74.000	93.24	127.000	11,260
75.000	109.25	128.000	11,859
76.000	127.43	129.000	12,480
77.000	147.99	130.000	13,125
78.000	171.15	131.000	13,793
79.000	197.13	132.000	14,486
80.000	226.18	133.000	15,203
81.000	258.55	134.000	15,946
82.000	294.50	135.000	16,715
83.000	334.31	136.000	17,510
84.000	378.25	137.000	18,333
85.000	426.62	138.000	19,183
86.000	479.71	139.000	20,062
87.000	537.83	140.000	20,970
88.000	601.30	141.000	21,909
89.000	670.44	142.000	22,877
90.000	745.58	143.000	23,877
90.180*b*	759.77	144.000	24,909
91.000	827.06	145.000	25,974
92.000	915.22	146.000	27,073
93.000	1010.4	147.000	28,206
94.000	1113.0	148.000	29,375
95.000	1223.4	149.000	30,580
96.000	1341.9	150.000	31,823
97.000	1468.8	151.000	33,105
98.000	1604.7	152.000	34,426
99.000	1749.8	153.000	35,789
100.000	1904.6	153.200	36,066
101.000	2069.5	153.400	36,345
102.000	2244.8	153.600	36,626
103.000	2430.9	153.800	36,909
104.000	2628.3	154.000	37,193
105.000	2837.3	154.200	37,479
106.000	3058.4	154.33*c*	37,666

[a] *t*, triple point; *b*, normal boiling point; *c*, critical point.

better, do not quite meet current standards. The careful works of Hoge (*8*), Henning (*7*), Travers, Senter, and Jaquerod (*12*), Dodge and Davis (*4*), and Kamerlingh Onnes, Dorsman, and Holst (*9*) are all associated with modest deviations which fall below the 1% level.

Table II includes experimental and calculated values which have been selected to properly represent the vapor pressure behavior of oxygen between the triple point and the critical point. These values are identified with their source and present a rapid survey of the better experimental values and calculated vapor pressures for oxygen. Equation 5 has also been used to calculate vapor pressures ranging from the triple point to the critical point using 1° K. increments up to 153.00° K. For temperatures above 153.00° K., temperature intervals of 0.2° K. were used. These calculated vapor pressures appear in Table III and are presented for convenience to minimize the calculations required by Equation 5.

NOMENCLATURE

a = van der Waals' constant, (cc./g.-mole)^2 atm.
A,B,C,D = constants for Equation 1
d_c = critical density, g./cc.
P = vapor pressure, mm. of Hg
P_1 = vapor pressure of reference point
P_c = critical pressure, atm.
P_t = triple point pressure, mm. of Hg
R = gas constant
T = temperature, ° K.
T_1 = temperature of reference point, ° K.
T_b = normal boiling point, ° K.
T_c = critical temperature, ° K.
T_t = triple point temperature, ° K.
X = temperature modulus, $[1/T - 1/T_1]/\log T/T_1$
Y = vapor pressure modulus, $\{\log(P/P_1) - D(P/T^2 - P_1/T_1^2)\}/\log(T/T_1)$

LITERATURE CITED

(1) Baly, E.C., *Phil. Mag.* **5**, 517 (1900).
(2) Bestelmeyer, A., *Ann. Physik* **14**, 87 (1904).
(3) Bulle, Fritz, *Physik. Z.* **14**, 860 (1913).
(4) Dodge, B.F., Davis, H.N., *J. Am. Chem. Soc.* **49**, 610 (1927).
(5) Estreicher, T., *Phil. Mag.* **5**, 454 (1895).
(6) Frost, A.A., Kalkwarf, D.R., *J. Chem. Phys.* **21**, 264 (1953).
(7) Henning, F., *Ann. Physik* **43**, 282 (1914).
(8) Hoge, H.J., *J. Res. Natl. Bur. Std.* **44**, 321 (1950).
(9) Kamerlingh Onnes, H., Dorsman, C., Holst, G., *Communs. Phys. Lab. Univ. Leiden* No. **145b** (1914).
(10) Michels, A., Blaisse, B., Michels, C., *Proc. Roy. Soc. (London)* **160A**, 358 (1937).
(11) Olszewski, M., *Nature* **54**, 377 (1896).
(12) Travers, M.W., Senter, G., Jaquerod, A., *Z. Physik. Chem.* **45**, 416 (1903).
(13) Wroblewski, M.S., *Compt. Rend.* **98**, 982 (1884).
(14) Wroblewski, M.S., *Ann. d. Phys. u. Chem.* **25**, 371 (1885).

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