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SHORT COMMUNICATION

ESTIMATION OF VAPOR PRESSURE OF LIQUID OXYGEN BETWEEN THE TRIPLE AND CRITICAL POINTS

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Abstract – The existing vapor pressure measurements available in the literature for the liquid oxygen between the triple and critical points have been utilized to establish the constants and exponent of the modified Frost-Kalkwarf vapor pressure equation in the reduced form as follows:

$$\ln P_r = 6.372408 - \frac{6.637925}{T_r} - 1.975760 \ln T_r + 0.265517\, T_r^5$$

In order to calculate the vapor pressure, only the normal boiling point (T_b=90.180 K) and the critical pressure (P_c=5037.17 kPa) and critical temperature (T_c=154.33 K)are necessary to obtain an overall average deviation of 0.36 % for 540 experimental vapor pressure data.

Key words: *Vapor Pressure, Liquid Oxygen, Modified Frost-Kalkwarf Equation, Critical Point, Triple Point*

INTRODUCTION

The Frost-Kalkwarf equation [Frost and Kalkwarf, 1953] is subject to a review to describe the behavior of vapor pressures of substances over the range between the triple point and the critical point. Their proposed equation shows that

$$\ln P = A' + B'/T + C' \ln T + D'P/T^2 \qquad (1)$$

The term $D'P/T^2$ on the right side of Eq. (1) requires a trial-and-error procedure to calculate a vapor pressure corresponding to a given temperature. Because the vapor pressure P is dependent on temperature, it is assumed that $D'P/T^2$ can be replaced by the term $D'T^n$ [Chung and Thodos, 1976]. With this substitution, Eq. (1) becomes

$$\ln P = A' + B'/T + C' \ln T + D'T^n \qquad (2)$$

This study has examined the vapor pressure measurements reported in the literature for liquid oxygen since the early studies of Wroblewski [1884] and includes in excess of 732 values. A screening procedure reduced this number to 540 reliable data which have been used to correlate experimental vapor pressure values. On the whole, 24 sources of information were considered to obtain vapor pressure data for liquid oxygen, including the work of Kamerlingh Onnes, Dorsman, and Holst [1914], that of Hoge [1950], and that of Wagner et al. [1976].

ESTABLISHMENT OF CONSTANTS OF REDUCED VAPOR PRESSURE EQUATION

Substituting $P=P_cP_r$ and $T=T_cT_r$ into Eq. (2) produces the reduced form of Eq. (2) as follows:

$$\ln P_r = A + B/T_r + C \ln T_r + DT_r^n \qquad (3)$$

where

$A=A' - \ln P_c + C' \ln T_c$

$B=B'/T_c$

$C=C'$

$D=D'T_c^n$

Eq. (3), when applied at the critical point, gives rise to the following relation, A=B − D. If the Plank-Riedel suggestion [Plank and Riedel, 1948, 1949] is accepted, it follows that $B=-Dn^2$, although the above suggestion is different from the viewpoint of Goodwin [1969]. Then the relationships, $A=-B-D$ and $B=-Dn^2$, are substituted into Eq. (3) to give the reduced form of vapor pressure relationship

$$\ln P_r = C \ln T_r + D\,[(T_r^n - 1) + n^2 (1 - 1/T_r)] \qquad (4)$$

Eq. (4), written for the special case of an arbitrarily selected reference point (T_{r1}, P_{r1}) , is subtracted from Eq. (4) itself, yielding:

$$Y = C + DX \qquad (5)$$

where

$$X = \frac{(T_r^n - T_{r1}^n) - n^2(1/T_r - 1/T_{r1})}{\ln(T_r/T_{r1})} \qquad (6)$$

$$Y = \frac{\ln (P_r/P_{r1})}{\ln (T_r/T_{r1})} \qquad (7)$$

To establish the temperature modulus X and the vapor pressure modulus Y, the normal boiling point (T_b=90.180 K) has been used throughout as the reference point. Although any reliable vapor pressure measurement can be arbitrarily employed as a reference point, the normal boiling point was adopted in this study because of its direct accessibility. Altogether 24 references were considered, from which vapor pressure data ranging from the triple point (T_t=54.363 K, P_t=0.149988 kPa) to the critical point (T_c=154.33 K, P_c=5037.17 kPa) were used.

Values of Y were calculated for each vapor pressure measurement. But a designated value of n is necessary in order to calculate the temperature modulus X. Values of n were assumed for the calculation of X and the X values were plotted against Y until Eq. (5) was satisfied. As an example, values of X and Y for the typical vapor pressure data of Hoge [1950] are shown for n=5 in Table 1. The resulting values of X and Y for 24 sources of data are shown in Fig. 1.

Table 1. Moduli X and Y for the typical vapor pressure data of Hoge [1950] (n=5)

Temp. [K]	Vapor pressure [mmHg]	Vapor pressure [kPa]	X	Y
54.363	1.125	0.15	55.8181	12.8472
65.002	17.60	2.35	50.7861	11.5013
67.956	31.90	4.25	49.6326	11.2060
70.141	47.90	6.39	48.8337	10.9996
75.150	111.00	14.80	47.1558	10.5516
85.913	473.30	63.10	44.1402	9.7703
89.558	710.90	94.78	43.2671	9.6495
90.827	811.80	108.23	42.9781	9.2232
94.804	1201.4	160.17	42.1188	9.1578
96.193	1366.2	182.15	41.8343	9.0857
100.116	1924.4	256.57	41.0712	8.8886
104.354	2702.3	360.28	40.3092	8.6897
115.654	5898.6	786.42	38.5531	8.2363
118.095	6846.8	912.83	38.2206	8.1512
124.725	9971.3	1329.4	37.3923	7.9375
127.357	11459	1527.7	37.0921	7.8601
131.540	14140	1885.2	36.6465	7.7442
135.048	16709	2227.7	36.3015	7.6528
140.329	21196	2825.9	35.8291	7.5269
144.396	25203	3360.1	35.5024	7.4379
150.163	31834	4244.2	35.0924	7.3247
153.553	36339	4844.8	34.8797	7.2662

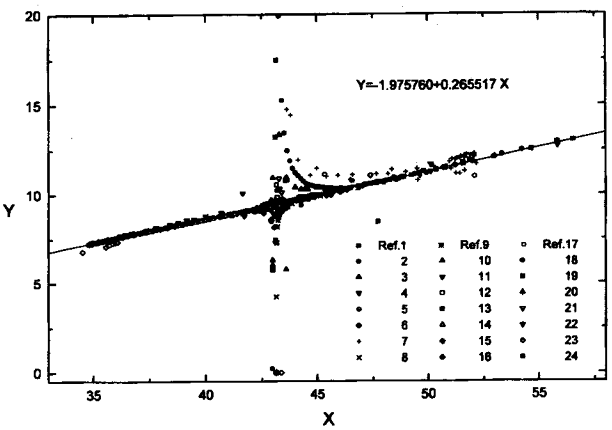

Fig. 1. Relationship between X and Y for the vapor pressure data of liquid oxygen (n=5).

Ref.
1. Aston et al. [1935]
2. Baly [1900]
3. Bestelmeyer [1904]
4. Bulle [1913]
5. Cath [1918]
6. Dodge and Davis [1927]
7. Estreicher [1895]
8. Giauque et al. [1927]
9. Henning [1914]
10. Henning and Heuse [1924]
11. Henning and Otto [1936]
12. Hoge [1950]

Ref.
13. Kamerlingh Onnes and Braak [1908]
14. Kamerlingh Onnes et al. [1914]
15. Keesom et al. [1929]
16. Muijlwijk et al. [1966]
17. Olszewski [1896]
18. Siemens [1913]
19. Stewart et al. [1991]
20. Stock et al. [1921]
21. Travers et al. [1903]
22. Wagner et al. [1976]
23. Wroblewski [1884]
24. Wroblewski [1885]

The significant scatter of values of Y in the vicinity of the reference point is noteworthy at $X \doteqdot 43.1$, which describes the point of discontinuity corresponding to the reference point. This value of X can be established by employing L'Hopital's rule:

$$\frac{d[(T_r^n - T_{r1}^n) - n^2(1/T_r - 1/T_{r1})]/dT_r}{d[(\ln T_r/T_{r1})]/dT_r} = nT_r^n + \frac{n^2}{T_r} \tag{8}$$

For the reference point (T_b=90.180 K and T_r=0.58433) and the exponent n=5, this limiting value comes to be X=43.12. Consequently a linear relationship between X and Y was found for n=5 as

$$Y = -1.975760 + 0.265517\ X \tag{9}$$

Comparison of Eq. (9) with Eq. (5) shows that C=−1.975760 and D=0.265517. The establishment of the constants C and D and exponent n satisfies the requirements of Eq. (4). Employing the relationships $A = -B - D$ and $B = -Dn^2$ it shows that A=6.372408 and B=−6.637925.

RESULTS AND DISCUSSIONS

The reliability of the numerical values of constants A, B, C, and D and exponent n was tested by examining all vapor pressure measurements adopted in this study. Table 2 includes a number of selected vapor pressures, which are compared with corresponding experimental observations ranging from the triple point to the critical point. The selection of these values was made arbitrarily by choosing them in the neighborhood of the straight line in Fig. 1. These values are identified with their sources and present a rapid survey of the better experimental values and calculated vapor pressures for liquid oxygen. For a total of 540 values, covering the range included between the triple point and the critical point, the average deviation was 0.36 %. The average deviation corresponding to each investigator is presented in Table 3 which shows the early work of Wroblewski [1885] to be considerably in error, the results of Kamerlingh Onnes and Braak [1908], Giauque et al. [1927], Henning and Otto [1936], Siemens [1913], Stewart et al. [1991], Bestelmeyer [1904], and Cath [1918], although considerably better, do not quite meet current standards. The careful works of Keesom et al. [1929], Hoge [1950], Wagner et al. [1976], Travers et al. [1903], Kamerlingh Onnes et al. [1914], Muijlwijk et al. [1966], Henning and Heuse [1924], Stock et al. [1921], Dodge and Davis [1927], and Henning [1914] are all associated with modest deviations which fall below 0.7 % .

In order to confirm the validity of the exponent n=5, this entire procedure was repeated for other values of n which produced different values of A, B, C, and D for each case. The average deviations arose for n=3, 4, 5, 6, and 7 are presented in Fig. 2 and indicate that the average deviation is minimum at 0.36 % when n=5.

CONCLUSIONS

The vapor pressure measurements for the liquid oxygen

Table 2. Experimental and calculated vapor pressures for liquid oxygen

Temp. [K]	Vapor pressure [kPa] Exptl.	Calc.	Dev. (%)	Source
54.363[a]	0.152	0.152	0.00	Hoge [1950]
56.538	0.293	0.290	1.00	Hoge [1950]
63.069	1.547	1.530	1.09	Hoge [1950]
65.246	2.462	2.461	0.05	Muijlwijk et al. [1966]
67.956	4.253	4.251	0.05	Hoge [1950]
70.141	6.386	6.391	-0.08	Hoge [1950]
75.150	14.80	14.79	0.03	Hoge [1950]
83.560	47.56	47.55	0.02	Travers et al. [1903]
83.750	48.62	48.68	-0.11	Travers et al. [1903]
85.913	63.10	63.08	0.03	Hoge [1950]
86.210	65.29	65.30	-0.01	Dodge and Davis [1927]
89.760	96.80	96.78	0.02	Dodge and Davis [1927]
90.150	101.33	100.85	0.47	Henning and Heuse [1924]
90.180[b]	101.33	101.17	0.15	Keesom et al. [1929]
90.269	102.66	102.12	0.52	Henning [1914]
90.387	103.39	103.39	0.00	Hoge [1950]
91.386	114.64	114.63	0.01	Hoge [1950]
92.503	128.25	128.29	-0.03	Wagner et al. [1976]
92.506	128.28	128.33	-0.04	Wagner et al. [1976]
94.090	149.81	149.80	0.01	Muijlwijk et al. [1966]
94.150	151.05	150.66	0.26	Stock et al. [1921]
96.108	180.89	181.00	-0.06	Muijlwijk et al. [1966]
98.760	228.99	229.19	-0.09	Dodge and Davis [1927]
100.116	256.57	257.27	-0.27	Hoge [1950]
104.354	360.28	361.69	-0.39	Hoge [1950]
107.392	471.79	473.77	-0.44	Hoge [1950]
110.142	548.42	550.95	-0.46	Hoge [1950]
115.654	786.42	790.00	-0.46	Hoge [1950]
118.095	912.83	916.69	-0.42	Hoge [1950]
120.260	1040.9	1040.7	0.02	Dodge and Davis [1927]
124.725	1329.4	1333.9	-0.34	Hoge [1950]
127.357	1527.7	1532.1	-0.29	Hoge [1950]
131.540	1885.2	1889.7	-0.24	Hoge [1950]
135.048	2227.7	2233.4	-0.25	Hoge [1950]
140.329	2825.9	2834.9	-0.32	Hoge [1950]
144.396	3360.1	3375.4	-0.45	Hoge [1950]
150.163	4244.2	4274.9	-0.72	Hoge [1950]
153.553	4844.8	4887.2	-0.88	Hoge [1950]
154.27	5029.8	5025.5	0.09	Kamerlingh Onnes et al. [1914]
154.33[c]	5037.2	5037.2	0.00	Kamerlingh Onnes et al. [1914]

[a]Triple point, [b]Normal boiling point, [c]Critical point.

between the triple point (T_t=54.363 K, P_t=0.149988 kPa) and the critical point (T_c=154.33 K, P_c=5037.17 kPa) have been employed to establish the modified Frost-Kalkwarf vapor pressure equation.

For the evaluation of the vapor pressures, the only data required are the normal boiling point (T_b=90.180 K) and the critical pressure (P_c=5037.17 kPa) and critical temperature (T_c=154.33 K) in order to acquire an overall average deviation of 0.36 % for 540 vapor pressure observations.

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Table 3. Average deviations between experimental and calculated vapor pressures of liquid oxygen

Source	No. of points	Average deviation (%)
Aston et al. [1935]	8	5.78
Baly [1900]	29	4.90
Bestelmeyer [1904]	22	2.73
Bulle [1913]	13	3.16
Cath [1918]	10	2.79
Dodge and Davis [1927]	53	0.51
Estreicher [1895]	44	11.89
Giauque et al. [1927]	5	0.88
Henning [1914]	18	0.67
Henning and Heuse [1924]	1	0.47
Henning and Otto [1936]	21	1.44
Hoge [1950]	210	0.29
Kamerlingh Onnes and Braak [1908]	1	0.85
Kamerlingh Onnes et al. [1914]	13	0.41
Keesom et al. [1929]	1	0.15
Muijlwijk et al. [1966]	34	0.46
Olszewski [1896]	5	13.62
Siemens [1913]	10	1.71
Stewart et al. [1991]	2	2.31
Stock et al. [1921]	7	0.48
Travers et al. [1903]	20	0.34
Wagner et al. [1976]	183	0.34
Wroblewski [1884]	7	14.35
Wroblewski [1885]	15	195.35

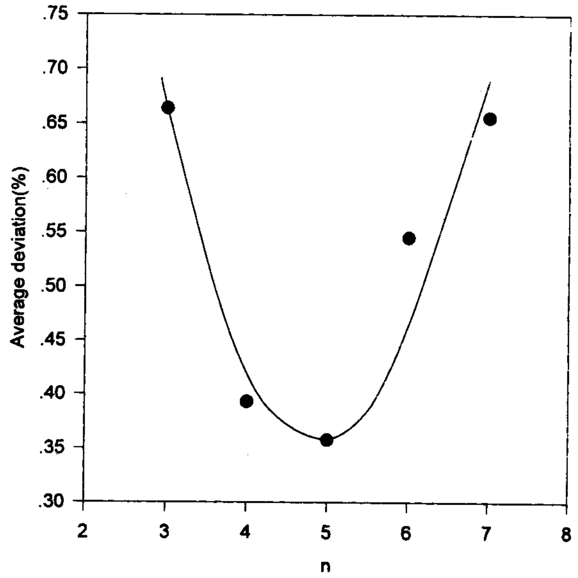

Fig. 2. Relationship between n and average deviation for liquid oxygen.

NOMENCLATURE

A, B, C, D : constants, Eq. (3) [-]
A', B', C', D' : constants, Eq. (1) [-]
n : exponent, Eq. (2) [-]
P : vapor pressure [atm, bar, kPa, MPa, mmHg]
P_r : reduced vapor pressure, P/P_c [-]
T : absolute temperature [K]
T_r : reduced temperature, T/T_c [-]

X : temperature modulus, $[(T_r^n - T_{r1}^n) - n^2(1/T_r - 1/T_{r1})]/\ln(T_r/T_{r1})$ [-]

Y : vapor pressure modulus, $\ln(P_r/P_{r1})/\ln(T_r/T_{r1})$ [-]

Subscripts

1 : reference point
b : normal boiling point
c : critical point
r : reduced value
t : triple point

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