A Vapor Pressure Equation for Oxygen

by

J. G. Hust and R. B. Stewart

GPO PRICE $ _________

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Hard copy (HC) 1.00

Microfiche (MF) .50

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A VAPOR PRESSURE EQUATION FOR OXYGEN

J. G. Hust and R. B. Stewart

Several vapor pressure equations have been considered to represent the vapor pressure data of oxygen. These equations have been fitted to the selected experimental data. The deviations of the calculated and experimental data are graphically illustrated. Rms deviations are also given. The selected equation is constrained to the critical, triple and normal boiling points. The selected vapor pressure equation reproduces the experimental data to within 0.01°K at the highest temperatures and 0.1°K at the lowest temperatures.

1.0 INTRODUCTION

As part of an extensive compilation of the thermodynamic properties of oxygen an appropriate analytical function for the representation of the experimental vapor pressure data has been determined. This function reproduces the experimental vapor pressure data with an accuracy comparable to the precision of the data. As the normal boiling point of oxygen is a primary fixed point of the International Temperature Scale, the selected equation has been constrained to reproduce this point exactly. In addition, the equation has been constrained to reproduce the critical and triple points in order to obtain consistency with the P-V-T surface.

The purpose of this report is to describe the study of vapor pressure relations for oxygen and to illustrate the deviations of the oxygen vapor pressure data from some commonly used representations.

2.0 EXPERIMENTAL DATA

Based on Hoge's [1950] comparisons and an examination of more recent data, the data presented by Hoge were selected as the most accurate measurements of the vapor pressure of oxygen. These data

† This report is a result of a study made by the Cryogenic Data Center of the Cryogenic Engineering Laboratory under a contract with the National Aeronautics and Space Administration.

* An interim table of thermodynamic properties of oxygen has been issued as NBS Report 7922, Stewart, et al. [1963].
points extend from the triple point to within 0.02°K of the critical point. The scatter of these data is estimated to be 0.01% in pressure near the critical point, 2% near the triple point, and varies approximately as the reciprocal of the square root of the pressure between these points. In this paper, Hoge's data are converted to the NBS 1955 Temperature Scale, by subtracting 0.01°.

3. MATHEMATICAL MODELS

The first reasonably successful vapor pressure equation is attributed to Wrede (See Partington [1951]). (For vapor pressure equation designations see Table I.) This equation may be derived from the Clapeyron relationship, by assuming that the latent heat divided by the volume of vaporization is proportional to pressure divided by absolute temperature. The Antoine equation (See Partington [1951]) represents an early attempt to account for the curvature commonly observed in plots of ln P versus 1/T (See Fig. 1). Gutman and Simmons [1950] derived a series representation for vapor pressure which simplifies to the Antoine equation by neglecting higher order terms. They also point out, however, that little is to be gained by retaining the higher order terms because of the rapid convergence of the series. Further attempts to approximate the vapor pressure behavior of substances are represented by the Cragoe [1928], Riedel [1954], and Frost-Kalkwarf [1953] equations. Gosman, et al. [1964] developed an equation on the assumption that the latent heat is quadratic in temperature and the volume of vaporization is \[ \Delta V = \frac{RT}{P} (1 - \frac{P}{P_c}). \]

Yang and Yang [1964] proposed that a vapor pressure equation must have an infinite curvature at the critical temperature and suggests the addition of the term \((T_c - T)^2 \ln (T_c - T)\). Equations (1) and (2) in Table I are power series in temperature and pressure, respectively; and with particular values of \(j\) and \(k\) these are the same as many of the equations appearing in the literature. Equations which could not be reduced to linear form in the coefficients have been omitted from this investigation.
### Table I. Vapor Pressure Equation Designations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Designation</th>
</tr>
</thead>
</table>
| \[
\ln P = \sum_{i=1}^{k} A_i T^{i-j-1} + A_{k+1} \ln T
\] | Equation (1) |
| \[
\frac{1}{T} = \sum_{i=1}^{k} A_i (i+1-1)^3 + A_{k+1} \ln P
\] | Equation (2) |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 T + A_4 T^3 + A_5 T^5
\] | Equation (3) |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 \ln T + A_4 T^4
\] | Wrede or Equation (1) with \( j = -1, k = 2 \) and \( A_{k+1} = 0 \) |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 \ln T + A_4 \ln T + A_5 T^2
\] | Antoine |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 \ln T + A_4 T^2
\] | Cragoe or Equation (1) with \( j = -1, k = 4 \) and \( A_{k+1} = 0 \) |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 \ln T + A_4 P/T^2
\] | Riedel |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 \ln T + A_4 P/T^2
\] | Frost-Kalkwarf |
| \[
\ln P = \frac{A_1}{T} + A_2 + A_3 \ln T + A_4 T + A_5 P
\] | Cosman |
| \[
\ln P = f(T) + B(T - T_c) \ln (T_c - T) + (d^2 f/dT^2 \text{ finite at } T = T_c)
\] | Yang |
4. COMPARISONS

Figures 2a, 2b, and 2c illustrate the deviations of several equations as fitted to the experimental data presented by Hoge [1950]. For convenience the deviations shown are with respect to the smoothed data presented by Hoge. These smoothed data behave well except in the region from 70 to 90\(^\circ\)K. This behavior is shown in more detail in Fig. 2b in the comparison with the Frost-Kalkwarf equation. The relationship of these smoothed data to the experimental data can best be seen in Fig. 5.

The number of coefficients for the equations illustrated in Figs. 2a, 2b, and 2c varies from 2 to 10, and generally the root-mean-square (rms) deviations become smaller with increasing number of coefficients. One exception is the deviation of the 4 term Cragoe equation which is comparable to the deviation of the 5 term equations considered. To improve the representation using the Cragoe equation the following fitting technique was also tried. The data were divided into \(n\) groups according to temperature and each group fitted to the Cragoe equation. The coefficients pertaining to adjacent groups were constrained so that the pressure and the first two derivatives with respect to temperature were equal at the boundaries. The effective number of coefficients in this procedure is determined by subtracting the total number of constraints from the total number of coefficients, e.g., with \(n = 2\), total coefficients = 8, total number of constraints = 3, and effective number of coefficients = 5. The results for \(n = 1, 2, 3,\) and 4 are illustrated in Fig. 3, and Table II. For \(n = 4\) the least squares matrix to be solved for the coefficients is of order 25. Considering the size of the matrix and the rate of convergence to zero of the rms deviation, the authors believe that the advantage of being able to use a simple 4 term equation does not offset the disadvantage of having to use \(n\) sets of coefficients, where \(n\) is at least 5. It is also suggested, however, that this method may be more advantageous with other vapor pressure equations or possibly with a different equation for each region.
The Yang equation with $F(T)$ from the Cragoe equation was also fitted, but no notable improvement resulted. Equation (3) gave results equivalent to the other 5 term equations.

Equation (1) was fitted to the data with various values of $j$ and $k$. The rms deviations became smaller as $j$ progressed from -5 to 0 and further improvement in the fit was observed by increasing $k$ by 1 while equating the coefficient $A_{k+1}$ to zero. The rate of convergence to zero, of the rms deviation, was observed to become noticeably smaller at about $k = 8$. For these reasons, equation (1) with $j = 0$, $k = 8$, and $A_{k+1} = 0$, was tentatively selected to represent the experimental data. The rms deviation of this selected equation with all points weighted equally, as shown in Table II, is 0.00331. This selected equation was fitted to the data in a least squares sense with the data weighted proportionately to pressure, and again with the same weight but also constrained to the following critical, normal boiling, and triple points.

- Critical point: 50.14 atm, 154.77°K
- Triple point: 0.0015 atm, 54.353°K
- Normal boiling point: 1 atm, 90.18°K

The weighted rms deviation of these two fits are 0.000158 and 0.000177, respectively. The effects of the weighting and the constraints are illustrated in Fig. 4. It is apparent from Fig. 4 and the above rms deviations that weighting the data is a distinct improvement, and further that the constraints produce no adverse effect on the fit. The deviations of the experimental data from the selected least squares fit constrained to the above points are shown in Fig. 5. The systematic trend which is apparent in these deviations is considered to be sufficiently small as compared to the probable uncertainty and precision of the data including the uncertainty of the temperature scale. The selected coefficients for equation (1) with $P$ in atm and $T$ in °K are:
\[ A_1 = -0.65081336 \times 10^2 \quad A_5 = -0.48321605 \times 10^{-5} \]
\[ A_2 = 0.26470838 \times 10 \quad A_6 = 0.23211203 \times 10^{-7} \]
\[ A_3 = -0.51911201 \times 10^{-1} \quad A_7 = -0.63554434 \times 10^{-10} \]
\[ A_4 = 0.62744705 \times 10^{-3} \quad A_8 = 0.75863527 \times 10^{-12} \]

Figure 6 illustrates the slope and curvature of the selected approximation. Because of the relative magnitudes of the terms in this equation, the user is cautioned to avoid excessive round off errors.

A least squares fit of equation (2) resulted in a representation of the experimental data which was about as good as with equation (1) but no significant advantage in the use of (2) was noted. The deviations of the data from equation (2) are illustrated in Fig. 4. This fit was accomplished with the same weighting and constraints as in the selected representation.

The rms deviations of various representations are collected in Table II. Each of the fits indicated in Table II was performed with all of the points weighted equally. The coefficients for each equation have been obtained by minimizing the sum of the squares of the deviation of the left hand side of the equation.
<table>
<thead>
<tr>
<th>Representation</th>
<th>Number of Terms</th>
<th>Rms Deviation in (ln P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrede</td>
<td>2</td>
<td>0.0474</td>
</tr>
<tr>
<td>Antoine</td>
<td>3</td>
<td>0.0114</td>
</tr>
<tr>
<td>Frost-Kalkwarf</td>
<td>4</td>
<td>0.00422</td>
</tr>
<tr>
<td>Riedel</td>
<td>4</td>
<td>0.00430</td>
</tr>
<tr>
<td>Cragoe</td>
<td>4</td>
<td>0.00371</td>
</tr>
<tr>
<td>Cragoe (2 sets of coefficients)</td>
<td>(5)*</td>
<td>0.00363</td>
</tr>
<tr>
<td>Cragoe (3 sets of coefficients)</td>
<td>(6)</td>
<td>0.00361</td>
</tr>
<tr>
<td>Cragoe (4 sets of coefficients)</td>
<td>(7)</td>
<td>0.00345</td>
</tr>
<tr>
<td>Gosman</td>
<td>5</td>
<td>0.00377</td>
</tr>
<tr>
<td>Yang</td>
<td>5</td>
<td>0.00368</td>
</tr>
<tr>
<td>Eq. (3)</td>
<td>5</td>
<td>0.00362</td>
</tr>
<tr>
<td>Eq. (1), ( j = -1, k = 6, A_7 = 0 )</td>
<td>6</td>
<td>0.00352</td>
</tr>
<tr>
<td>Eq. (1), ( j = -1, k = 7, A_8 = 0 )</td>
<td>7</td>
<td>0.00336</td>
</tr>
<tr>
<td>Eq. (1), ( j = 0, k = 8, A_9 = 0 )</td>
<td>8</td>
<td>0.00331</td>
</tr>
<tr>
<td>Eq. (1), ( j = 0, k = 10, A_{11} = 0 )</td>
<td>10</td>
<td>0.00329</td>
</tr>
</tbody>
</table>

* The numbers in parenthesis refer to the effective number of coefficients, as noted on page 4.
5. REFERENCES


Figure 2b: Deviations of Hayes Spectral Data from the Indicated Equations.
Figure 4. Deviations of Moyes Smoothed Data from Eq. 1 with $\gamma=0$, $\alpha=0$, $\mu_1=9$ and Eq. 2 with $\gamma=1$, $\alpha=0$. Weight +13.

Weight +0.5

Weight +0.1

Weight -0.1

Weight -0.5

Concentrated at critical, normal boiling, and triple points.

(Freez./Rac.)/100/Pa.

Temperature, °K
Figure 3: Deviation of Nappé data from Eq. 1. 
with \( f(x, K_n) = 0 \). 
• Experimental data 
= Calculated data.