Vapor Pressure and Latent Heat of Vaporization of Parahydrogen from the Triple to the Critical Point

JOSEPH V. De PALMA and GEORGE THODOS

Northwestern University, Evanston, Ill.

The existing vapor pressure measurements reported in the literature for parahydrogen have been utilized to establish the constants of the Frost-Kalkwarf equation applicable between the triple point and the critical point. For refinement, this equation has been applied specifically to vapor pressures above 1 atm. For vapor pressures below 1 atm. a truncated form of this equation has been used. These refined equations, along with the saturated vapor and liquid density relationships of Roder, Diller, Weber, and Goodwin were used with the Clapeyron equation to calculate the latent heats of vaporization. A plot of latent heats of vaporization is presented along with a table of comparison with the values of others.

CURRENT INTEREST in the use of parahydrogen as a fuel for rocket propulsion has stimulated interest for the accurate establishment of several of its physical properties. Two such interdependent properties that have practical usage are the vapor pressure and the latent heat of vaporization. Therefore, this study has been concerned with the procurement from the literature of experimental vapor pressure values to be used for the establishment of an analytical relationship capable of defining accurately the vapor pressure behavior of parahydrogen from its triple point to its critical point. Furthermore, such a relationship permits the calculation of the latent heat of vaporization of this substance through the use of the Clapeyron equation,

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\lambda}{T(v_g - v_l)} \tag{1}$$

Equation 1 is thermodynamically exact and consequently the accuracy of the latent heat of vaporization, λ, depends directly on the ability to obtain accurate values for $(\partial P/\partial T)_v$ and the quantity, $v_g - v_l$.

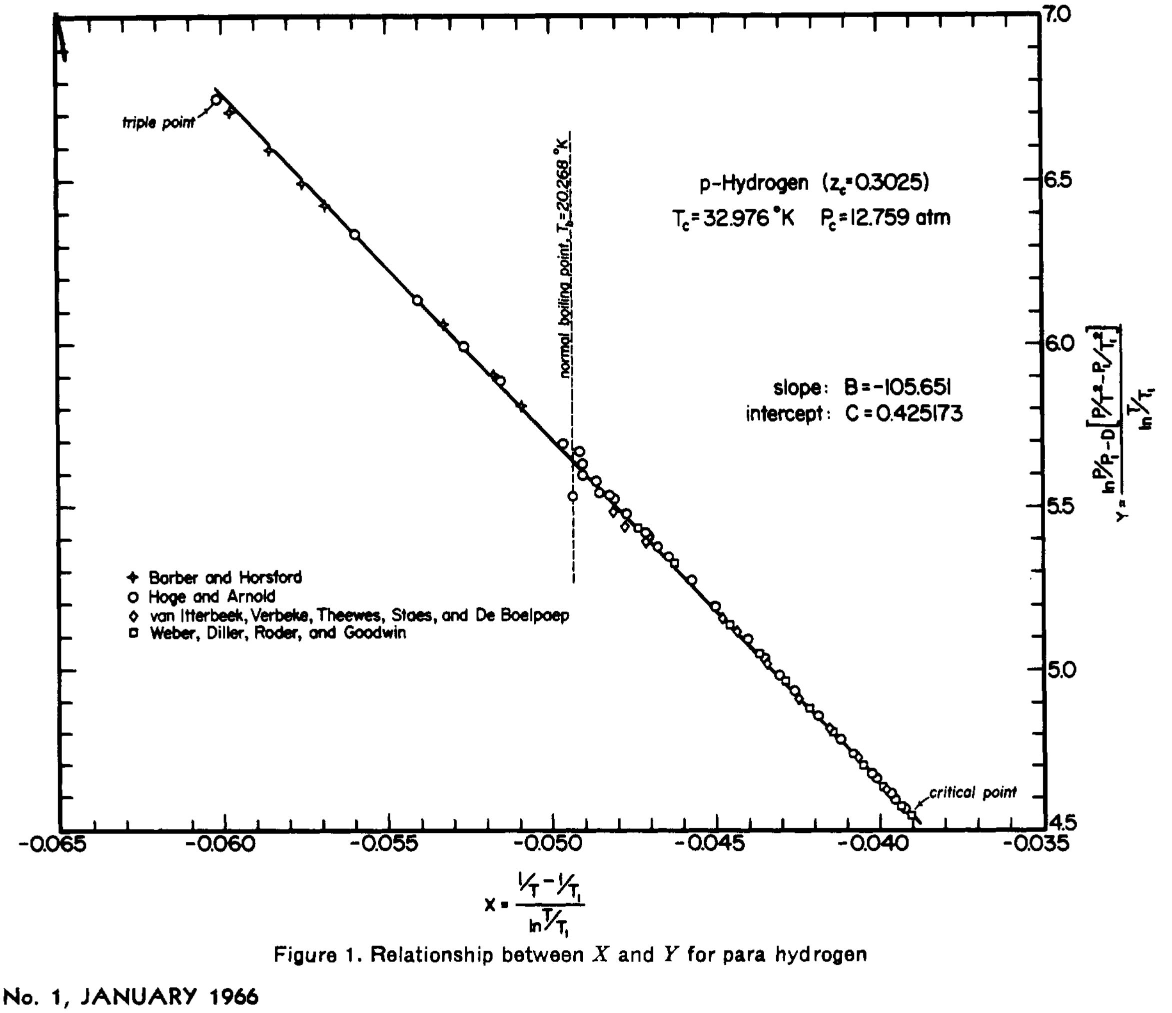

Figure 1. Relationship between X and Y for para hydrogen

VAPOR-PRESSURE BEHAVIOR

A number of vapor pressure equations are presented in the literature. In a recent critical review, Miller (*4*) points out the superiority of the Frost-Kalkwarf equation (*2*) to represent accurately the vapor-pressure behavior of a substance over the complete range included between its triple and critical points. Consequently, this equation was applied to the existing vapor pressure meassurements presented in the literature. A critical literature survey reveals the extensive experimental vapor pressure measurements of Hoge and Arnold (*3*), which cover the range from the triple point to the near critical point vicinity. These data were adjusted to the N.B.S.-1955 temperature scale by subtracting 0.01° K. from the temperatures reported. These adjusted temperatures are used throughout this study. The recent contributions of the National Bureau of Standards (*11*) cover the range between the normal boiling point and the critical point of parahydrogen. Hoge and Arnold (*3*) report a triple point value of $T_t = 13.803°$ K., $P_t = 52.82$ mm. (adjusted to N.B.S.-1955 temperature scale). In 1963, Barber and Horsford (*1*) reported experimental measurements from the triple point to the normal boiling point. The triple point obtained by Barber and Horsford is 13.816° K. and 52.95 mm. The temperatures of the investigation by Barber and Horsford (*1*) are consistent with the N.B.S.-1955 temperature scale. These three references constitute the basic core of experimental data used to develop the constants of the Frost-Kalkwarf equation,

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

In their original development, Frost and Kalkwarf point out the $D = a/R^2$, where a is the pressure van der Waals constant and R is the universal gas constant. The critical constants of parahydrogen reported by Roder, Diller, Weber, and Goodwin (*7*) are as follows: $T_c = 32.976 \pm 0.015°$ K, $P_c = 12.759 \pm 0.028$ atm., and $\rho_c = 0.01559 \pm 0.00005$ gram-moles/cc. Thus, the critical volume of parahydrogen becomes $v_c = 1/0.01559 = 64.144$ cc/gram-mole. The molecular weight of parahydro-

Table I. Comparison of Experimental and Calculated Vapor Pressures of Parahydrogen Using Equation 7

$$\ln P = 10.4791 - \frac{105.651}{T} + 0.425173 \ln T + 0.047310\frac{P}{T^2}$$

		Millimeters of Mercury			
	T, ° K.	P_{exptl}	P_{calcd}	ΔP	Dev. %
W	32.976[a]	9696.8	9762.3	65.5	0.68
W	32.900	9589.6	9654.0	64.4	0.67
H	32.883	9566.2	9630.4	64.2	0.67
H	32.884	9564.4	9630.8	66.4	0.69
H	32.883	9559.3	9629.4	70.1	0.73
W	32.800	9449.5	9513.1	63.6	0.67
W	32.700	9312.0	9373.8	61.8	0.66
H	32.636	9219.5	9285.2	65.7	0.71
W	32.600	9176.8	9236.2	59.4	0.65
W	32.500	9042.8	9100.2	57.4	0.63
H	32.375	8875.1	8932.8	57.7	0.65
H	32.129	8557.7	8609.6	51.9	0.61
W	32.000	8399.0	8443.6	44.6	0.53
H	31.881	8255.1	8293.0	37.9	0.46
W	31.500	7792.5	7824.7	32.2	0.41
H	31.392	7660.2	7695.8	35.6	0.46
V	31.238	7503.2	7514.4	11.2	0.15
H	31.072	7302.5	7323.1	20.6	0.28
W	31.000	7221.1	7241.2	20.1	0.28
V	30.971	7200.2	7208.2	8.0	0.11
H	30.892	7102.8	7119.7	16.9	0.24
W	30.500	6679.2	6691.5	12.3	0.18
H	30.368	6544.6	6551.3	6.7	0.10
V	30.172	6357.3	6348.0	−9.3	−0.15
W	30.000	6169.0	6173.6	4.6	0.07
H	29.907	6080.2	6081.0	0.8	0.01
H	29.386	5583.9	5578.9	−5.0	−0.09
V	29.238	5453.3	5442.3	−11.0	−0.02
W	29.000	5233.6	5227.9	−5.7	−0.11
H	28.870	5121.5	5113.0	−8.5	−0.17
H	28.376	4705.7	4694.2	−11.5	−0.24
W	28.000	4401.9	4392.8	−9.1	−0.21
H	27.864	4299.6	4287.5	−12.1	−0.28
V	27.540	4049.9	4043.0	−6.9	−0.17
H	27.398	3952.7	3939.5	−13.2	−0.33
V	27.072	3718.2	3708.2	−10.0	−0.27
W	27.000	3669.7	3658.7	−11.0	−0.30
H	26.771	3517.5	3504.0	−13.5	−0.38
H	26.188	3142.6	3131.0	−11.6	−0.37
W	26.000	3026.7	3017.0	−9.7	−0.32
H	25.885	2960.3	2949.1	−11.2	−0.38
H	25.561	2773.5	2762.5	−11.0	−0.40
V	25.209	2578.1	2569.6	−8.5	−0.33
H	25.037	2488.5	2479.2	−9.3	−0.37
W	25.000	2467.1	2459.9	−7.2	−0.29
H	24.890	2414.1	2403.6	−10.5	−0.44
V	24.680	2301.5	2298.2	−3.3	−0.15
H	24.440	2189.4	2182.1	−7.3	−0.33
H	23.634	1827.1	1822.4	−4.7	−0.26
W	23.000	1572.3	1570.6	−1.7	−0.11
H	22.896	1534.9	1531.7	−3.2	−0.21
V	22.772	1488.7	1486.4	−2.4	−0.16
H	22.569	1416.1	1414.3	−1.8	−0.13
H	22.270	1313.8	1312.4	−1.4	−0.10
H	22.250	1308.4	1306.0	−2.4	−0.19
W	22.000	1225.4	1225.1	−0.3	−0.02
H	21.677	1127.2	1126.3	−0.9	−0.08
H	21.328	1026.8	1025.8	−1.0	−0.10
H	21.195	989.8	989.2	−0.6	−0.06
H	20.943	922.5	922.7	0.2	0.03
H	20.941	922.1	922.2	0.1	0.01
H	20.855	900.7	900.3	−0.4	−0.05
H	20.507	815.2	815.0	−0.2	−0.03
H	20.502	813.7	813.8	0.1	0.01
H	20.397	789.6	789.3	−0.3	−0.03
B	20.270	760.0	760.6	0.6	0.07
H	20.268	760.0	760.0	0.0	0.00
W	20.268	760.0	760.0	0.0	0.00
H	20.255	757.1	757.0	−0.1	−0.01
H	20.030	707.7	707.9	0.2	0.03
H	19.114	530.7	531.2	0.5	0.09
B	19.050	519.5	520.1	0.6	0.11
H	18.571	442.1	442.8	0.7	0.16
B	18.447	423.3	424.2	0.9	0.23
H	17.819	338.4	338.7	0.3	0.10
B	17.429	291.3	292.3	1.0	0.36
H	16.965	243.1	243.6	0.5	0.19
H	16.945	241.4	241.6	0.2	0.07
H	15.831	149.7	149.6	−0.1	−0.04
B	15.348	119.4	119.2	−0.2	−0.16
B	15.005	100.8	100.6	−0.3	−0.27
B	14.524	78.6	78.2	−0.4	−0.47
B	13.977	58.3	57.7	−0.6	−0.97
B	13.816[b]	52.95	52.5	−0.4	−0.77
W	13.803[b]	52.82	52.1	−0.7	−1.29
H	13.803[b]	52.80	52.1	−0.7	−1.25

[a] Reported critical point.
[b] Reported triple point.

gen reported by Roder *et al.* (*7*) is $M = 2.01572$ grams/gram-mole. The evaluation of constant D follows directly from the van der Waals constant, $a = 27R^2T_c^2/64P_c$. Thus,

$$D = \frac{a}{R^2} = \frac{27T_c^2}{64P_c} = \frac{27}{64}\frac{(32.976)^2}{(12.759 \times 760)} = 0.047310(^\circ\text{K.})^2/\text{mm.}$$

When a reference point (T_1,P_1), selected from a set of data, is substituted into Equation 2, the following expression results:

$$\ln P_1 = A + \frac{B}{T_1} + C \ln T_1 + D\frac{P_1}{T_1^2} \tag{3}$$

By subtracting Equation 3 from Equation 2, and rearranging, it follows that:

$$\frac{\ln\dfrac{P}{P_1} - D\left[\dfrac{P}{T^2} - \dfrac{P_1}{T_1^2}\right]}{\ln\dfrac{T}{T_1}} = B\,\frac{\dfrac{1}{T} - \dfrac{1}{T_1}}{\ln\dfrac{T}{T_1}} + C \tag{4}$$

If Equation 2 truly represents the behavior of the vapor pressure function and the reference is reliable, a plot of the vapor pressure modulus,

$$Y = \frac{\ln\dfrac{P}{P_1} - D\left[\dfrac{P}{T^2} - \dfrac{P_1}{T_1^2}\right]}{\ln\dfrac{T}{T_1}} \tag{5}$$

against the temperature modulus,

$$X = \frac{\dfrac{1}{T} - \dfrac{1}{T_1}}{\ln\dfrac{T}{T_1}} \tag{6}$$

should produce a straight line of slope B and an intercept C. This premise has been substantiated with several substances (*6*), including the aliphatic hydrocarbons (*8*, *9*).

The above procedure was followed in this study using the normal boiling point reported by each experimenter as the reference point for the corresponding set of data. The X and Y values resulting from the data of Hoge and Arnold (*3*), Weber, Diller, Roder, and Goodwin (*11*), and Barber and Horsford (*1*) were plotted as shown in Figure 1. The recent data of van Itterbeek *et al.* (*10*) have been used to calculate X and Y values which are also included for comparison in Figure 1. This was done to screen out any vapor pressure points that were in significant disagreement with the general trend of the data. Furthermore, this approach would indicate how well the behavior of parahydrogen conforms to Equation 2, as shown by the linearity of the Y *vs.* X relationship. The data of the three sources produce a relationship that is linear from the critical point to nearly the triple point. As T approaches T_1, Equation 6 becomes indeterminate. Application of L'Hospital's rule yields the limiting value

$$\mathop{\pounds}_{T \to T_1} X = -1/T_1 = -1/20.268 = -0.04934.$$

Because of the high sensitivity of the vapor pressure modulus, Y, near the reference point, some scatter can be encountered in its vicinity.

The method of least squares was applied to the values of Figure 1 to obtain a slope of $B = -105.651$ and an intercept of $C = 0.425173$ to represent best the data of the three references. The value of $A = 10.4791$ was established by substituting the normal boiling point reported by Hoge and Arnold (*3*), adjusted to the N.B.S.-1955 temperature scale, $T_b = 20.268^\circ$ K. into Equation 2 along with the already established values for B, C, and D. The final equation for parahydrogen over the complete range included between the triple and critical points becomes:

$$\ln P = 10.4791 - \frac{105.651}{T} + 0.425173 \ln T + 0.047310\frac{P}{T^2} \tag{7}$$

where P is in millimeters of mercury and T is in degrees Kelvin. Vapor pressures calculated with Equation 7 are presented in

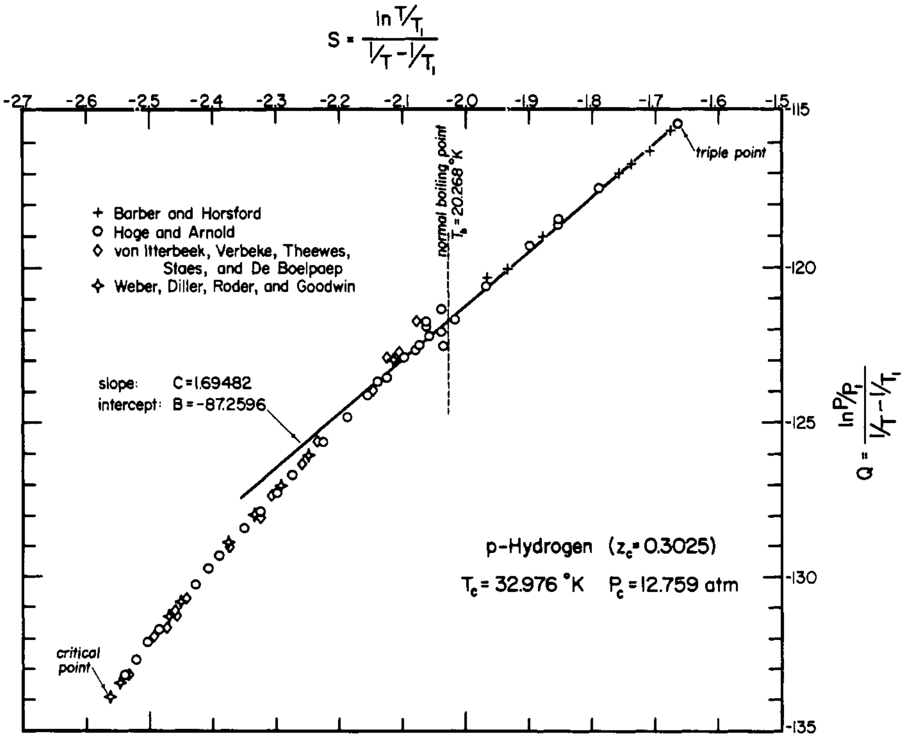

Figure 2. Relationship between Q and S for para hydrogen

Table II. Comparison of Experimental and Calculated Vapor Pressures of Parahydrogen Using Equation 8

$$\ln P = 11.2586 - \frac{110.157}{T} + 0.240055 \ln T + 0.047310 \frac{P}{T^2}$$

		Millimeters of Mercury			
	T, ° K.	P_{exptl}	P_{calcd}	ΔP	Dev. %
W	32.976^a	9696.8	9690.2	−6.6	−0.07
W	32.900	9589.6	9585.0	−4.6	−0.05
H	32.883	9566.2	9561.9	−4.3	−0.04
H	32.884	9564.4	9562.4	−2.0	−0.02
H	32.883	9559.3	9561.0	1.7	0.02
W	32.800	9449.5	9447.8	−1.7	−0.02
W	32.700	9312.0	9312.2	0.2	0.00
H	32.636	9219.5	9225.8	6.3	0.07
W	32.600	9176.8	9178.1	1.3	0.01
W	32.500	9042.8	9045.4	2.6	0.03
H	32.375	8875.1	8882.1	7.0	0.08
H	32.129	8557.7	8566.3	8.6	0.10
W	32.000	8399.0	8403.9	4.9	0.06
H	31.881	8255.1	8256.5	1.4	0.02
W	31.500	7792.5	7797.3	4.8	0.06
H	31.392	7660.2	7670.8	10.6	0.14
V	31.238	7503.2	7492.5	−10.7	−0.14
H	31.074	7302.5	7304.5	2.0	0.03
W	31.000	7221.1	7223.9	2.8	0.04
V	30.971	7200.2	7191.3	−8.9	−0.12
H	30.892	7102.8	7104.2	1.4	0.02
W	30.500	6679.2	6682.2	3.0	0.04
H	30.368	6544.6	6543.8	−0.8	−0.01
V	30.172	6357.3	6343.1	−14.2	−0.22
W	30.000	6169.0	6170.7	1.7	0.03
H	29.907	6080.2	6079.1	−1.1	−0.02
V	29.238	5453.3	5446.4	−6.9	−0.13
H	29.386	5583.9	5581.8	−2.1	−0.04
W	29.000	5233.6	5233.6	0.0	0.00
H	28.870	5121.5	5119.5	−2.0	−0.04
H	28.376	4705.7	4703.2	−2.5	−0.05
W	28.000	4401.9	4403.1	1.2	0.03
H	27.864	4299.6	4298.2	−1.4	−0.03
V	27.540	4049.9	4054.3	4.4	0.11
H	27.398	3952.7	3951.1	−1.6	−0.04
V	27.072	3718.2	3720.2	2.0	0.05
W	27.000	3669.7	3670.7	1.0	0.03
H	26.771	3517.5	3516.0	−1.5	−0.04
H	26.188	3142.6	3142.9	0.3	0.01
W	26.000	3026.7	3028.7	2.0	0.07
H	25.885	2960.3	2960.7	0.4	0.01
H	25.561	2773.5	2773.7	0.2	0.01
V	25.209	2578.1	2580.3	2.2	0.08
H	25.037	2488.5	2489.6	1.1	0.04
W	25.000	2467.1	2470.1	3.0	0.12
H	24.890	2414.1	2413.6	−0.5	−0.02
V	24.680	2301.5	2307.8	6.3	0.27
H	24.440	2189.4	2191.2	1.8	0.08
H	23.634	1827.1	1829.6	2.5	0.14
W	23.000	1572.3	1576.3	4.0	0.26
H	22.896	1534.9	1537.2	2.3	0.15
V	22.772	1488.7	1491.6	2.9	0.19
H	22.569	1416.1	1419.0	2.9	0.20
H	22.270	1313.8	1316.5	2.7	0.20
H	22.250	1308.4	1310.0	1.6	0.12
W	22.000	1225.4	1228.6	3.2	0.26
H	21.677	1127.2	1129.0	1.8	0.16
H	21.328	1026.8	1027.8	1.0	0.10
H	21.195	989.8	990.9	1.1	0.11
H	20.943	922.5	924.0	1.5	0.16
H	20.941	922.1	923.5	1.4	0.15
H	20.855	900.7	901.4	0.7	0.08
H	20.507	815.2	815.5	0.3	0.03
H	20.502	813.7	814.3	0.6	0.07
H	20.397	789.6	789.7	0.1	0.01
B	20.270	760.0	760.7	0.7	0.09
H	20.268	760.0	760.1	0.1	0.01
W	20.268	760.0	760.1	0.1	0.01
H	20.255	757.1	757.1	0.0	0.00
H	20.030	707.7	707.7	0.0	0.00
H	19.114	530.7	529.8	−0.9	−0.17
B	19.050	519.5	518.7	−0.8	−0.16
H	18.571	442.1	440.9	−1.2	−0.27
B	18.447	423.3	422.3	−1.0	−0.24
H	17.819	338.4	336.4	−2.0	−0.59
B	17.429	291.3	289.9	−1.4	−0.49
H	16.965	243.1	241.0	−2.1	−0.87
H	16.945	241.4	239.0	−2.4	−1.00
H	15.831	149.7	147.1	−2.6	−1.72
B	15.348	119.4	116.8	−2.6	−2.14
B	15.005	100.8	98.3	−2.5	−2.50
B	14.524	78.6	76.2	−2.4	−3.08
B	13.977	58.3	55.9	−2.4	−4.05
B	13.816^b	52.95	50.8	−2.1	−4.01
W	13.803^b	52.82	50.4	−2.4	−4.52
H	13.803^b	52.80	50.4	−2.4	−4.49

[a] Reported critical point.

[b] Reported triple point.

Table I along with the corresponding experimental values and resulting deviations. Each point is identified in this table by B for Barber and Hosford (*1*), H for Hoge and Arnold (*3*), V for van Itterbeek *et al.* (*10*) and W for Weber *et al.* (*11*). These calculations were carried out by an iterative scheme on a digital computer. These iterations were carried out until the correction between successive values of P was less than 0.01 mm. The deviations reported in Table I between experimental and calculated values are small, but deviate, systematically from the triple point to the critical point. A maximum deviation of 1.29% is encountered at the triple point.

Despite the fact that Equation 7 is capable of producing vapor pressures well within ordinary limits of accuracy, improvements could be made to represent more precisely the vapor pressure behavior of parahydrogen.

The values in the low pressure region of the Y, X relationship are slightly offset from the otherwise straight line. On the basis of this observation, it was decided to fit this low pressure region with a separate vapor pressure–temperature relationship. Therefore, a new straight line was fitted through the (Y, X) values corresponding to vapor pressures above 1 atm. and placing more weight on the values in the high pressure region. Again the method of least squares was applied to produce a slope of $B = -110.157$ and an intercept of $C = 0.240055$. Constant A was determined using the vapor pressure value of Weber *et al.* (*11*), $T = 29.000°$ K. and $P = 6.8863$ atm. (5233.6 mm.). This procedure yielded $A = 11.2586$. Therefore, the vapor pressure equation for the high pressure range becomes,

$$\ln P = 11.2586 - \frac{110.157}{T} + 0.240055 \ln T + 0.047310 \frac{P}{T^2} \quad (8)$$

Vapor pressures calculated with Equation 8 are presented in Table II along with the corresponding experimental values and their deviations. These deviations remain small for pressures down to the normal boiling point and then increase to a maximum of 4.52% at the triple point. In view of this, the application of Equation 8 should be restricted to vapor pressures above 760 mm. of mercury.

Since the last term of Equation 2 accounts for the reversal in curvature of the $\ln P$ *vs.* $1/T$ relationship in the vicinity of the

Table III. Comparison of Experimental and Calculated Vapor Pressures of Parahydrogen Using Equation 11

$$\ln P = 5.83882 - \frac{87.2596}{T} + 1.69482 \ln T$$

Millimeters of Mercury

	T, ° K.	P_{exptl}	P_{calcd}	ΔP	Dev. %
H	13.803[a]	52.80	52.76	−0.04	−0.08
W	13.803[a]	52.82	52.76	−0.06	−0.11
B	13.816[a]	52.95	53.16	0.21	0.39
B	13.977	52.28	58.30	0.02	0.03
B	14.524	78.62	78.70	0.08	0.10
B	15.005	100.84	100.87	0.02	0.02
B	15.348	119.38	119.36	−0.01	−0.01
H	15.831	149.70	149.62	−0.08	−0.05
B	16.288	183.03	183.28	0.25	0.14
H	16.945	241.40	241.17	−0.23	−0.10
H	16.965	243.10	243.15	0.05	0.02
B	17.429	291.29	291.81	0.52	0.18
H	17.819	338.40	338.15	−0.25	−0.07
B	18.447	423.28	423.65	0.37	0.08
H	18.571	442.10	442.21	0.11	0.02
B	19.050	519.53	519.63	0.10	0.02
H	19.114	530.70	530.70	0.00	0.00
H	20.030	707.70	707.81	0.11	0.02
H	20.255	757.10	757.03	−0.07	−0.01
W	20.268	760.00	760.00	0.00	0.00
H	20.268	760.00	760.00	0.00	0.00
B	20.270	760.00	760.56	0.56	0.07
H	20.397	789.60	789.40	−0.20	−0.02
H	20.502	813.70	813.91	0.21	0.02
H	20.507	815.20	815.07	−0.13	−0.02
H	20.855	900.70	900.57	−0.13	−0.01
H	20.941	922.10	922.54	0.44	0.05
H	20.943	922.50	923.08	0.58	0.06
H	21.195	989.80	989.60	−0.20	−0.52
H	21.328	1026.8	1026.2	−0.6	−0.05
H	21.677	1127.2	1126.8	−0.4	−0.03
W	22.000	1225.4	1225.7	0.3	0.02
H	22.250	1308.4	1306.4	−2.0	−0.15
H	22.270	1313.8	1312.9	−0.9	−0.07
H	22.569	1416.1	1414.5	−1.5	−0.11
H	22.896	1534.9	1531.6	−3.3	−0.22

[a] Reported triple point.

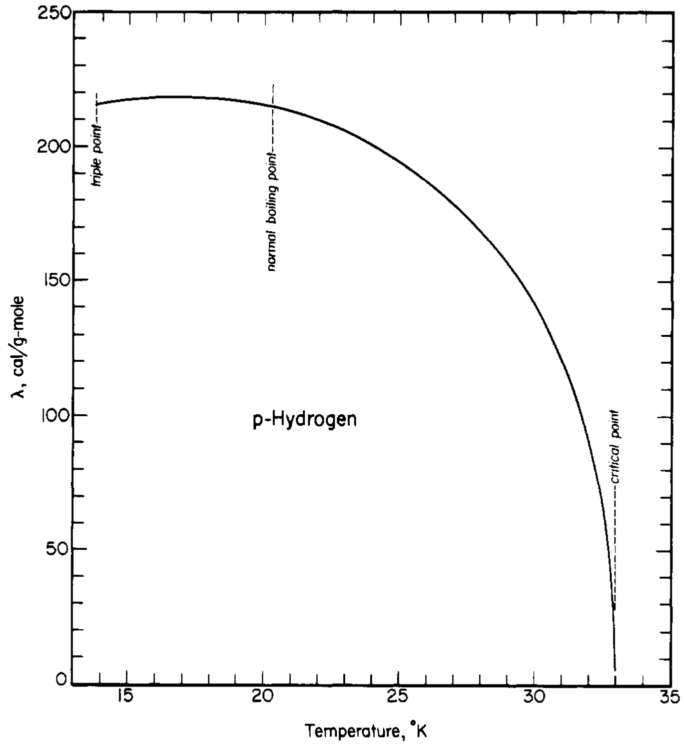

Figure 3. Latent heat of vaporization for parahydrogen

critical point (*9*), it becomes unnecessary to carry it along for the establishment of a vapor pressure relationship in the low pressure region. Therefore, the truncated form of Equation 2 becomes,

$$\ln P = A + \frac{B}{T} + C \ln T \tag{9}$$

Again, a reference point (P_1, T_1) is chosen and substituted into Equation 9. The resulting equation is then subtracted from Equation 9 and rearranged to yield the expression,

$$\frac{\ln \dfrac{P}{P_1}}{\dfrac{1}{T} - \dfrac{1}{T_1}} = B + C \frac{\ln \dfrac{T}{T_1}}{\dfrac{1}{T} - \dfrac{1}{T_1}} \tag{10}$$

The reference point selected for this procedure was again the normal boiling point.

The vapor pressure modulus, $Q = (\ln P/P_1)/(1/T - 1/T_1)$ was plotted against the temperature modulus $S = (\ln T/T_1)/(1/T - 1/T_1)$ as shown in Figure 2. The fact that the Q,S relationship is linear in the low pressure region and curved in the high pressure region supports the assumption that the term DP/T^2 is negligible at low pressure. Application of L'Hospital's rule to the temperature modulus yields $\underset{T \to T_1}{\mathcal{L}} (\ln T/T_1)/(1/T - 1/T_1) = -T = -20.268$. The method of least squares was applied to the values from the triple point to the normal boiling point. The results of this analysis produced an intercept $B = -87.2596$ and a slope of $C = 1.69482$. The normal boiling point was then used to determine constant $A = 5.83882$. Thus the vapor pressure function for parahydrogen covering the range from the triple point to the normal boiling point becomes,

$$\ln P = 5.83882 - \frac{87.2596}{T} + 1.69482 \ln T \tag{11}$$

Values calculated with Equation 11, along with corresponding experimental values and deviations are presented in Table III. A review of these comparisons indicates that Equation 11 is capable of predicting accurate vapor pressures up to almost 1400 mm. Since the objective of Equation 11 is to define the vapor pressure behavior of parahydrogen up to the boiling point, this equation more than fulfills its purpose. Therefore, the combined results of Equations 11 and 8 enable the calculation of accurate vapor pressures from the triple point to the critical point. At the normal boiling point, these equations properly blend into each other as indicated by their derivatives at this point. For Equation 8, $dP/dT = 226.0$ mm./° K, and for Equation 11, $dP/dT = 225.0$ mm./° K.

LATENT HEATS OF VAPORIZATION

Equations 8 and 11 have been used to obtain values of the slope, dP/dT, along the vapor pressure curve. For pressures above the normal boiling point, the differentiated form of Equation 8,

$$\frac{dP}{dT} = \frac{0.240055/T + 110.157/T^2 + 0.094620P/T^3}{1/P - 0.047310/T^2} \tag{12}$$

Table IV. Derived Quantities Used to Calculate Latent Heats of Vaporization

		Cc./Gram-Mole			λ
T, ° K.	P, mm.	v_g	v_l	dP/dT Atm./° K.	Cal./Gram-Mole
13.803[a]	52.8	16,025	26.173	0.0403	215.6
14.000	59.1	14,503	26.230	0.0440	216.0
14.500	77.7	11,378	26.376	0.0544	216.8
15.000	100.6	9055.3	26.526	0.0663	217.4
15.500	128.3	7301.9	26.682	0.0798	217.9
16.000	161.4	5959.5	26.842	0.0949	218.2
16.500	200.6	4917.7	27.008	0.1117	218.4
17.000	246.6	4098.8	27.179	0.1303	218.4
17.500	299.9	3447.5	27.357	0.1507	218.4
18.000	361.3	2923.7	27.542	0.1728	218.2
18.500	431.5	2498.1	27.734	0.1968	217.8
19.000	511.1	2149.0	27.933	0.2225	217.2
19.500	600.8	1860.1	28.141	0.2501	216.4
20.000	701.4	1619.1	28.358	0.2795	215.4
20.268	760.0	1506.8	28.479	0.2960	214.8
20.500	813.8	1417.1	28.586	0.3123	215.3
21.000	938.8	1245.3	28.824	0.3456	213.8
21.500	1076.8	1098.8	29.073	0.3809	212.2
22.000	1228.5	973.39	29.335	0.4181	210.3
22.500	1394.8	865.34	29.612	0.4573	208.2
23.000	1576.3	771.82	29.903	0.4984	206.0
23.500	1773.8	690.48	30.212	0.5415	203.5
24.000	1988.1	619.37	30.539	0.5866	200.8
24.500	2219.9	556.93	30.887	0.6338	197.8
25.000	2470.1	501.84	31.259	0.6832	194.6
25.500	2739.4	453.04	31.656	0.7346	191.2
26.000	3028.7	409.62	32.084	0.7883	187.4
26.500	3338.8	370.81	32.545	0.8442	183.3
27.000	3670.6	336.00	33.045	0.9025	178.8
27.250	3844.9	319.91	33.311	0.9325	176.4
27.500	4025.0	304.62	33.590	0.9632	173.9
27.750	4211.0	290.08	33.882	0.9945	171.2
28.000	4402.9	276.24	34.188	1.0264	168.5
28.250	4601.0	263.03	34.510	1.0590	165.6
28.500	4805.4	250.43	34.850	1.0923	162.5
28.750	5016.2	238.38	35.208	1.1263	159.3
29.000	5233.4	226.85	35.588	1.1609	155.9
29.100	5322.2	222.37	35.747	1.1750	154.5
29.200	5412.0	217.97	35.910	1.1892	153.1
29.300	5503.0	213.64	36.076	1.2035	151.6
29.400	5595.0	209.38	36.247	1.2179	150.1
29.500	5688.1	205.19	36.423	1.2325	148.6
29.600	5782.3	201.06	36.604	1.2472	147.0
29.700	5877.7	197.00	36.789	1.2620	145.4
29.800	5974.1	193.00	36.981	1.2769	143.8
29.900	6071.8	189.05	37.178	1.2919	142.1
30.000	6170.5	185.16	37.380	1.3071	140.4
30.100	6270.4	181.33	37.590	1.3225	138.6
30.200	6371.5	177.55	37.806	1.3379	136.7
30.300	6473.8	173.82	38.030	1.3535	134.9
30.400	6577.3	170.13	38.261	1.3692	132.9
30.500	6681.9	166.49	38.501	1.3851	130.9
30.600	6787.8	162.89	38.749	1.4011	128.9
30.700	6894.9	159.34	39.008	1.4172	126.8
30.800	7003.2	155.82	39.277	1.4335	124.6
30.900	7112.8	152.33	39.557	1.4500	122.4
31.000	7223.6	148.88	39.849	1.4666	120.0
31.100	7335.7	145.45	40.155	1.4833	117.6
31.200	7449.1	142.05	40.476	1.5002	115.1
31.300	7563.8	138.67	40.813	1.5173	112.6
31.400	7679.7	135.31	41.168	1.5345	109.9
31.500	7797.0	131.96	41.543	1.5519	107.0
31.600	7915.6	128.62	41.941	1.5695	104.1
31.700	8035.6	125.29	42.365	1.5872	101.0
31.800	8156.9	121.94	42.818	1.6051	97.81
31.900	8279.6	118.59	43.305	1.6232	94.40
32.000	8403.6	115.21	43.832	1.6414	90.79
32.100	8529.1	111.79	44.406	1.6599	86.95
32.200	8655.9	108.32	45.038	1.6785	82.83
32.300	8784.2	104.78	45.742	1.6973	78.38
32.400	8913.9	101.13	46.536	1.7163	73.52
32.500	9045.1	97.334	47.452	1.7355	68.14
32.600	9177.7	93.315	48.538	1.7549	62.04
32.700	9311.8	88.949	49.884	1.7745	54.90
32.800	9447.5	83.969	51.687	1.7944	46.01
32.900	9584.6	77.567	54.571	1.8144	33.24
32.976[b]	9689.8	64.144	64.144	1.8298	0.00

[a] Triple point. [b] Critical point

Table V. Comparison of Latent Heats of Vaporization Resulting from this Study with Experimental and Calculated Values of Others

	λ, Cal./Gram-Mole			
T, ° K.	This study	White *et al.* (*11*)[a]	Mullins *et al.* (*5*)	Roder *et al.* (*7*)
13.803	215.6	...	216.87	216.8
13.990	216.0	...	217.07	217.1
14.000	216.0	...	...	217.1
14.990	217.4	...	217.93	218.3
15.000	217.4	...	...	218.3
15.990	218.2	...	218.44	218.6
16.000	218.2	...	...	218.5
16.990	218.4	...	218.50	218.4
17.000	218.4	...	...	218.4
17.990	218.2	...	218.05	217.9
18.000	218.2	...	...	217.9
18.990	217.2	...	217.03	216.8
19.000	217.2	...	...	216.8
19.990	215.4	...	215.38	215.3
20.000	215.4	...	...	215.2
20.268	214.8	...	214.80[b]	214.8[b]
21.000	213.8	...	214.03	212.5
22.000	210.3	...	209.94	209.5
23.000	206.0	...	...	205.6
24.000	200.8	...	...	200.8
24.41	198.4	204.7	...	198.5
25.000	194.6	...	...	195.0
26.000	187.4	...	...	187.8
26.33	184.7	193.4	...	185.2
27.000	178.8	...	...	179.2
28.000	168.5	...	...	168.7
28.12	167.1	177.5	...	167.3
29.000	155.9	...	...	155.8
29.65	146.2	145.2	...	145.9
30.000	140.4	...	...	140.1
30.97	120.8	116.5	...	120.5
31.000	120.0	...	...	119.8
31.85	96.13	93.8	...	96.1
32.000	90.79	...	...	90.8
32.400	73.52	...	...	73.9
32.69	55.67	51.8	...	56.4
32.700	54.90	...	...	55.6
32.900	33.24	...	...	33.9

[a] Recalculated by Roder *et al.* (*7*) as suggested by White *et al.* (*11*).
[b] Defined by Roder *et al.* (*7*).

was used to calculate these slopes at convenient temperature intervals. From the triple point up to and including the normal boiling point, the differentiated form of Equation 11,

$$\frac{dP}{dT} = \frac{P}{T}\left[1.69482 + \frac{87.2596}{T}\right] \tag{13}$$

was used to obtain the values of the slopes at convenient intervals. The saturated vapor and liquid molar volumes, v_g and v_l, respectively, were obtained from the saturated density relationships of Roder *et al.* (*7*), which were developed from their experimental studies. Using this information, the latent heats of vaporization for parahydrogen were calculated from the rearranged Clapeyron equation,

$$\lambda = (v_g - v_l)T\frac{dP}{dT} \tag{14}$$

The resulting latent heats of vaporization in cc. mm./gram-mole were divided by the conversion factors 760 mm./atm. and 41.2929 cc. atm./cal. to produce values in cal./gram-mole. Values of slopes, saturated vapor, and liquid molar volumes, and latent heats of vaporization are presented for convenient temperatures in Table IV. These calculated latent heats of vaporization have been plotted to produce Figure 3. It will be noted in this figure that the latent heat function of parahydrogen reaches a maximum at approximately 17.0° K.

To compare these results with the experimental latent heats of vaporization of White, Hu, and Johnston (*2*), values were calculated at their corresponding experimental temperatures. These comparisons are presented in Table V. Also included in this table are the calculated values of Mullins, Ziegler, and Kirk (*5*) and Roder *et al.* (*7*).

The latent heats of vaporization of this investigation presented in Table V show good agreement when compared with the experimental and calculated values reported by others (*5, 7, 12*). Mullins, Ziegler, and Kirk (*5*) calculated latent heats of vaporization from the triple point up to and including 22.0° K., using a virial-type equation of state. The only experimental values for temperatures above the normal boiling point are presented by White, Hu, and Johnston (*12*). The values reported by Roder, Diller, Weber, and Goodwin (*7*) were calculated using the Clapeyron equation and three separate vapor pressure relationships applicable in different regions included between the triple point and the critical point. The values resulting from this study also cover the complete vapor-liquid range and were found to be in good agreement with those already reported in the literature. These findings add creditability to the work already cited (*5, 7, 12*) in which the equations utilized to calculate the latent heat of vaporization of parahydrogen differed in each case.

ACKNOWLEDGMENT

The authors express gratitude to the National Aeronautics and Space Administration for support through NASA Grant SC-3467. Also thanks are due the Northwestern University Computing Center for the allocation of computing time for this study.

NOMENCLATURE

a = van der Waals constant, (cc./gram-mole)^2 atm.
A, B, C, D = constants for Frost-Kalkwarf equation, Equation (2)
M = molecular weight
P = vapor pressure, mm of mercury
P_1 = vapor pressure of reference point, mm. of mercury
P_c = critical pressure, atm.
P_t = triple point pressure, mm. of mercury
Q = vapor pressure modulus, $(\ln P/P_1)/(1/T - 1/T_1)$
R = gas constant
S = temperature modulus, $(\ln T/T_1)/(1/T - 1/T_1)$
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.
v_c = critical volume, cc./gram-mole
v_g = molar volume of saturated vapor, cc./gram-mole
v_l = molar volume of saturated liquid, cc./gram-mole
X = temperature modulus, $(1/T - 1/T_1)/(\ln T/T_1)$
Y = vapor pressure modulus, $\{\ln P/P_1 - D(P/T^2 - P_1/T_1^2)\}/(\ln T/T_1)$

Greek

λ = latent heat of vaporization, cal./gram-mole
ρ_c = critical density, gram-moles/cc.

LITERATURE CITED

(1) Barber, C. R., Horsford, A., *Brit. J. Appl. Phys.* **14,** 920 (1963).
(2) Frost, A. A., Kalkwarf, D. R., *J. Chem. Phys.* **21,** 264 (1953).
(3) Hoge, H. J., Arnold, R. D., *J. Res. Natl. Bur. Stds.* **47,** 63 (1951).
(4) Miller, D. G., *Ind. Eng. Chem.* **56,** No. 3, 46 (1964).
(5) Mullins, J. C., Ziegler, W. T., Kirk, B. S., Tech. Rept. **1,** Eng. Expt. Station, Georgia Institute of Technology, Nov. 1, 1961.
(6) Reynes, E. G., Thodos, George, *Ind. Eng. Chem. Fundamentals* **1,** 127 (1962).
(7) Roder, H. M., Diller, D. E., Weber, L. A., Goodwin, R. D., *Cryogenics* **3,** 16 (1963).
(8) Smith, C. H., Thodos, George, *A.I.Ch.E. J.* **6,** 569 (1960).
(9) Sondak, N. E., Thodos, George, *Ibid.*, **2,** 347 (1956).
(10) van Itterbeek, A., Verbeke, O., Theewes, F., Staes, K., De Boelpacp, J., *Physica* **30,** 1238 (1964).
(11) Weber, L. A., Diller, D. E., Roder, H. M., Goodwin, R. D., *Cryogenics* **2,** 236 (1962).
(12) White, D., Hu, J. H., Johnston, H. L., *J. Phys. Chem.* **63,** 1181 (1959).

RECEIVED for review January 26, 1965. Accepted October 11, 1965.