

TABLE 1. Summary of P-V-T data

Number of points	Temperature or volume	Pressure range (atm)	Source
8	-140 °C	6 to 160	Michels, Levelt, and de Graaff [1]
10	-135	7 to 200	[1]
13	-130	7 to 240	[1]
17	-125	7 to 280	[1]
20	-122.5	7 to 300	[1]
24	-120	7 to 320	[1]
26	-110	8 to 400	[1]
26	-100	8 to 480	[1]
26	-85	9 to 600	[1]
27	-70	6 to 700	[1]
27	-50	7 to 850	[1]
28	-25	7 to 1030	[1]
41	Near coexistence region		[1]
48	0 °C	19 to 930	Michels, Wijker, and Wijker [6]
46	25	20 to 870	[6]
15	50 to 150 °C	27 to 750	[6]
7	-183.02 °C	26 to 165	Rogovaya and Kaganer [7]
8	-150.08	25 to 185	[7]
6	-135.03	72 to 196	[7]
6	-120.02	73 to 166	[7]
7	-110.04	47 to 176	[7]
9	-100.01	49 to 192	[7]
7	-90.03	50 to 190	[7]
8	-75.03	26 to 194	[7]
8	-49.93	28 to 197	[7]
8	-24.98	27 to 184	[7]
8	86.63 K	17 to 90	van Itterbeek and Verbeke [8]
14	87.91	13 to 147	[8]
14	89.13	22 to 150	[8]
14	90.55	18 to 146	[8]
8	90.15 K	10 to 242	van Itterbeek, Verbeke, and Staes [9]
12	96.99	11 to 280	[9]
12	108.18	19 to 260	[9]
8	117.10	16 to 284	[9]
7	127.05	30 to 290	[9]
7	130.85	21 to 266	[9]
11	134.40	30 to 258	[9]
16	136.02	40 to 257	[9]
14	138.98	33 to 285	[9]
11	146.63	58 to 248	[9]
9	148.25	45 to 288	[9]

TABLE 1. Summary of P-V-T data—Continued

Number of points	Temperature or volume	Pressure range (atm)	Source
1	93.15 K	320	van Witzenburg [10]
5	98.15	78 to 350	[10]
7	103.15	76 to 330	[10]
12	123.15	303 to 1042	[10]
12	128.15	302 to 1908	[10]
15	133.15	207 to 1941	[10]
7	108.15	322 to 1210	[10]
3	113.15	74 to 967	[10]
10	118.15	296 to 1590	[10]
13	138.15	315 to 1957	[10]
16	148.15	66 to 1902	[10]
13	153.15	315 to 1925	[10]
14	29.2 cm ³ /g-mol	21 to 488	Walker [11]
15	29.6	25 to 494	[11]
17	29.8	43 to 520	[11]
20	31.3	39 to 500	[11]
17	33.8	16 to 515	[11]
24	35.7	24 to 500	[11]
22	37.8	27 to 506	[11]
16	39.5	34 to 286	[11]
16	41.2	34 to 483	[11]
23	42.0	38 to 506	[11]
24	43.6	45 to 316	[11]
25	45.5	43 to 272	[11]
14	50.7	45 to 139	[11]
22	58.3	61 to 209	[11]
13	66.5	45 to 122	[11]

A preliminary comparison of Walker's [11] experimental data showed an inconsistency in the published density values. Private communication from Walker [13] indicated that there were errors in the density values quoted in the original paper [11]. A more complete discussion of Walker's [11] data will be given later.

4. Summary of Vapor Pressure Data

Some of the vapor pressure data which are available in the literature were published in the early part of the century. Wherever possible, these early data were replaced by more recent data if there appeared to be sufficient evidence that the recent data were of higher reliability.

Modern experimental instrumentation and techniques generally permit a higher order of accuracy and precision than did the earlier work. In addition, the temperature scales and basic standards which were used in much of the older work were substantially different from those used today. Some of the earlier work may have been conducted with variations in the temperature scales of as much as 0.06 deg. Much of the time, the early investigator did not clearly state which temperature scale was in current use and the results therefore lead to confusion and uncertainty.

As a result of the above considerations, the vapor pressure data which were selected for further analysis are shown in table 2.

In addition to the vapor pressure data shown above, two sources of coexistence or saturation densities were examined. These are indicated in table 3.

TABLE 2. Summary of vapor pressure data

Number of points	Temperature range—K	Source
23	90 to 150	van der Waals Laboratory data reported by Clark, Din, Robb, Michels, Wassenaar, and Zwietering [14].
17	86 to 150	British Oxygen Co. Ltd. data reported by Clark et al. [14].
23	117 to 150	Michels, Levelt, and de Graaff [1].
6	84 to 87	Flubacher, Leadbetter, and Morrison [15].
34	85 to 148	van Itterbeek, de Boelpaep, Verbeke, Theeuwes, and Staes [16].
9	129 to 147	van Itterbeek, Verbeke, and Staes [9].

TABLE 3. Coexistence density data

Number of points	Temperature range—K	Source
23	117–150	Michels, Levelt, and de Graaff [1].
16	90–148	Mathias, Onnes, and Crommelin [17].

5. Saturated Liquid Density

In this analysis, it frequently was found convenient to have an expression which could be used to predict approximate values for the density of the saturated liquid. This type of expression was not needed for the determination of the equation of state or the calculation of the thermodynamic properties. However, it would prove useful in the preliminary analysis, where saturation data were evaluated for consistency. Such an expression also would be useful for obtaining initial approximations in iterative solutions of the equation of state. For these purposes a simple expression, based upon the principle of corresponding states, was developed.

Using the critical point as the reducing parameter, the principle of corresponding states assumes a universal function which may be expressed as

$$P_r = f(T_r, V_r) \quad (1)$$

where

$$\begin{aligned} P_r &= P/P_c \\ T_r &= T/T_c \\ V_r &= V/V_c. \end{aligned}$$

However, in the coexistence region where the saturated liquid and saturated vapor are in mutual equilibrium, the pressure and temperature are not independent properties. Thus if eq (1) were examined in accordance with the thermodynamic requirements of the coexistence line, it may be deduced that there also exists a universal function for the saturated liquid such that

$$\rho^l/\rho_c = F(T_r). \quad (2)$$

Using a coordinate system of reduced temperature versus reduced density, Guggenheim [18] plotted experimental data points for a number of pure substances and verified the universal form of eq (2). For the data which Guggenheim [18] had available, he found that the coexistence line could be adequately expressed by the relationships

$$\frac{\rho^l + \rho^g}{2\rho_c} = 1 + a(1 - T_r) \quad (3)$$

and

$$\frac{\rho^l - \rho^g}{\rho_c} = b(1 - T_r)^{1/3}, \quad (4)$$

where a and b are constants. Equation (3) represents the "law" of the rectilinear diameter which states that the average of the saturated liquid and saturated vapor densities appears as a straight line on the reduced coordinate system of temperature versus density.

Combining eqs (3) and (4) yields an equation for the saturated liquid density, expressed as

$$\rho^l/\rho_c = 1 + a(1 - T_r) + C(1 - T_r)^{1/3} \quad (5)$$

where $C = b/2$.

In order to represent the data with more accuracy than eq (5) permits, an expanded form of eq (5) was proposed. Physical requirements demand that the derivative

$$\frac{d(T_r)}{d(\rho^l/\rho_c)} = 0 \text{ at } \rho^l = \rho_c, \text{ and } T_r = 1 \quad (6)$$

Thus the possibility of an equation with the saturated liquid density as a function of only integer powers of temperature is ruled out, since such an equation would not fulfill the requirements of eq (6). It then appears that a fractional power term such as the last term in eq (5) is necessary so that zero slope may exist at the critical point. An expanded form of eq (5) may then be written as

$$\rho^l/\rho_c = \sum_{n=0, 1, 2, 3, \dots} d_n (1 - T_r)^{n/3}. \quad (7)$$

For eq (7) to satisfy critical point behavior, the coefficient d_0 should be essentially equal to unity. In addition, if the derivative of eq (7) is written

$$\frac{d(T_r)}{d(\rho^l/\rho_c)} = - \frac{1}{\sum_{n=0, 1, 2, 3, \dots} \frac{n}{3} d_n (1 - T_r)^{\frac{n}{3}-1}}, \quad (8)$$

it is seen that the requirements of eq (6) are satisfied. In eq (7), fractional exponents other than multiples of $1/3$ were investigated. The results showed no apparent advantages, and the $1/3$ exponent was retained.

Equation (7) was fitted to the saturated liquid data by least square techniques. A series of successive fits was performed with increasing values of " n ." Examination of these fits revealed a continued decrease in the deviations between the calculated density and experimental density until the fit with $n=6$. For fits with " n " greater than six, the results appeared to be approaching the precision of the data, and, therefore, the final form for the equation was selected to be

$$\rho^l/\rho_c = \sum_{n=0}^6 d_n K^n \quad (9)$$

where $K = (1 - T_r)^{1/3}$ and T_r is calculated from temperatures in Kelvin units.

An examination of the saturated liquid density data demonstrates that the data from Michels et al. [1] and Mathias et al. [17] are consistent with each other, with Michels' data showing somewhat more precision. This may be seen in figure 1, where