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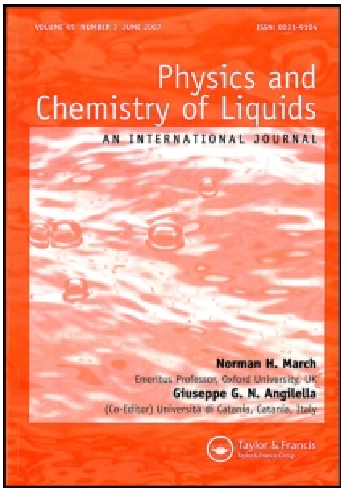

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Saturated Liquid Densities of Cryogenic Fluids

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Abstract—Experimental saturated liquid densities available in the literature for the cryogenic fluids, hydrogen, neon, argon, nitrogen, oxygen, carbon monoxide, and methane show that their temperature dependence can be expressed by the relationship,

$$\rho_R = 1 + k(1 - T_R)^{\beta}.$$

With the exception of hydrogen, the saturated liquid density of all the other polyatomic cryogenic fluids can be represented with $\beta = 0.408$ and $k = 2.36$ giving rise to an average deviation of 0.99% (127 points). For the monatomic cryogenic fluids, $\beta = 0.410$ and $k = 2.21$ from which an average deviation of 0.49% (29 points) results. For the specific case of hydrogen, $\beta = 0.378$ and $k = 1.82$ which produce an average deviation of 0.54% (85 points).

The development of a background capable of predicting the density of saturated liquids finds considerable utility in the design of heat exchangers, distillation columns, and in general, equipment handling liquid processing streams. With the advent of the space programs, information on the properties of hydrogen, nitrogen, and oxygen in their liquid state becomes indispensable. Furthermore, the increasing trend for storing natural gas in the liquefied state makes it imperative to have accessible information on the physical properties of the light hydrocarbons and in particular for methane. For the sake of comprehensiveness, a study of the density behaviour of these cryogenic fluids in their saturated liquid state, of necessity, must also include other common cryogenic fluids such as neon, argon, and carbon monoxide.

The density of liquids, calculated from equations of state, are

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difficult to obtain and frequently these calculated values are not as reliable. Perhaps the most direct quantitative approach to the volumetric behaviour of the liquid state is that of Watson (1) who introduced the concept of the expansion factor, ω, to account for the variation of liquid density as follows:

$$\frac{\rho}{\rho_1} = \frac{\omega}{\omega_1} \qquad (1)$$

where $\omega = \rho_R/zRT_R$. In Eq. (1), ω_1 is the expansion factor for the liquid state corresponding to the temperature and pressure at which the density of the liquid is ρ_1. For $T_R < 0.65$ and pressures not exceeding 10 atm, the liquid expansion factor, ω_1 is satisfactorily expressed by the relationship (2),

$$\omega = 0.1745 - 0.0838 T_R. \qquad (2)$$

At higher temperatures and pressures, values of ω must be obtained from a plot of ω versus T_R with P_R as parameter.

Guggenheim (3) examined experimental densities for the saturated liquid state of the cryogenic fluids, neon, argon, krypton, xenon, nitrogen, oxygen, carbon monoxide, and methane. Using these data, he developed the three parameter relationship,

$$\rho_{R_l} = 1 + \tfrac{3}{4}(1 - T_R) + \tfrac{7}{4}(1 - T_R)^{1/3} \qquad (3)$$

which satisfies the boundary condition at the critical point, $\rho_{R_l} = 1$ at $T_R = 1$. Using experimental densities for the saturated vapor state of these substances, Guggenheim (3) developed a similar relationship

$$\rho_{R_v} = 1 + \tfrac{3}{4}(1 - T_R) - \tfrac{7}{4}(1 - T_R)^{1/3}. \qquad (4)$$

Subtraction of Eq. (4) from Eq. (3) yields the coexistence relationship for densities

$$\rho_{R_l} - \rho_{R_v} = \tfrac{7}{2}(1 - T_R)^{1/3}. \qquad (5)$$

The exponent, 1/3, of Eq. (5) obtained from experimental density measurements is considerably different from the value of 1/2 which results from all analytical equations of state, as pointed out by Pings (4).

1. Treatment of Available Density Data

Experimental values available in the literature for the density of cryogenic fluids, in their saturated liquid state, were collected and reduced to establish corresponding relationships of ρ_R versus T_R. Such a relationship resulting from the data of Herz (5) and Michels et al (6) is presented for argon in Fig. 1. A number of attempts were made to express the relationship of this figure in the form of a simple equation. When $\rho_R - 1$ was plotted against $1 - T_R$, using log-log coordinates, the experimental data for argon produced a straight line over the complete range included between $T_R = 0.597$ and $T_R = 1.00$, as shown in Fig. 2. The relationship of this figure can be expressed as follows:

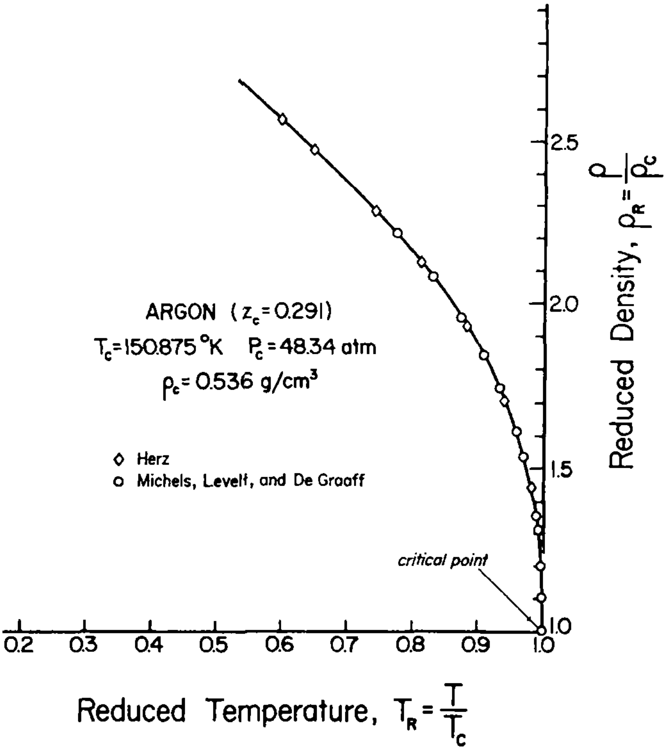

Figure 1. Reduced density-reduced temperature relationship for saturated liquid argon.

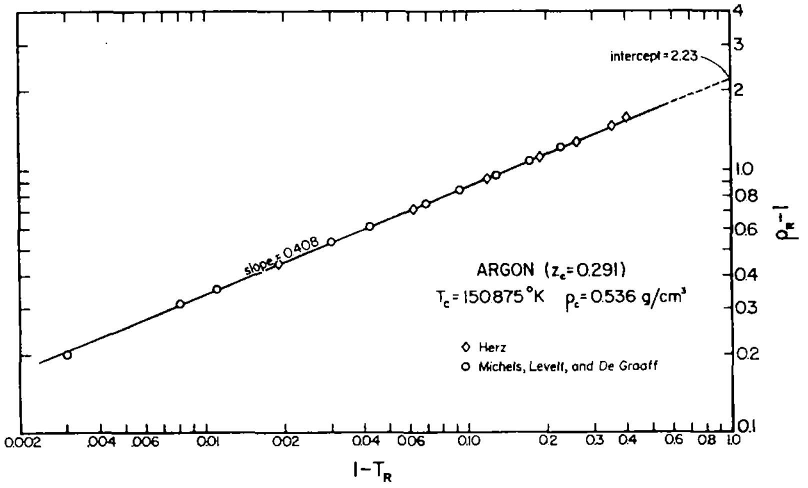

Figure 2. Linear relationship between $\rho_R - 1$ and $1 - T_R$ resulting from the saturated liquid density data for argon.

$$\log(\rho_R - 1) = \beta \log(1 - T_R) + \log k$$

or

$$\rho_R = 1 + k(1 - T_R)^\beta. \tag{6}$$

From Fig. 2, $\beta = 0.408$ and $k = 2.23$, for argon. The same behavior was found to exist with the other cryogenic fluids which include, hydrogen, neon, nitrogen, oxygen, carbon monoxide, and methane. Figure 3 presents this behavior for methane from which the values $\beta = 0.404$ and $k = 2.30$ were obtained. Table 1 lists the values of β and k obtained, as well as the sources of data, for all the seven substances included in this study.

Equation (6) when applied at $T_R = 0$, gives the value of k as $\rho_{R_0} - 1$ and therefore the hypothetical reduced density of the liquid at absolute zero becomes

$$\rho_{R_0} = 1 + k. \tag{7}$$

On the other hand, at the critical point, $T_R = 1$, Eq. (3) produces the value, $\rho_R = 1$.

2. Results and Conclusions

A careful examination of the values of β and k presented in Table 1

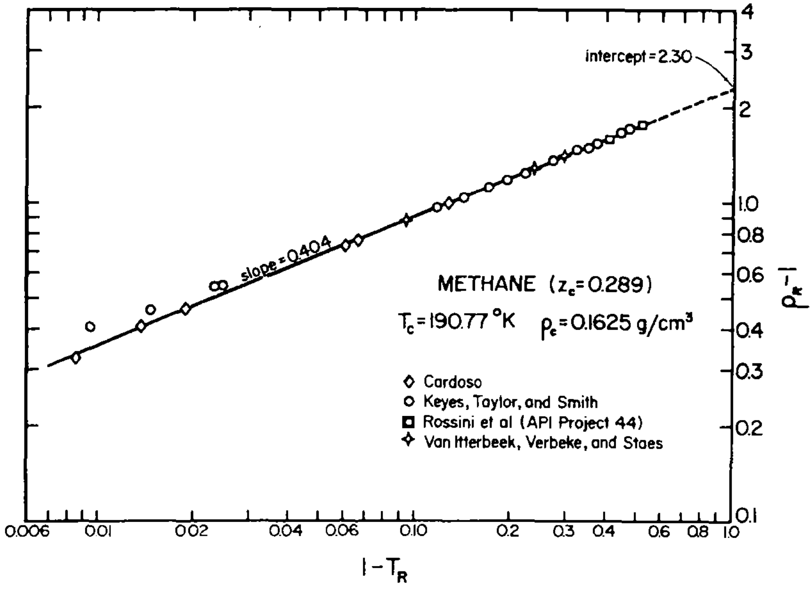

Figure. 3 Linear relationship between $\rho_R - 1$ and $1 - T_R$ resulting from the saturated liquid density data for methane.

shows that a corresponding state behavior almost exists for all the cryogenic fluids, except for hydrogen. The departure for this substance is not unexpected because of the excessive quantum deviations associated with it. Thus, the temperature dependence of the saturated liquid density for hydrogen becomes,

$$\rho_R = 1 + 1.82(1 - T_R)^{0.378} \quad \text{(hydrogen)}. \tag{8}$$

As seen from Table 1, the respective values of β and k are essentially the same for neon and argon. For these monatomic substances average values of β and k may be used. Hence, for them, Eq. (6) becomes,

$$\rho_R = 1 + 2.21(1 - T_R)^{0.410} \quad \text{(monatomic)}. \tag{9}$$

The remaining substances which include nitrogen, oxygen, carbon monoxide, and methane can be treated as a group since their respective parameters are nearly alike. For them, the average values are $\beta = 0.408$ and $k = 2.36$, and therefore, the saturated liquid density for this group of substances becomes,

TABLE 1 Critical Constants and Parameters β and k Obtained for Eq. (6)

	z_c	T_c°K	ρ_c g/cm^3	β	k	Source of Data
Neon	0.298	44.50	0.4835	0.413	2.20	(7)
Argon	0.291	150.875	0.536	0.408	2.23	(5), (6)
Hydrogen	0.305	33.3	0.0310	0.378	1.82	(8), (9), (10), (11), (12), (13), (14), (15), (16), (17), (18), (19), (20)
Nitrogen	0.291	126.2	0.311	0.409	2.37	(21), (22), (23), (24)
Oxygen	0.292	154.33	0.430	0.410	2.39	(21), (25), (26)
Carbon Monoxide	0.294	133	0.301	0.408	2.36	(21), (27)
Methane	0.289	190.77	0.1625	0.404	2.30	(28), (29), (30), (31)

$$\rho_R = 1 + 2.36(1 - T_R)^{0.408}. \qquad (10)$$

The parameters in Eq. (9) and (10) are nearly alike. The exponents 0.410 and 0.408 are for all practical purposes identical. The average value of the exponents, $\beta = 0.409$, is specific for the saturated liquid state. On the other hand, the exponent, $\beta = 1/3$, for the Guggenheim relationship, Eq. (5), is applicable to the coexistence curve. However, the slight difference in the constants 2.21 and 2.36 may be attributed to the difference in molecular complexity of the liquid state between monatomic and polyatomic species. The slightly higher value for the polyatomic molecules could well be the result of rotational and vibrational contributions that are absent in the case of the monatomic substances.

Equations (8), (9), and (10) were used to calculate saturated liquid densities which were compared with corresponding experimental values. Equation (8) yielded saturated liquid densities for hydrogen with an average deviation of 0.54% (85 points). In this comparison the 85 experimental points represent the values reported in the 13 references cited in Table 1. Typical experimental and calculated values covering the entire temperature range are presented in Table 2.

Using Eq. (9), saturated liquid densities for neon and argon were calculated and compared with corresponding experimental measurements which produced average deviations of 0.40% (10 points) and 0.54% (19 points), respectively. For comparison, typical calculated and corresponding experimental values, over the complete temperature range of neon and argon are shown in Table 2. The overall average deviation obtained with Eq. (9) is 0.49% (29 points).

Saturated liquid densities for nitrogen, oxygen, carbon monoxide, and methane were calculated using Eq. (10) and were compared with corresponding experimental values. The average deviations were found to be 0.47% (30 points), 0.82% (26 points), 1.20% (29 points), and 1.32% (42 points), respectively. The overall average deviation obtained from the use of Eq. (10) is 0.99% (127 points).

Typical experimental and calculated densities, rounded to the third decimal point, are presented in Table 2 for all the fluids of this study. The deviations presented in this table indicate that the general form of Eq. (6) properly defines saturated liquid densities

TABLE 2 Comparison Between Experimental and Calculated Saturated Liquid Densities of Cryogenic Fluids

T°K	Density, g/cm^3			
	expt'l	calc'd	%dev.	Source
Hydrogen				
(T_c= 33.3°K ρ_c= 0.0310g/cm^3)				
13.3	0.0763	0.0775	−1.61	6
14.0	0.0772	0.0769	0.36	15
14.64	0.0765	0.0763	0.19	10
14.89	0.0763	0.0761	0.28	7
15.0	0.076	0.076	0.01	13
15.47	0.0770	0.0768	0.23	11
16.0	0.0754	0.0750	0.49	18
16.3	0.0749	0.0748	0.19	9
17.97	0.0734	0.0731	0.49	7
18.24	0.0731	0.0728	0.41	16
19.0	0.0725	0.0720	0.68	15
20.35	0.0710	0.0705	0.72	12
22.0	0.0690	0.0685	0.67	18
23.11	0.0672	0.0671	0.27	17
25.21	0.0642	0.0641	0.17	17
27.27	0.0605	0.0606	−0.12	17
30.06	0.0540	0.0544	−0.68	8
31.26	0.0500	0.0506	−1.24	8
Nitrogen				
(T_c= 126.2°K ρ_c= 0.311g/cm^3				
64.80	0.862	0.858	0.41	21
67.71	0.850	0.847	0.31	20
71.0	0.839	0.835	0.50	22
73.13	0.826	0.826	−0.05	21
74.21	0.825	0.822	0.36	19
77.0	0.811	0.811	0.03	22
80.13	0.798	0.798	0.12	19
87.04	0.766	0.766	−0.01	19
90.65	0.743	0.749	−0.80	21
99.43	0.692	0.701	−1.25	20
111.96	0.607	0.612	−0.86	20
119.51	0.533	0.532	0.15	20
Carbon Monoxide				
(T_c= 133°K ρ_c= 0.301g/cm^3)				
68.12	0.847	0.831	1.90	25
72.20	0.839	0.817	2.58	19
78.01	0.806	0.796	1.24	25
82.77	0.794	0.778	1.95	19
86.97	0.775	0.762	1.76	19
90.26	0.754	0.748	0.85	25
100.91	0.700	0.699	0.12	25
107.59	0.662	0.663	−0.13	25
120.88	0.566	0.568	−0.44	25
127.79	0.492	0.490	0.30	25
130.53	0.440	0.441	−0.10	25
131.36	0.422	0.419	0.66	25

T°K	Density, g/cm^3			
	expt'l	calc'd	%dev.	Source
Neon				
(T_c= 44.50°K ρ_c= 0.4835g/cm^3)				
25.24	1.238	1.241	−0.26	5
27.22	1.204	1.208	−0.36	5
33.16	1.088	1.093	−0.48	5
37.90	0.967	0.971	−0.50	5
41.14	0.854	0.852	0.03	5
43.09	0.749	0.739	0.76	5
Argon				
(T_c= 150.875°K ρ_c= 0.536g/cm^3)				
90.01	1.374	1.352	1.57	3
97.77	1.325	1.308	1.27	3
116.84	1.186	1.180	0.56	4
122.40	1.138	1.134	0.40	3
131.63	1.048	1.046	0.27	4
140.44	0.935	0.932	0.30	4
141.62	0.915	0.913	0.20	3
144.46	0.864	0.859	0.40	4
148.04	0.772	0.769	0.49	4
150.78	0.590	0.592	−0.63	4
Oxygen				
(T_c= 154.33°K ρ_c= 0.430g/cm^3)				
62.76	1.275	1.250	1.92	23
68.7	1.246	1.228	1.44	24
72.59	1.226	1.213	1.03	19
74.0	1.221	1.207	1.11	24
77.17	1.204	1.195	0.79	19
83.6	1.174	1.168	0.50	24
86.06	1.163	1.158	0.43	19
90.2	1.143	1.139	0.33	24
118.65	0.976	0.988	−1.28	23
132.96	0.874	0.883	−1.00	23
143.26	0.778	0.776	0.23	23
149.86	0.678	0.669	1.28	23
Methane				
(T_c= 190.77°K ρ_c= 0.1625g/cm^3)				
93.2	0.445	0.454	−1.00	28
103.2	0.436	0.442	−1.24	28
110.02	0.426	0.433	−1.44	27
119.25	0.413	0.419	−1.62	27
128.70	0.399	0.405	−1.59	27
134.1	0.390	0.396	−1.72	29
145.3	0.370	0.376	−1.63	29
153.19	0.354	0.360	−1.68	27
166.15	0.324	0.329	−1.43	26
178.15	0.286	0.289	−1.20	26
186.05	0.251	0.247	1.48	27
189.15	0.216	0.217	−0.79	26

for these substances from the triple point up to and through the critical point. In particular, this relationship appears to apply very well in the vicinity of the critical point.

The Guggenheim relationship, Eq. (3), has also been used to calculate corresponding liquid densities for the fluids of this study. Since Eq. (3) does not apply to hydrogen, no attempt has been made to include this substance in this comparison. The deviations between experimental and calculated values are summarized in Table 3 and are also compared with the corresponding deviations obtained from the relationships of this study. With the exception of methane, the method of the present study possesses the capability of producing more exacting values for the saturated liquid densities. Also, a careful review of the densities predicted by this method shows positive and negative deviations from corresponding experimental values for all these substances. This consistency holds true only for carbon monoxide and methane when using the relationship of Guggenheim.

TABLE 3 Summary of Overall Average Deviations Resulting from Method of This Study and That of Guggenheim

		Average Deviation, %	
	No. of Points	Guggenheim	This Study
Neon	10	2.22	0.40
Argon	19	1.97	0.54
Nitrogen	30	1.38	0.47
Oxygen	26	1.37	0.82
Carbon Monoxide	29	2.43	1.20
Methane	42	0.57	1.32

The consequence of the present study has resulted in the development of a relationship represented by Eq. (6). This relationship requires that parameters β and k be established in order to define the density of a saturated liquid for temperatures extending up to the critical point. On the other hand, the Guggenheim form, if considered for substances other than cryogenic fluids will require three parameters to accomplish this objective. Furthermore, the present study treats the important cryogen, hydrogen, with its specific parameters, $\beta = 0.378$ and $k = 1.82$, while that of Guggenheim does not include this substance.

Nomenclature

k	constant, Equation (6)
P	absolute pressure
P_c	critical pressure
P_R	reduced pressure, P/P_c
R	gas constant
T	absolute temperature
T_c	critical temperature
T_R	reduced temperature, T/T_c
v	molar volume
z	compressibility factor, Pv/RT

Greek Letters

β	parameter, Equation (6)
ρ	density, g/cm^3
ρ_c	critical density, g/cm^3
ρ_R	reduced density for saturated liquid, ρ_l/ρ_c
ω	liquid expansion factor, P_R/zRT_R

Subscripts

l	saturated liquid state
v	saturated vapor state

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