Table I. Methyl Borate Liquid Compressibility Data

Temp., °C.	Press., Atm.	Density, Gram Moles/Liter
180.00	17.00	5.380
	20.00	5.408
	25.00	5.445
	30.00	5.476
	35.00	5.504
	40.00	5.530
202.17	25.00	4.821
	30.00	4.899
	35.00	4.975
	40.00	5.031
209.79	28.50	4.597
	30.00	4.647
	35.00	4.754
	40.00	4.824

The compressibility data are given in Table I. No comparison is possible since no other such data exist.

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Pressure-Volume-Temperature Behavior of Methyl Alcohol in the Gaseous and Liquid States

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P-V-T data available in the literature for methyl alcohol have been used to develop a reduced density correlation for this substance. The critical constants used are those determined by Young (22): T_c = 513.2° K., P_c = 78.50 atm., and ρ_c = 0.272 gram/cc. In order to extend the P-V-T information for methyl alcohol over the complete range of temperatures up to T_R = 2.0 and pressures up to P_R = 40, the Nelson-Obert compressibility factor charts (14) and the available reduced density correlations for water (21) and ammonia (6) have been used. The resulting reduced density plots for methyl alcohol are capable of reproducing experimental values within 1.1%.

CONTINUED INTEREST in the transport and thermodynamic properties of polar and nonpolar substances requires that their P-V-T behavior be accurately known over a wide range of temperatures and pressures. Lydersen, Greenkorn, and Hougen (13) have made an extensive study using 82 different substances, and they have utilized the critical compressibility factor, z_c, as the third correlating parameter in order to represent the P-V-T behavior of both polar and nonpolar substances. In their studies, they classified all substances in the following four categories: 0.28 < z_c < 0.30, 0.26 < z_c < 0.28, 0.24 < z_c < 0.26, and z_c = 0.231, to represent the P-V-T behavior of water which is highly polar and exhibits strong hydrogen bonding tendencies. Despite the fact that the critical compressibility factor has been applied extensively for the correlation of the P-V-T behavior of substances, little effort has been made to extend these studies to polar substances having values of z_c < 0.231, and particularly in the compressed gaseous and liquid regions. In this regard, methyl alcohol with z_c = 0.219 represents a polar molecule with strong hydrogen bonding tendencies.

Hobson and Weber (10) produced unique saturation density envelopes for substances having similar z_c values. Their conclusions are well demonstrated for a number of substances having values ranging from z_c = 0.219 for methyl alcohol to z_c = 0.291 for nitrogen. Hall and Ibele (7), in their compressibility studies of polar gases, introduced the dipole moment as an additional parameter to account for the polar contributions of molecules, and they developed correction charts to account for the deviation from a standard compressibility chart obtained from the P-V-T data of the rare gases. Lydersen, Greenkorn, and Hougen (13) plotted z_c values against the reduced dipole moment, $\mu(P_c)^{1/2}/RT_c$, and concluded that no suitable correlation exists between these variables.

Thodos and coworkers comprehensively investigated the P-V-T behavior of substances of similar critical compressibility factors. For the monatomic gases, argon, krypton, and xenon (9), and the diatomic gases, nitrogen, oxygen, and carbon monoxide (3), the critical compressibility factor of which ranges from z_c = 0.290 for xenon to z_c = 0.294 for carbon monoxide, a single correlation of reduced density vs. reduced temperature, with constant reduced pressure as a parameter, applies equally well for the dense gaseous and liquid states. Similar reduced density correlations have been developed specifically for carbon dioxide (11), ammonia (6), and water (21) having z_c values of 0.275, 0.242, and 0.231, respectively.

To cover the complete spectrum of P-V-T behavior, methyl alcohol, with z_c = 0.219, was selected for investiga-
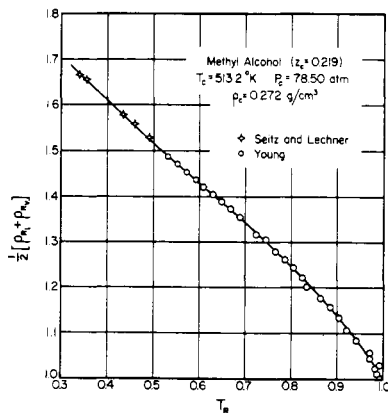
530

Figure 1. Cailletet-Mathias relationship for
methyl alcohol

tion because this substance is polar in nature and also
exhibits a very low z_c value. Methyl alcohol possesses a
dipole moment because the electron pair required to make
up the bonds between oxygen and hydrogen lies closer to
the oxygen atom. Consequently, the hydrogen portion of
the molecule is positively charged and the remainder of the
molecule is negatively charged. Alcohols and ammonia
belong to this category, since these substances contain both
active hydrogen atoms and donor atoms (oxygen and
nitrogen). On the other hand, water forms a three dimen-
sional network of strong hydrogen bonds. Ordinarily, simple
substances having critical compressibility factors of low
order of magnitude are polar. A dipole moment of 1.66 D.
is reported for methyl alcohol (8), while those of water and
ammonia (23) are 1.87 and 1.44 D., respectively.

DEVELOPMENT OF REDUCED DENSITY CORRELATION

A comprehensive literature survey revealed eight per-
tinent references which included P-V-T measurements of
methyl alcohol in limited temperature and pressure ranges
of the gaseous and liquid states. To maintain consistency
with previous work of this type dealing with the P-V-T
behavior of the monatomic gases, helium, neon, argon,
krypton, and xenon (9), the diatomic gases, nitrogen,
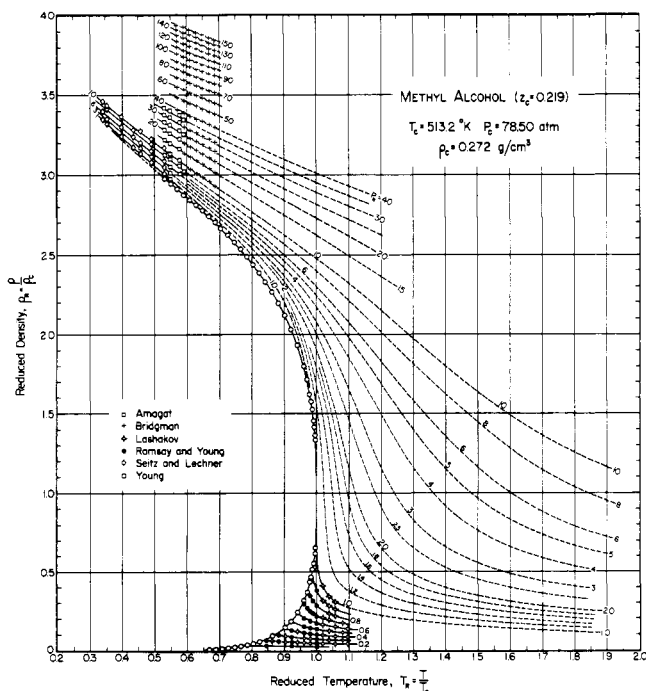oxygen, and carbon monoxide (3), hydrogen (18), carbon

dioxide (11), ammonia (6), and water (21), reduced density,
reduced temperature, and reduced pressure have been used
as the variables to describe the P-V-T behavior of methyl
alcohol. The available experimental P-V-T data of methyl
alcohol were transformed into these reduced quantities
using the critical values reported by Young (22), T_c =
513.2° K., P_c = 78.50 atm. and ρ_c = 0.272 gram/cc.

The experimental measurements of Young (22) permitted
the construction of the saturation density envelope for
reduced temperatures ranging from T_R = 0.532 up to the
critical point. These saturated density values were used to
construct a Cailletet-Mathias relationship by plotting
$\frac{1}{2}[\rho_{R_i} + \rho_{R_v}]$ vs. T_R, which is presented in Figure 1. For
reduced temperatures of T_R < 0.529, the atmospheric
pressure liquid densities of Seitz and Lechner (20) were used
to extend the Cailletet-Mathias relationship as low as
T_R = 0.341. Densities for the gaseous state were experi-
mentally established by Ramsay and Young (15) in 1887,
by Lashakov (12) in 1939, and by Russell and Maass (17)
(low pressure region only) in 1931. The work of Ramsay
and Young (15), together with vapor pressure data avail-
able in the literature (4,5,15,16,19,22), was utilized to
establish the intersections of the gaseous region isotherms
with the saturation density envelope. Since the P-V-T data
of all these investigators are reported at constant tempera-
tures, it became necessary to cross plot them in order to
obtain the ρ_R vs. T_R values used to develop the final constant
pressure relationships presented in Figures 2 and 3. Figure 3
shows that the experimental data lie in the limited range
between the saturated vapor curve and T_R = 1.097 and
pressures as low as P_R = 0.006.

The experimental compressibility data of Amagat (1),
Bridgman (2), and Seitz and Lechner (20) constitute the
liquid density data available for this region. Figures 2 and 3
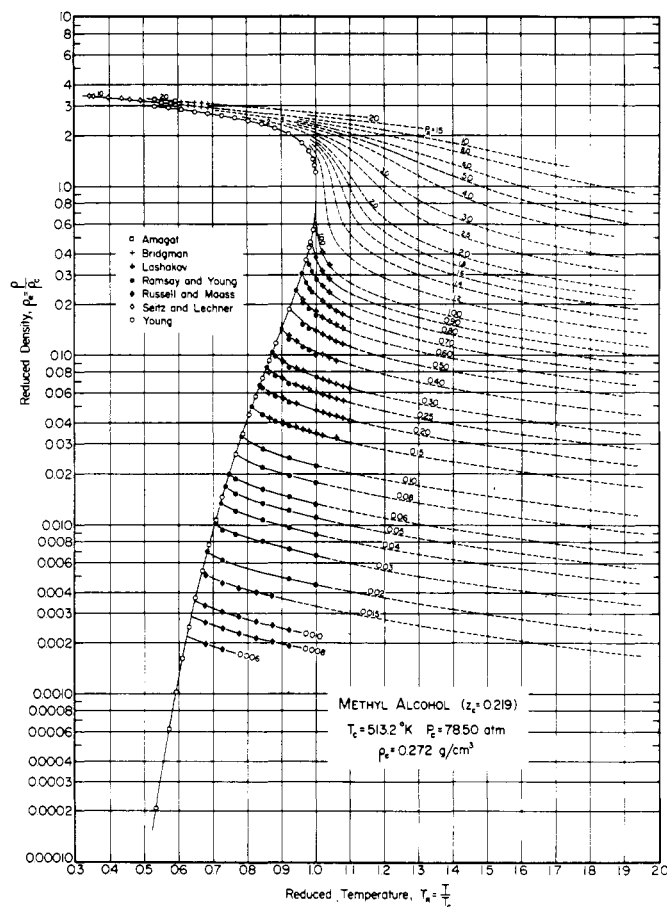include the cross-plotted values resulting from their original

Figure 2. Reduced density correlation of methyl alcohol
(rectilinear coordinates)

Figure 3. Reduced density correlation of methyl alcohol
(semilogarithmic coordinates)

Table I. Reduced Density Values for Methyl Alcohol

$T_c = 513.2°$ K. $P_c = 78.50$ atm. $\rho_c = 0.272$ gram/cc. $z_c = 0.219$

T_R	Saturated Liquid	Saturated Vapor	$P_R=0.006$	$P_R=0.008$	$P_R=0.010$	$P_R=0.015$	$P_R=0.020$	$P_R=0.03$	$P_R=0.04$	$P_R=0.06$	$P_R=0.08$	$P_R=0.10$
0.35	3.318											
0.40	3.221											
0.50	3.040											
0.60	2.860	0.00127										
0.70	2.674	0.00940	0.00189	0.00253	0.00320	0.00480	0.00660					
0.80	2.450	0.0420		0.00220	0.00277	0.00412	0.00554	0.00840	0.0113	0.0174	0.0239	0.0313
0.85	2.305	0.0800		0.00208	0.00259	0.00390	0.00520	0.00789	0.0106	0.0160	0.0217	0.0279
0.90	2.130	0.145		0.00195	0.00243	0.00369	0.00490	0.00740	0.00990	0.0150	0.0200	0.0256
0.925	2.020	0.195				0.00358	0.00479	0.00720	0.00960	0.0145	0.0194	0.0247
0.95	1.882	0.270				0.00349	0.00468	0.00700	0.00932	0.0140	0.0189	0.0238
0.975	1.680	0.392				0.00340	0.00455	0.00680	0.00908	0.0137	0.0183	0.0230
1.000	1.000	1.000				0.00330	0.00444	0.00662	0.00880	0.0133	0.0178	0.0225
1.025						0.00322	0.00432	0.00645	0.00860	0.0129	0.0173	0.0218
1.050						0.00314	0.00421	0.00630	0.00840	0.0126	0.0168	0.0212
1.075						0.00307	0.00412	0.00611	0.00820	0.0123	0.0164	0.0208
1.10						0.00300	0.00402	0.00599	0.00800	0.0120	0.0160	0.0201
1.15						0.00287	0.00387	0.00570	0.00761	0.0115	0.0152	0.0193
1.20						0.00274	0.00370	0.00541	0.00729	0.0110	0.0145	0.0185
1.30						0.00252	0.00340	0.00499	0.00670	0.0102	0.0134	0.0170
1.40						0.00233	0.00316	0.00460	0.00624	0.00949	0.0125	0.0157
1.50						0.00218	0.00290	0.00430	0.00583	0.00880	0.0116	0.0145
1.60						0.00202	0.00270	0.00404	0.00549	0.00820	0.0109	0.0136
1.80						0.00180	0.00240	0.00361	0.00489	0.00723	0.00965	0.0121
2.00						0.00163	0.00218	0.00327	0.00439	0.00658	0.00860	0.0110
Saturated at T_R			0.00221	0.00284	0.00352	0.00520	0.00696	0.0102	0.0134	0.0199	0.0262	0.0330
			0.623	0.636	0.648	0.667	0.682	0.705	0.721	0.747	0.766	0.783

T_R	Liquid	Vapor	$P_R=0.15$	$P_R=0.20$	$P_R=0.25$	$P_R=0.30$	$P_R=0.40$	$P_R=0.50$	$P_R=0.60$	$P_R=0.70$	$P_R=0.80$	$P_R=0.90$
0.35	3.318											
0.40	3.221											
0.50	3.040											
0.60	2.860	0.00127										
0.70	2.674	0.00940										
0.80	2.450	0.0420										
0.85	2.305	0.0800	0.0440	0.0632								
0.90	2.130	0.145	0.0393	0.0559	0.0732	0.0935						
0.925	2.020	0.195	0.0379	0.0530	0.0690	0.0870	0.128					
0.95	1.882	0.270	0.0365	0.0510	0.0660	0.0823	0.118	0.167	0.232			
0.975	1.680	0.392	0.0352	0.0490	0.0630	0.0782	0.111	0.153	0.198	0.260		
1.000	1.000	1.000	0.0343	0.0472	0.0605	0.0750	0.105	0.140	0.179	0.228	0.285	0.380
1.025			0.0331	0.0455	0.0580	0.0718	0.0995	0.131	0.165	0.204	0.249	0.302
1.050			0.0322	0.0440	0.0560	0.0690	0.0950	0.123	0.153	0.187	0.225	0.269
1.075			0.0314	0.0443	0.0540	0.0660	0.0910	0.118	0.144	0.175	0.208	0.247
1.10			0.0305	0.0412	0.0522	0.0640	0.0870	0.112	0.138	0.165	0.197	0.231
1.15			0.0290	0.0390	0.0494	0.0600	0.0820	0.104	0.126	0.151	0.179	0.208
1.20			0.0278	0.0370	0.0469	0.0568	0.0770	0.0975	0.199	0.141	0.165	0.192
1.30			0.0255	0.0338	0.0422	0.0515	0.0692	0.0870	0.105	0.124	0.145	0.168
1.40			0.0238	0.0310	0.0390	0.0475	0.0635	0.0800	0.0960	0.118	0.131	0.149
1.50			0.0220	0.0290	0.0363	0.0442	0.0583	0.0740	0.0888	0.103	0.120	0.136
1.60			0.0204	0.0270	0.0340	0.0415	0.0545	0.0690	0.0817	0.095	0.111	0.126
1.80			0.0180	0.0240	0.0301	0.0363	0.0480	0.0606	0.0715	0.0839	0.0964	0.108
2.00			0.0161	0.0217	0.0270	0.0322	0.0430	0.0540	0.0640	0.0745	0.0860	0.096
			0.0498	0.0665	0.0850	0.103	0.143	0.189	0.241	0.304	0.385	0.498
			0.812	0.836	0.856	0.873	0.899	0.923	0.942	0.959	0.974	0.987

data. Figure 2 presents best these data in the liquid region, which are confined to temperatures of $T_R < 0.688$ and pressures as high as $P_R = 150$. Amagat's data are somewhat higher than those of Bridgman, particularly in the high pressure region. Good agreement existed between the data of Bridgman (2) and Seitz and Lechner (20).

The density data, presented in Figures 2 and 3, constitute the only experimental P-V-T information available to date for methyl alcohol. Although this density information is valuable to studies concerned with the thermodynamic and transport properties of this substance, its application is limited to temperatures of $T_R \leq 1.097$ and an incomplete range of pressures. To extend the isobars of Figures 2 and 3, the compressibility data of water (21) and ammonia (6) have been used.

The extension of the isobar, $P_R = 1.00$, was accomplished by the use of the reduced density plots of ammonia and water (6,21) and the following relationship, applicable at constant reduced density:

$$\frac{T_R}{T_{R_i}} = \left(\frac{T_R}{T_{R_i}}\right)_{H_2O, NH_3} \tag{1}$$

Equation 1 refers to the saturated state and assumes that the temperature ratio, T_R/T_{R_i}, at constant reduced density is the same for methyl alcohol, ammonia, and water. In this equation, the reduced temperature, T_R, refers to the same reduced pressures for these three substances. Both water and ammonia gave practically the same results up to $T_R = 0.9$. A comparison with experimental values produced an average deviation of 2.6% in this region. For $T_R > 0.9$, the values resulting from the use of the water plot were nearly consistent with the data of Lashakov (12), and therefore they were extended from the highest value of Lashakov, $T_R = 1.058$, to $T_R = 2.00$.

To check the calculated values for the critical isobar, $P_R = 1.00$, the compressibility factor correlations of Nelson and Obert (14), together with the theorem of corresponding states, have been applied, using the following generalized P-V-T relationship:

$$\frac{\rho_R}{\rho'_R} = z' \frac{P_R}{P'_R} \frac{T'_R}{T_R} \tag{2}$$

Table I. Reduced Density Values for Methyl Alcohol (Continued)

$T_c = 513.2°$ K. $P_c = 78.50$ atm. $\rho_c = 0.272$ gram/cc. $z_c = 0.219$

T_R	Saturated Liquid	Vapor	$P_R = 1.0$	$P_R = 1.2$	$P_R = 1.4$	$P_R = 1.6$	$P_R = 1.8$	$P_R = 2.0$	$P_R = 2.5$	$P_R = 3.0$	$P_R = 4.0$	$P_R = 5.0$
0.35	3.318		3.331							3.360		3.383
0.40	3.221		3.241							3.270		3.300
0.50	3.040		3.061							3.101		3.131
0.60	2.860	0.00127	2.889					2.911		2.935		2.972
0.70	2.674	0.00940	2.708					2.735		2.762	2.789	2.811
0.80	2.450	0.0420	2.503					2.545		2.582	2.615	2.648
0.85	2.305	0.0800	2.376					2.438		2.481	2.522	2.559
0.90	2.130	0.145	2.210					2.300	2.339	2.370	2.420	2.468
0.925	2.020	0.195	2.095		2.168			2.222	2.270	2.310	2.365	2.417
0.95	1.882	0.270	1.950	2.005	2.050			2.136	2.194	2.241	2.305	2.363
0.975	1.680	0.392	1.750	1.840	1.905			2.035	2.109	2.166	2.243	2.305
1.000	1.000	1.000	1.000	1.590	1.703	1.795	1.863	1.912	2.012	2.081	2.174	2.248
1.025			0.380	0.960	1.433	1.593	1.683	1.762	1.900	1.990	2.100	2.183
1.050			0.320	0.510	0.980	1.320	1.483	1.572	1.770	1.890	2.020	2.119
1.075			0.289	0.420	0.640	0.960	1.231	1.374	1.619	1.779	1.942	2.050
1.10			0.269	0.378	0.521	0.731	0.950	1.171	1.461	1.650	1.858	1.982
1.15			0.240	0.321	0.422	0.538	0.663	0.824	1.163	1.400	1.679	1.847
1.20			0.220	0.288	0.367	0.450	0.542	0.650	0.919	1.160	1.500	1.700
1.30			0.190	0.242	0.300	0.351	0.416	0.481	0.653	0.830	1.158	1.414
1.40			0.170	0.211	0.260	0.301	0.349	0.400	0.526	0.659	0.917	1.158
1.50			0.154	0.190	0.230	0.269	0.308	0.349	0.450	0.558	0.767	0.970
1.60			0.142	0.174	0.208	0.243	0.277	0.311	0.400	0.489	0.660	0.836
1.80			0.124	0.149	0.176	0.206	0.232	0.262	0.332	0.404	0.537	0.669
2.00			0.110	0.132	0.156	0.173	0.208	0.232	0.288	0.350	0.469	0.570
			1.000									
1.000												

T_R	Liquid	Vapor	$P_R = 6.0$	$P_R = 8.0$	$P_R = 10.0$	$P_R = 15$	$P_R = 20$	$P_R = 25$	$P_R = 30$	$P_R = 35$	$P_R = 40$
0.35	3.318		3.398	3.419	3.443						
0.40	3.221		3.315	3.335	3.365						
0.50	3.040		3.149	3.171	3.208	3.265					
0.60	2.860	0.00127	2.990	3.018	3.059	3.130	3.195	3.248	3.296	3.341	3.384
0.70	2.674	0.00940	2.833	2.870	2.913	3.000	3.070	3.132	3.188	3.240	3.289
0.80	2.450	0.0420	2.674	2.726	2.771	2.872	2.952	3.020	3.083	3.140	3.192
0.85	2.305	0.0800	2.592	2.650	2.700	2.810	2.899	2.969	3.032	3.093	3.148
0.90	2.130	0.145	2.504	2.570	2.630	2.750	2.840	2.914	2.984	3.046	3.100
0.925	2.020	0.195	2.458	2.530	2.590	2.719	2.815	2.890	2.960	3.021	3.079
0.95	1.882	0.270	2.408	2.490	2.558	2.688	2.790	2.863	2.938	3.000	3.057
0.975	1.680	0.392	2.357	2.445	2.519	2.657	2.760	2.840	2.914	2.978	3.033
1.000	1.000	1.000	2.303	2.400	2.480	2.623	2.734	2.813	2.890	2.955	3.013
1.025			2.249	2.354	2.440	2.591	2.708	2.790	2.870	2.932	2.992
1.050			2.190	2.309	2.400	2.560	2.679	2.768	2.847	2.911	2.971
1.075			2.134	2.260	2.362	2.530	2.650	2.744	2.825	2.890	2.950
1.10			2.076	2.211	2.320	2.498	2.620	2.720	2.800	2.870	2.930
1.15			1.953	2.115	2.238	2.430	2.563	2.671	2.760	2.828	2.890
1.20			1.828	2.018	2.150	2.366					
1.30			1.583	1.818	1.975	2.231					
1.40			1.358	1.629	1.800	2.100					
1.50			1.160	1.450	1.638	1.974					
1.60			1.001	1.282	1.488						
1.80			0.790	1.035	1.251						
2.00			0.673	0.879							

where the primed values refer to a dependable density value for methyl alcohol. For the same reduced pressure, $P_R = P'_R$, Equation 2 simplifies to the following expression:

$$\rho_R = \frac{z'}{z} \frac{T'_R}{T_R} \rho'_R \qquad (3)$$

Using the experimental density of methyl alcohol for the highest temperature reported by Lashokov (12), $T_R = 1.058$ at $P_R = 1.00$, this approach produced densities that were consistent with those obtained earlier by the use of the water density correlation.

For reduced pressures of $P_R < 1.00$, the application of the Nelson-Obert compressibility factor charts produced densities that were in agreement with the experimental values of Ramsay and Young (15), Lashakov (12), and Russell and Maass (17). The average deviation resulting from these comparisons was 1.8% only, and consequently this approach was used to extend all the isobars below $P_R = 1.00$ to $P_R = 0.10$ for reduced temperatures up to $T_R = 2.00$. For the low pressure region, $0.04 < P_R < 0.09$, the isobars were extended up to $T_R = 1.8$, again using the Nelson-Obert compressibility charts. For temperatures from $T_R = 1.8$ to

$T_R = 2.0$, these extensions were made by assuming that the perfect gas law applied in this region. A cross-plot of ρ_R vs. P_R on log-log coordinates, at constant reduced temperatures, produced linear relationships that permitted the extension of the isobars below $P_R = 0.04$.

In the dense gaseous region above $T_R = 1.1$ and reduced pressures between $P_R = 1.00$ and $P_R = 2.5$, Equation 3 with the Nelson-Obert charts and the water-density correlation, together with Equation 1, produced consistent reduced density values for methyl alcohol up to $T_R = 2.00$. To check the validity of these isobars, Equation 2 was applied using the isothermal conditions, $T_R = T'_R$, and the resulting relationship,

$$\rho_R = \frac{z'}{z} \frac{P_R}{P'_R} \rho'_R \qquad (4)$$

The density values for methyl alcohol, produced from this isothermal condition, were in good agreement with those developed previously when using the isobaric approach for $T_R > 1.00$. In the compressed liquid region ($T_R < 0.9$), the application of the ammonia density correlation produced densities that were in agreement within 1.7% with the

available experimental data of methyl alcohol. For the temperature range $0.9 < T_R < 1.1$, the water density correlation produced densities that permitted the values below $T_R = 0.9$ and above $T_R = 1.1$ to be properly connected with a smooth curve.

The reduced density correlations of ammonia and water were used to develop the isobars above $P_R = 2.5$. The density correlation for ammonia, using Equation 1, applied well in the compressed liquid region and produced values that were within 1.0% of the experimental values. All the isobars up to $P_R = 40$, for temperatures up to $T_R = 1.1$, were developed from the ammonia correlation. However, the ammonia plot was assumed not to apply for reduced temperatures above $T_R = 1.1$, since this correlation failed to produce results that were consistent with available experimental densities, with values resulting from the water-density correlation, and with the Nelson-Obert compressibility charts for pressures below $P_R = 2.5$. On the other hand, the use of the water-density correlation at elevated temperatures produced isobars that properly joined with those obtained at lower temperatures when using the ammonia-density correlation.

CONCLUSIONS

Figures 2 and 3 present the final plots of density for methyl alcohol, which resulted from P-V-T data available in the literature and from their extension into regions of pressure and temperature where no data are currently available. Reduced density values read from enlarged plots of Figures 2 and 3 are presented in Table I. The accuracy of the reduced density correlation for methyl alcohol cannot be checked over the complete range of temperature and pressure, but has been checked in regions where data are available, to produce an over-all average deviation of 1.1% resulting from a total of 45 experimental points. The Lydersen, Greenkorn, and Hougen (13) density development cannot be properly compared with the results of Figures 2 and 3, since these investigators did not include the behavior of substances with critical compressibility factors below that of water, $z_c = 0.231$.

NOMENCLATURE

P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 82.055 cm.^{3} atm./gram-mole ° K.

T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c
T_{R_s} = reduced temperature at saturated conditions
v = molar volume, cm.^{3}/gram-mole
v_c = critical molar volume, cm.^{3}/gram-mole
z = compressibility factor, Pv/RT
z_c = critical compressibility factor, $P_c v_c / RT_c$

Greek

μ = dipole moment, debye units
ρ = density, grams/cm.^{3}
ρ_c = critical density, grams/cm.^{3}
ρ_R = reduced density, ρ/ρ_c
ρ_{R_l} = reduced density for saturated liquid
ρ_{R_v} = reduced density for saturated vapor

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Standard Heats of Formation of Paraperiodic Acid at 25°

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PERIODIC ACIDS are important compounds representative of the highest oxidation state of iodine, +7. The stable room temperature form in the solid state is paraperiodic acid, H_5IO_6. Its aqueous solution is widely used in iodimetric analytical procedures as an oxidizing agent which is powerful enough to quantitatively oxidize manganous ion to permanganate.

Very little thermodynamic information is available for any forms of periodic acid. Circular 500 of the National Bureau of Standards (3) lists some heats of formation based on Thomsen's data (6) which are more than 80 years old. Heats of formation of other halogen compounds and ions based on results from the older literature have sometimes been found to be in conflict with more recent values.