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

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TO BROADEN the background of the *P-V-T* behavior of substances, the application of the critical compressibility factor, z_c, as the third correlating parameter has been extended to include a substance not belonging to the class of the inert gases, diatomic gases, or hydrocarbons. A review of the order of magnitude of z_c values shows a variation from 0.291 to 0.231 for substances not possessing any quantum deviations.

The *P-V-T* behavior of the inert gases has been comprehensively studied by Hamrin and Thodos (*14*). Comparable studies on the diatomic gases have been presented by Byrne (*7*). For argon, krypton, and xenon as well as for nitrogen, oxygen, and carbon monoxide, the available literature *P-V-T* data indicate a variation in z_c from 0.294 to 0.290. These substances produced reduced state correlations for density that were essentially the same. Kennedy (*19*) developed a reduced density correlation for carbon dioxide from literature data. The resulting correlation was considerably different from that developed for the inert and diatomic gases, despite the fact that carbon dioxide is essentially a nonpolar substance. This behavior must be due to the substantially different critical compressibility factor for carbon dioxide ($z_c = 0.275$).

To extend these studies to substances having lower z_c values, ammonia was arbitrarily selected for investigation. Ammonia has a critical compressibility factor of $z_c = 0.242$, which is close to the lower limiting value reported for water, $z_c = 0.231$. Ordinarily, simple substances having critical

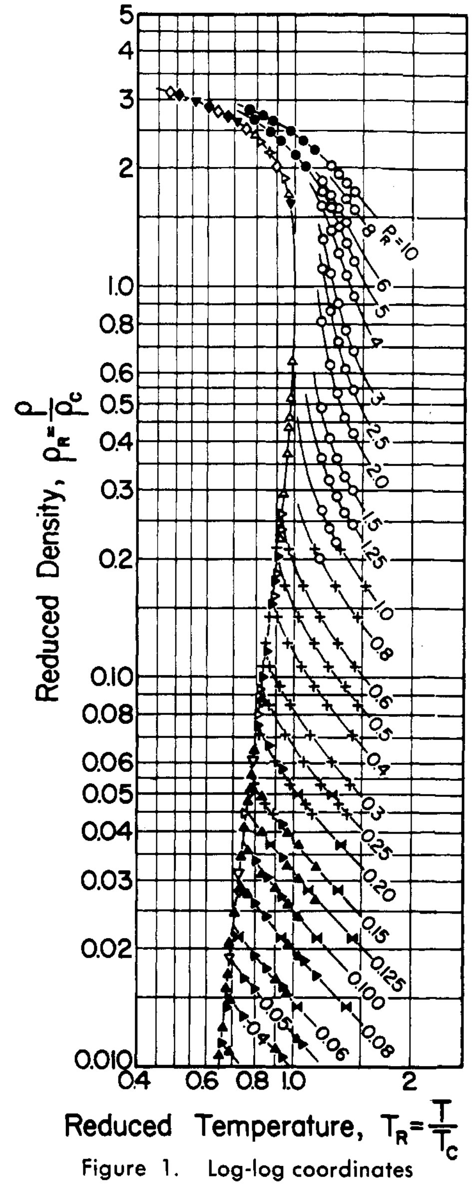

Figure 1. Log-log coordinates

For legend, see Figure 2

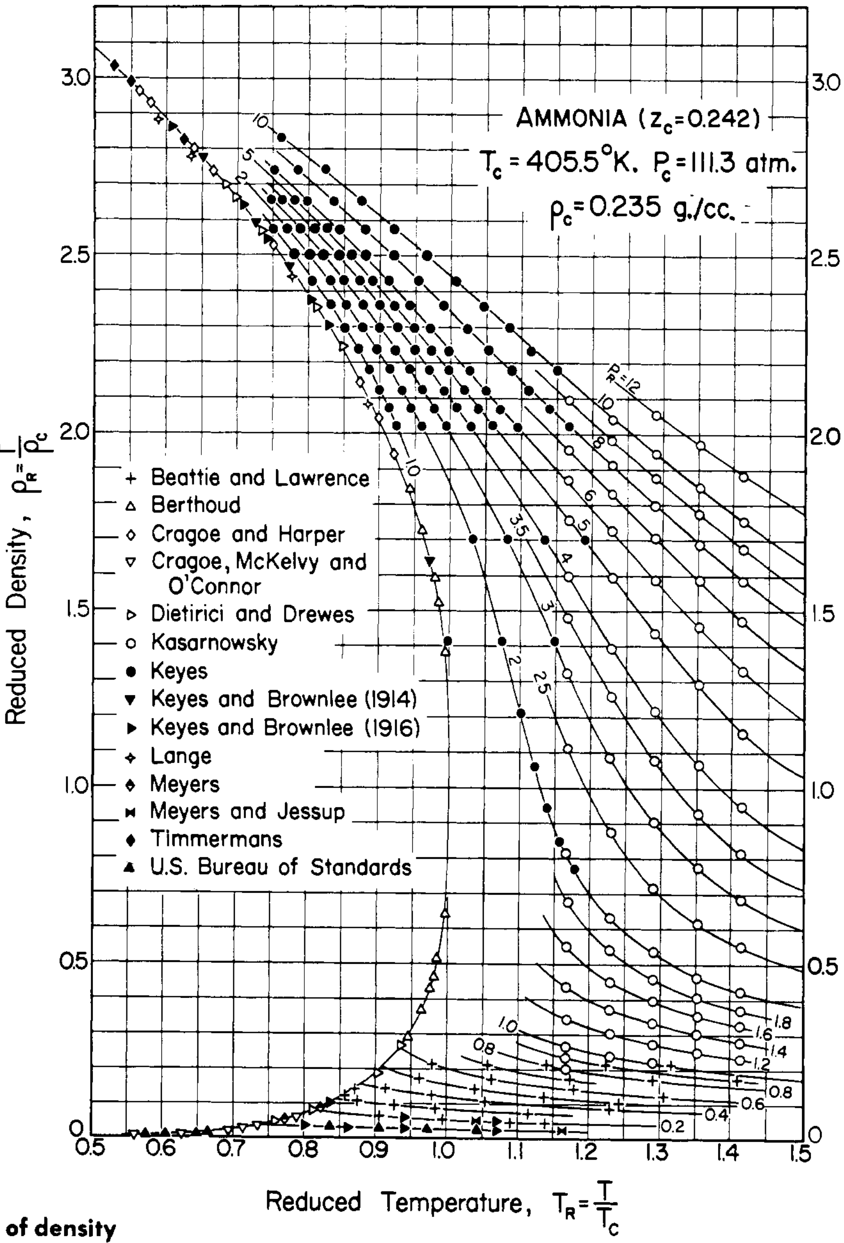

Figure 2. Rectilinear coordinates

Development of density correlation for ammonia from literature values

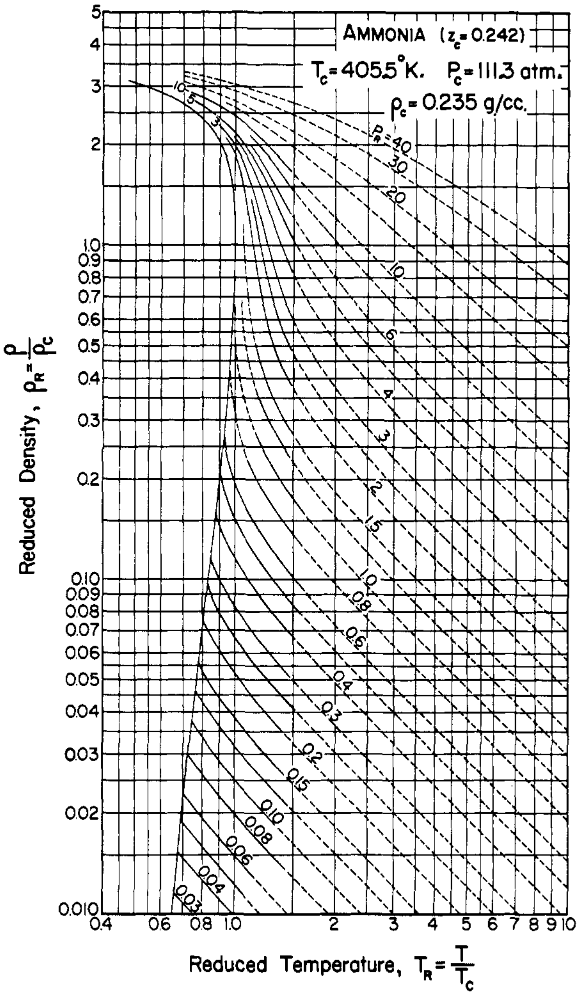

Figure 3. Log-log coordinates

compressibility factors of this order of magnitude are polar. A dipole moment of 1.437 debyes is reported for ammonia (*16, 26*), while that for water is found to be 1.87 debyes.

CORRELATION OF P-V-T DATA

The available experimental data in the literature for ammonia have been comprehensively examined, to eliminate inconsistent values. Several of the references required cross-plotting of the data to obtain the variation of density with temperature at constant pressure. The critical constants reported by Kobe and Lynn (*25*) have been used to produce reduced temperature, pressure, and density values. The critical values of ammonia are T_c = 405.5° K., P_c = 111.3 atm., and ρ_c = 0.235 gram per cc. From these values a critical compressibility factor of z_c = 0.242 was obtained.

Considerable density information is available for the saturated vapor and liquid states, permitting a complete definition of the saturated envelope. Of interest are the low temperature data for the liquid state presented by Timmermans (*36*) and Cragoe and Harper (*8*). Additional data for both the saturated liquid and vapor states of Berthoud (*3*) and Keyes and Brownlee (*22, 24*) as well as the excellent work of Meyers (*29*) and Meyers and Jessup (*30*) permit the complete definition of the saturated envelope.

The P-V-T behavior of ammonia for pressures below P_R = 1.0 and temperatures up to T_R = 1.5 is defined from the works of Beattie and Lawrence (*1*), Keyes and Brownlee (*23*), and Meyers and Jessup (*30*). From their data, isobars for pressures less than P_R = 1.0 were established and extended to the saturated vapor curve using vapor pressure data to define the saturated density of each isobar. Data for ammonia (*2, 4, 5, 10-12, 15, 17, 20, 23, 31, 33, 35*) were treated along the lines proposed by Sondak and Thodos (*34*) to produce the vapor pressure equation

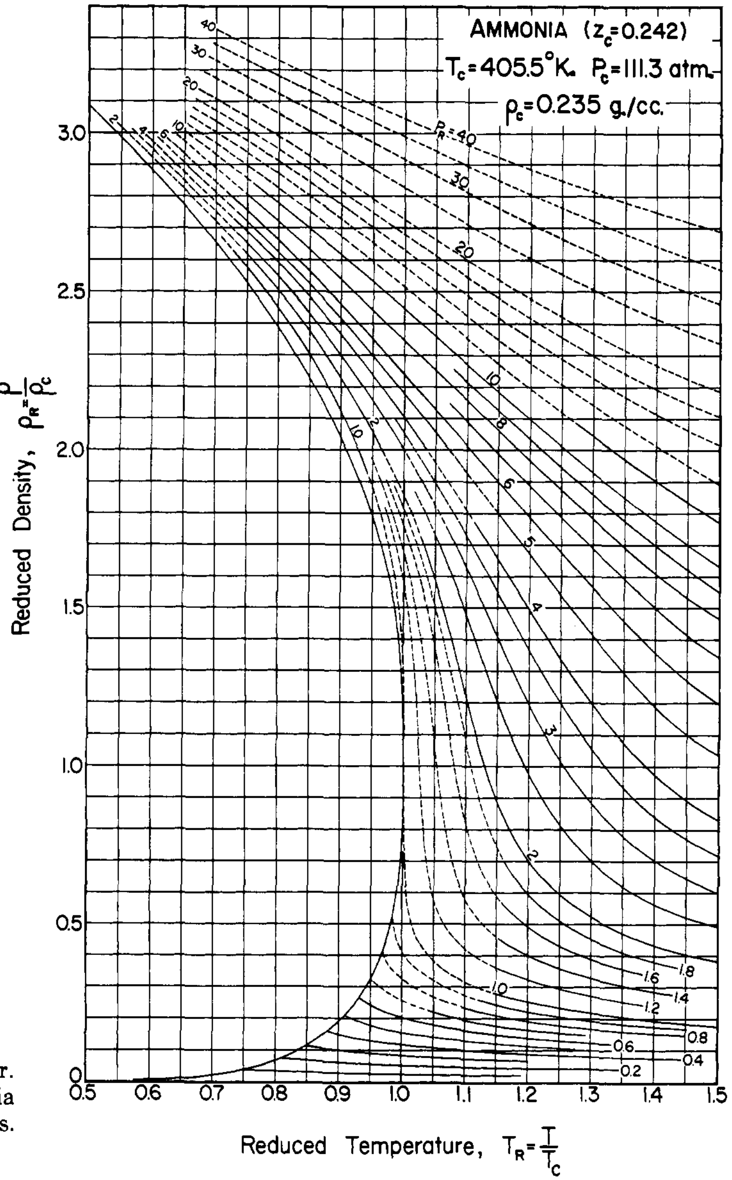

Figure 4. Rectilinear coordinates

$$\log p = 21.28466 - \frac{1728.18}{T} - 4.70589 \log T + 0.35603 \frac{p}{T^2} \qquad (1)$$

which is applicable from the triple point to the critical point.

The dense phase region is established from the contributions of the only two available sources of Keyes (*21*) and Kasarnowsky (*18*). Without this information the behavior of ammonia in the dense phase region would highly speculative. The regions investigated by Keyes and Kasarnowsky do not overlap. The data of Keyes are restricted to the region between the saturated liquid line and the isobar P_R = 10 for temperatures ranging from T_R = 0.75 to T_R = 1.15. Consistent with the work of Keyes is that of Kasarnowsky which extends the isobars up to T_R = 1.42, except the region in the vicinity of the critical point. To obtain the behavior in this region, the P-V-T data available for water (*6*) were used to extend the isobars. For this operation, water was selected as a reference substance because its critical compressibility factor and polarity values and those of ammonia are nearly alike.

Table I. Reduced Density Values for Ammonia

	Saturated								
T_R	Liquid	Vapor	$P_R = 0.03$	$P_R = 0.04$	$P_R = 0.05$	$P_R = 0.06$	$P_R = 0.08$	$P_R = 0.10$	$P_R = 0.15$
0.50	3.086								
0.60	2.881								
0.70	2.653	0.023	0.0108	0.0147	0.0186				
0.80	2.386	0.070		0.0126	0.0158	0.0193	0.0261	0.0335	0.0528
0.85	2.227	0.114		0.0118	0.0148	0.0180	0.0241	0.0308	0.0476
0.90	2.040	0.192		0.0111	0.0138	0.0168	0.0225	0.0287	0.0440
0.95	1.793	0.328		0.0104	0.0130	0.0157	0.0211	0.0268	0.0410
0.975	1.612	0.450		0.0101	0.0126	0.0153	0.0205	0.0260	0.0394
1.00	1.000	1.000			0.0123	0.0149	0.0199	0.0251	0.0382
1.05					0.0116	0.0141	0.0188	0.0238	0.0361
1.10					0.0110	0.0134	0.0179	0.0227	0.0342
1.20					0.0100	0.0123	0.0162	0.0205	0.0310
1.30						0.0112	0.0149	0.0188	0.0285
1.40						0.0103	0.0138	0.0175	0.0262
1.50							0.0128	0.0163	0.0244
1.75							0.0110	0.0138	0.0209
2.00								0.0121	0.0182
2.50									0.0146
3.00									0.0121

T_R	$P_R = 0.20$	$P_R = 0.30$	$P_R = 0.40$	$P_R = 0.60$	$P_R = 0.80$	$P_R = 1.00$	$P_R = 1.2$	$P_R = 1.4$	$P_R = 1.6$
0.85	0.0673	0.114							
0.90	0.0608	0.0995	0.144						
0.95	0.0562	0.0900	0.128	0.242				1.970	
0.975	0.0540	0.0867	0.121	0.221	0.383		1.783	1.839	1.891
1.00	0.0523	0.0825	0.116	0.198	0.323	1.000	1.580	1.677	1.758
1.05	0.0489	0.0773	0.107	0.175	0.262	0.383	0.579	1.078	1.380
1.10	0.0461	0.0722	0.0995	0.158	0.230	0.317	0.423	0.580	0.818
1.20	0.0413	0.0644	0.0879	0.138	0.189	0.253	0.325	0.400	0.493
1.30	0.0377	0.0585	0.0793	0.122	0.167	0.218	0.271	0.329	0.389
1.40	0.0349	0.0537	0.0726	0.111	0.149	0.193	0.239	0.286	0.333
1.50	0.0322	0.0497	0.0672	0.102	0.137	0.175	0.211	0.253	0.290
1.75	0.0276	0.0420	0.0562	0.0843	0.113	0.143			
2.00	0.0242	0.0363	0.0489	0.0728	0.0965	0.122			
2.50	0.0193	0.0291	0.0388	0.0573	0.0763	0.0954			
3.00	0.0161	0.0242	0.0321	0.0478	0.0634	0.0790			
4.00	0.0120	0.0182	0.0242	0.0361	0.0477	0.0591			
5.00		0.0144	0.0194	0.0288	0.0382	0.0472			
6.00		0.0119	0.0161	0.0241	0.0318	0.0396			
8.00			0.0120	0.0180	0.0239	0.0296			
10.0				0.0144	0.0190	0.0237			

T_R	$P_R = 1.8$	$P_R = 2.0$	$P_R = 2.5$	$P_R = 3.0$	$P_R = 3.5$	$P_R = 4.0$	$P_R = 5.0$	$P_R = 6.0$	$P_R = 8.0$
0.60		2.920		2.948		2.970	2.998		
0.70		2.720		2.751		2.780	2.811	2.842	2.889
0.80		2.501		2.546		2.589	2.623	2.661	2.719
0.85		2.374		2.430		2.482	2.522	2.562	2.630
0.90		2.227		2.299		2.364	2.416	2.460	2.537
0.95		2.055		2.155		2.236	2.297	2.351	2.441
0.975		1.961		2.080		2.170	2.236	2.294	2.393
1.00	1.812	1.859		2.000	2.052	2.101	2.178	2.239	2.346
1.05	1.504	1.587	1.731	1.724	1.897	1.960	2.055	2.127	2.253
1.10	1.079	1.218	1.479	1.627	1.730	1.810	1.930	2.014	2.157
1.20	0.596	0.700	0.978	1.192	1.365	1.493	1.670	1.788	1.968
1.30	0.453	0.522	0.700	0.883	1.056	1.195	1.414	1.564	1.783
1.40	0.381	0.429	0.564	0.702	0.840	0.974	1.188	1.359	1.608
1.50	0.338	0.377	0.483	0.600	0.718	0.830	1.035	1.196	1.467
1.75		0.294	0.367	0.453		0.625	0.805	0.960	1.21
2.00		0.246	0.306	0.374		0.516	0.663	0.798	1.03
2.50		0.188	0.233	0.284		0.390	0.500	0.602	0.807
3.00		0.154	0.191	0.233		0.318	0.409	0.496	0.665
4.00		0.116	0.142	0.173		0.236	0.302	0.367	0.494
5.00		0.0923	0.114	0.138		0.188	0.243	0.292	0.398
6.00		0.0772	0.0953	0.115		0.158	0.203	0.245	0.333
8.00		0.0581	0.0717	0.0868		0.119	0.154	0.187	0.256
10.0		0.0464	0.0571	0.0695		0.0954	0.124	0.151	0.207

T_R	$P_R = 10.0$	$P_R = 12$	$P_R = 14$	$P_R = 16$	$P_R = 18$	$P_R = 20$	$P_R = 25$	$P_R = 30$	$P_R = 40$
0.70	2.930	2.964	3.001	3.034	3.070	3.107	3.173	3.229	3.329
0.80	2.777	2.825	2.870	2.909	2.946	2.987	3.060	3.126	3.231
0.85	2.697	2.750	2.800	2.843	2.882	2.923	3.004	3.074	3.183
0.90	2.618	2.674	2.727	2.774	2.817	2.859	2.943	3.023	3.136
0.95	2.530	2.593	2.652	2.700	2.747	2.791	2.886	2.968	3.089
0.975	2.489	2.555	2.615	2.665	2.712	2.759	2.855	2.941	3.068
1.00	2.446	2.514	2.576	2.629	2.679	2.726	2.827	2.914	3.046
1.05	2.358	2.433	2.500	2.558	2.613	2.661	2.769	2.864	3.002
1.10	2.270	2.351	2.422	2.486	2.544	2.598	2.712	2.811	2.961
1.20	2.097	2.194	2.274	2.351	2.418	2.478	2.603	2.712	2.883
1.30	1.931	2.045	2.141	2.228	2.298	2.367	2.504	2.621	2.816
1.40	1.773	1.901	2.014	2.114	2.193	2.270	2.417	2.538	2.750
1.50	1.629	1.769	1.891	2.016	2.108	2.188	2.338	2.462	2.689
1.75	1.38					1.99		2.28	2.53
2.00	1.21					1.81		2.13	2.38
2.50	0.960					1.55		1.88	2.16
3.00	0.801					1.35		1.68	1.96
4.00	0.602					1.08		1.39	1.65
5.00	0.488					0.896		1.19	1.43
6.00	0.412					0.767		1.04	1.27
8.00	0.314					0.601		0.840	1.04
10.00	0.255					0.500		0.702	0.876

The available information derived from the experimental data is presented for the several references in both Figures 1 and 2. Figure 1 is presented in logarithmic coordinates to define clearly the low density region, whereas Figure 2 is presented in rectilinear coordinates to accentuate the liquid and dense phase regions. The information presented in Figure 1 is expressed as solid lines in Figure 3. The effect of pressure on the density of the compressed liquid region has been extended from $P_R = 10$ to $P_R = 40$ by using nitrogen data (7) available for this compressed region.

Ratios of reduced densities for nitrogen and ammonia at common reduced temperatures were plotted against reduced pressure to produce essentially linear relationships. Extrapolation of these lines allowed the compressed liquid region of ammonia to be defined up to pressures of $P_R = 40$ in the temperature interval $0.70 \leqq T_R \leqq 1.50$.

All isobars were extended through the use of the Nelson-Obert (*32*) compressibility factor charts and the relation

$$\frac{\rho_R}{\rho_{R_1}} = \frac{z_1}{z}\,\frac{P_R}{P_{R_1}}\,\frac{T_{R_1}}{T_R} \tag{2}$$

When $P_R = P_{R_1}$, Equation 2 represents the dependence of density on temperature. Thus a single density value and corresponding compressibility factors permit the extension of an isobar. Following this procedure, all isobars were extended to $T_R = 10$.

To present the liquid and dense phase regions comprehensively, a rectilinear plot is presented in Figure 4. This detailed correlation for ammonia is capable of accurately defining density values in the vicinity of the critical point and dense phase region. Reduced density values extracted from enlarged plots of Figures 3 and 4 are in Table I.

Representative experimental density values from each reference were checked with values obtained from enlarged plots of Figures 3 and 4. The results of these comparisons were as follows:

	Points	% Deviation
Beattie and Lawrence (*1*)	25	0.93
Berthoud (*3*)	5	0.76
Cragoe and Harper (*8*)	8	0.11
Cragoe, McKelvy, and O'Connor (*9*)	4	1.11
Dieterici and Drewes (*13*)	12	2.35
Kasarnowsky (*18*)	23	0.38
Keyes (*21*)	24	0.28
Keyes and Brownlee (*22*)	5	0.33
Keyes and Brownlee (*24*)	15	0.80
Lange (*27*)	8	0.88
Meyers (*29*)	7	1.40
Meyers and Jessup (*30*)	13	1.02
Timmermans (*36*)	6	0.13
Natl. Bur. Standards (*31*)	9	0.76
	164	0.78

These comparisons indicate that the saturated density data of Dieterici and Drews (*13*) show a maximum deviation of 2.35% for 12 saturated vapor and liquid densities considered, while the data of Cragoe and Harper (*8*) and Timmermans (*36*) for saturated liquid produced deviations of only 0.11 and 0.13%, respectively.

In addition, reduced density values derived from these studies on ammonia have been compared to the generalized values reported by Lyderson, Greenkorn, and Hougen (*28*). These comparisons indicate that the values from this study agree within 0.87% for the range of temperature and pressure where these values could be compared. Above $T_R = 1.50$ and $P_R = 1.00$, no comparisons are possible. On the whole, the density values of this study and those produced from the generalized study of Lydersen, Greenkorn, and Hougen (*28*) are in good agreement, except the saturated density values that show an average deviation of 7.4%.

Figures 3 and 4 should be of value in extending our knowledge of the *P-V-T* behavior of fluids and in calculating thermodynamic functions and transport properties for ammonia and substances possessing comparable critical compressibility factors and polarity values. The critical compressibility factor, z_c, is defined by the critical constants as $z_c = P_cV_c/RT_c$, while the contributions due to the dipole moment are reflected in the dimensionless polarity parameter, $\Delta^* = \mu^2/V_cRT_c$ as defined by Krieger (*26*). Thus, for ammonia $z_c = 0.242$ and $\Delta^* = 0.306$. The introduction of the polarity parameter, Δ^*, in *P-V-T* studies deserves further investigation as a possible fourth correlating parameter.

NOMENCLATURE

p = vapor pressure, mm. of mercury
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
= reduced pressure for experimental density value, P_1/P_c
R = gas constant, 82.055 (cc.)(atm.) per(gram mole)(° K.)
T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c
T_{R_1} = reduced temperature for experimental density, T_1/T_c
V = molar volume, cc. per gram mole
V_c = critical molar volume, cc. per gram mole
z = compressibility factor, PV/RT
z_1 = compressibility factor corresponding to experimental density value
z_c = critical compressibility factor, P_cV_c/RT_c
Δ^* = dimensionless polarity parameter, μ^2/V_cRT_c
μ = dipole moment, debye units
ρ = density, grams per cc.
ρ_c = critical density, grams per cc.
ρ_R = reduced density, ρ/ρ_c
ρ_{R_1} = experimental reduced density at P_{R_1} and T_{R_1}

LITERATURE CITED

(1) Beattie, J.A., Lawrence, C.K., *J. Am. Chem. Soc.* **52**, 6 (1930).
(2) Bergstrom, F.W., *J. Phys. Chem.* **26**, 358 (1922).
(3) Berthoud, A., *Helv. Chim. Acta* **1**, 84 (1918).
(4) Brill, Otto, *Ann. Physik.* [4] **21**, 170 (1906).
(5) Burrell, G.A., Robertson, I.W., *J. Am. Chem. Soc.* **37**, 2482 (1915).
(6) Byrne, Robert, *A.I.Ch.E. Journal* **5**, 551 (1959).
(7) Byrne, Robert, M.S. thesis, Northwestern University, Evanston, Ill., 1959.
(8) Cragoe, C.S., Harper, D.R., Bur. Standards, Sci. Papers **17**, 287 (1921).
(9) Cragoe, C.S., McKelvy, E.C., O'Connor, C.F., *Ibid.*, **18**, 707 (1923).
(10) Cragoe, C.S., Meyers, C.H., Taylor, C.S., *Ibid.*, **16**, 1 (1920).
(11) Cragoe, C.S., Meyers, C.H., Taylor, C.S., *J. Am. Chem. Soc.* **42**, 206 (1920).
(12) Davies, J.H., *Proc. Roy. Soc.* (*London*) **A78**, 41 (1906).
(13) Dieterici, C.H., Drewes, *Z. ges. Kalte-Ind.* **11**, 21 (1904).
(14) Hamrin, C.E., Jr., Thodos, George, *A.I.Ch.E. Journal* **4**, 480 (1958).
(15) Henning, Fritz, Stock, Alfred, *Z. Physik.* **4**, 226 (1921).
(16) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(17) Holst, Gilles, *Bull. assoc. internationale du froid* **6**, 27 (1915).
(18) Kasarnowsky, J. S., *Acta Physicochim. U.R.S.S.* **12**, 513 (1940).
(19) Kennedy, J.T., M.S. thesis, Northwestern University, Evanston, Ill., 1958.
(20) Keyes, F.G., *Am. Soc. Refrig. Engrs. J.* **7**, 371 (1921).
(21) Keyes, F.G., *J. Am. Chem. Soc.* **53**, 965 (1931).
(22) Keyes, F.G., Brownlee, R.B., *Am. Soc. Refrig. Engrs. J.* **1**, 34 (1914).
(23) Keyes, F.G., Brownlee, R.B., *J. Am. Chem. Soc.* **40**, 25 (1918).
(24) Keyes, F.G., Brownlee, R.B., "Thermodynamic Properties of Ammonia," Wiley, New York, 1916.
(25) Kobe, K.A., Lynn, R.E., Jr., *Chem. Revs.* **52**, 117 (1953).
(26) Krieger, F.J., "Viscosity of Polar Gases," U.S. Air Force Project **RAND RM-646**, (July 1, 1951).
(27) Lange, A., *Chem. Ind.* **21**, 191 (1898).
(28) Lydersen, A.L., Greenkorn, R.A., Hougen, O.A., Wisconsin, Univ. Eng. Expt. Sta. Rept. **4**, Madison, Wis., (1955).
(29) Meyers, C.H., *Bur. Standards J. Research* **11**, 691 (1933).
(30) Meyers, C.H., Jessup, R.S., *Refrig. Eng.* **11**, 345 (1925).
(31) Natl. Bur. Standards (U.S.), Circ. **142**, 1st ed., 1923.
(32) Nelson, L.C., Obert, E.F., *Trans. Am. Soc. Mech. Engrs.* **76**, 1057 (1954).
(33) Overstreet, Roy, Giauque, W.F., *J. Am. Chem. Soc.* **59**, 254 (1937).
(34) Sondak, N.E., Thodos, George, *A. I. Ch. E. Journal* **2**, 347 (1956).
(35) Thode, H.G., *J. Am. Chem. Soc.* **62**, 581 (1940).
(36) Timmermans, Jean, *Bull. soc. chim. Belg.* **32**, 299 (1923).

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