Densities of the Liquid and Dense Phase Regions

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The expansion factor correlation introduced in 1943 by Watson (*21*) has received considerable interest and application for the calculation of thermodynamic properties and densities of the liquid state. In this connection, the saturated liquid density data of Young (*23*) for isopentane and the high pressure data of Sage and Lacey (*18, 19*) for propane and *n*-pentane were used to calculate values of the expansion factor, defined as:

$$\omega = \frac{T_c}{MP_c}\rho \qquad (1)$$

where

T_c = critical temperature, °K.
P_c = critical pressure, atm.
M = molecular weight
ρ = density, grams per cc.

Watson points out that a correlation of the expansion factor with reduced temperature and pressure failed to produce a generalized relationship, as ω values at the same reduced conditions were found to vary by more than 20% for different substances. To overcome this limitation, Watson proposed to calculate densities of other substances from a single liquid density, ρ_1, through the relationship,

$$\rho = \frac{\rho_1}{\omega_1}\omega \qquad (2)$$

where ω_1 is the expansion factor corresponding to conditions of density ρ_1. Equation 2 has proved of considerable utility for the calculation of liquid densities over extended ranges of temperature and pressure.

The recent introduction of the compressibility factor at the critical point, z_c, as the third correlating parameter (*7, 9, 11, 16*) suggests that a correlation of the expansion factor with reduced temperature and pressure could become generalized if related to this parameter. Accordingly, for the direct calculation of densities, the correlation presented by Watson (*21*) should be restricted to substances having z_c values comparable to those of isopentane ($z_c = 0.268$), *n*-pentane ($z_c = 0.269$), and propane ($z_c = 0.278$).

DEVELOPMENT OF EXPANSION FACTOR PLOT FOR NITROGEN

The saturated liquid density data of Mathias, Kamerlingh Onnes, and Crommelin (*17*), van Itterbeek, de Bock and Verhaegen (*13*), and Baly and Donnan (*3*) have been used to establish the saturated liquid line presented in Figure 1. The density values of these investigators are in good agreement at the lower temperatures. At the higher temperatures, the density values of Mathias, Kamerlingh Onnes, and Crommelin (*17*) represent the only source of data which permit an extension of the saturated liquid line to the critical point. The critical density of nitrogen, $\rho_c = 0.311$ gram per cc., reported by Kobe and Lynn (*15*) has been used to produce the expansion factor for nitrogen at the critical point, $\omega_c = 0.0418$.

The comprehensive experimental nitrogen density determinations of Benedict (*5, 6*) have proved invaluable in this study. Benedict presents nitrogen densities for pressures ranging from 100 to 5835 atm. and for temperatures ranging from −183° to 200°C. The experimental density values of Benedict are plotted in Figure 2 and cover the pressure range included between $P_R = 2.98$ and $P_R = 174$ and the temperature range included between $T_R = 0.714$ and $T_R = 3.749$.

The density values of the saturated liquid state presented in Figure 1 and those of Benedict presented in Figure 2 have been converted with Equation 1 to produce expansion factors, for the corresponding temperature and pressure conditions. For these calculations, the critical constants used for nitrogen were $T_c = 126.2$°K. and $P_c = 33.5$ atm (*15*). A cross plot of these calculated ω values permitted the construction of Figures 3 and 4. Figure 3 presents expansion factors for nitrogen as functions of reduced temperature and pressure on rectilinear coordinates. In this figure, the high pressure data of Benedict (*5, 6*) made possible the calculation of ω values up to a reduced pressure of $P_R = 180$ and a reduced temperature of $T_R = 1.4$. Figure 4 presents an extension of this temperature range up to $T_R = 4.0$, on a logarithmic coordinate.

GENERALIZED APPLICATION OF EXPANSION FACTOR CORRELATIONS

In accordance with the recent introduction of the compressibility factor, z_c, as the third correlating parameter, Brock and Bird (*9*) apply the principle of corresponding states to the correlation of surface tension. Hobson and Weber (*11*) utilize this parameter for the correlation of compressibility factors of the saturated vapor and liquid states. Similarly, Lydersen, Greenkorn, and Hougen (*16*) adapt this parameter for the correlation of reduced densities applicable to the liquid and gaseous phases.

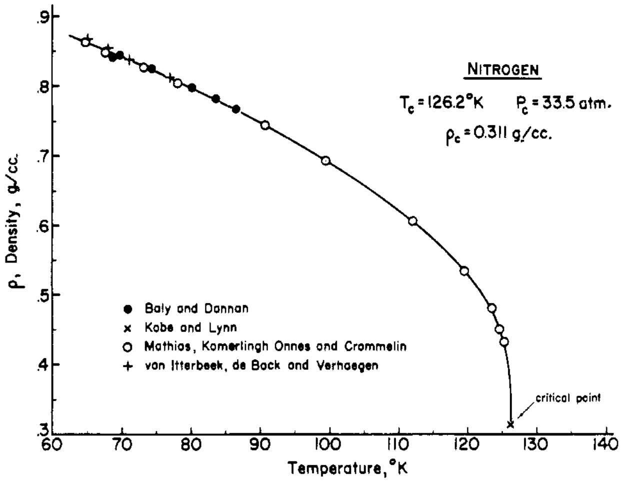

Figure 1. Density-temperature relationship for saturated liquid nitrogen

The dependence of the expansion factor on the z_c parameter is well illustrated in Figure 5 in which are presented the expansion factor lines resulting for the saturated liquid data of nitrogen ($z_c = 0.291$) and that of isopentane ($z_c = 0.268$). The data for isopentane used by Watson (*21*) to produce the original ω factor correlation have been utilized to produce the isopentane relationship of Figure 5. This relationship is found to diverge from the corresponding nitrogen curve with decreasing temperature. The dis-

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parity of these relationships can be attributed to differences in critical compressibility factors.

Accordingly, Figures 3 and 4 should be capable of producing densities directly for substances having the same compressibility factor at the critical point as that of nitrogen, $z_c = 0.291$. A cursory literature examination indicates that argon, carbon disulfide, carbon monoxide, chloroform, methane, oxygen, and phosgene have critical compressibility factors near 0.291. The exact z_c values and corresponding critical constants for these substances are presented in Table I.

A number of density values for the substances presented in Table I have been calculated for the saturated liquid and dense phase regions. These calculated values have been compared with experimental densities reported in the literature to produce the deviations presented in Table I. For argon, carbon monoxide, methane, and oxygen, the resulting deviations were found to be close to 1%, whereas those of chloroform and phosgene were −8.42 and −7.58%, respectively.

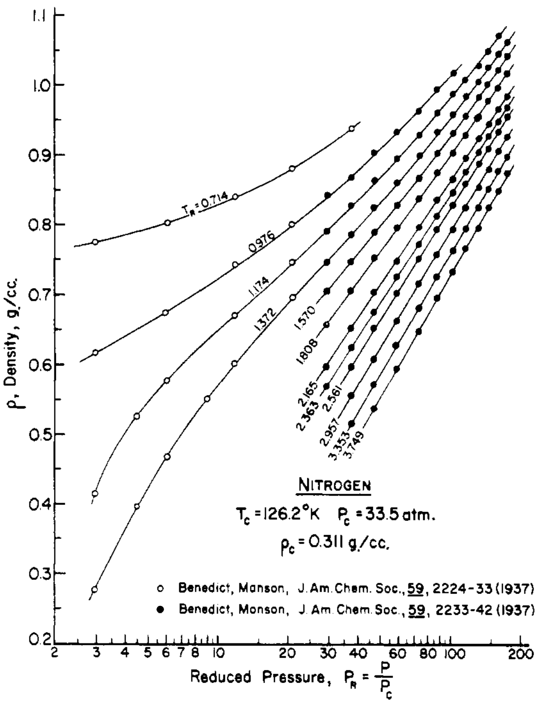

Figure 2. Experimental density data for nitrogen in dense phase region used in this investigation

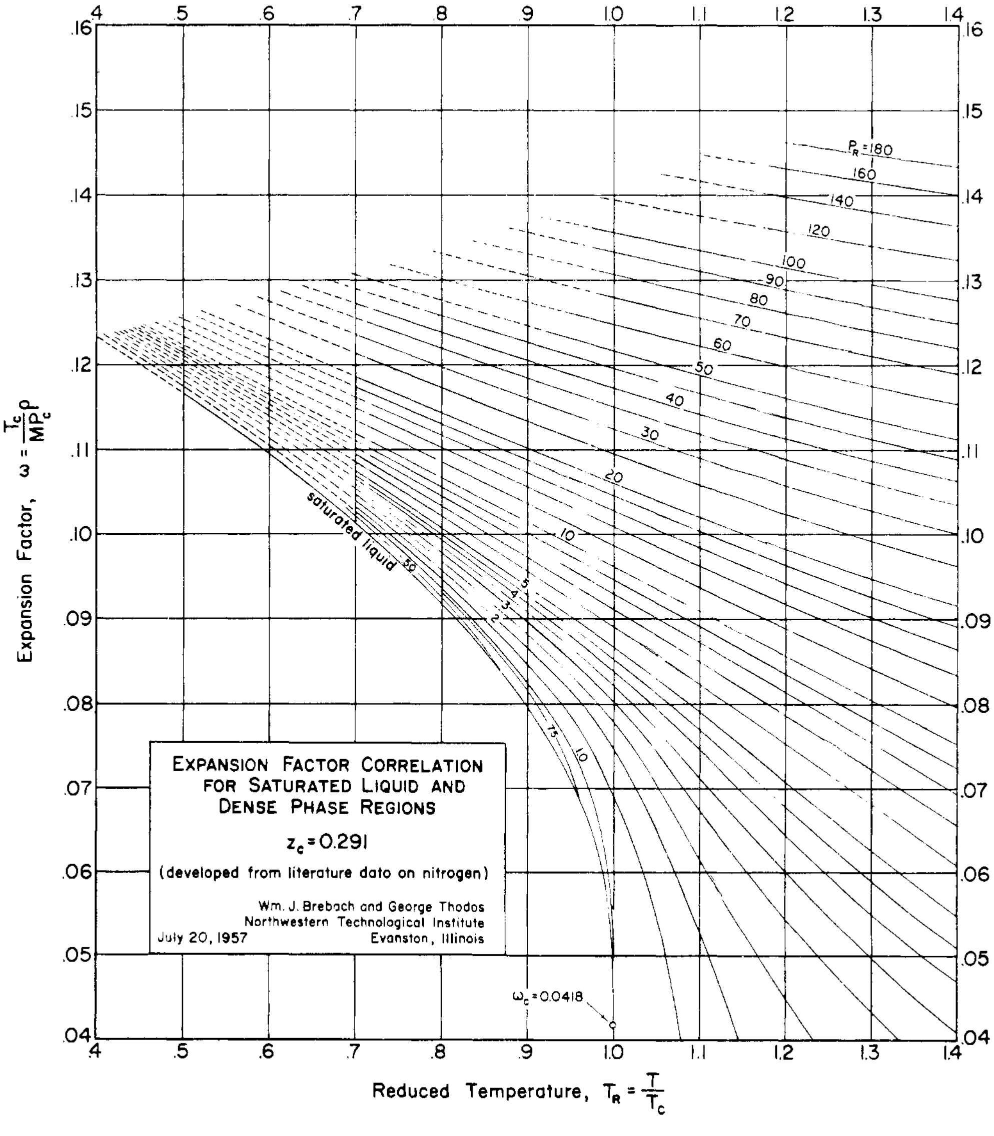

Figure 3. Expansion factor correlation for saturated liquid and dense phase regions ($z_c = 0.291$)

Low temperature range

Table I. Fundamental Constants and Resulting Per Cent Density Deviations for a Number of Substances ($z_c \sim 0.291$)

	M	Critical Constants			μ, Dipole Moment, Debye Units	Ranges Investigated		% Density Deviations		
		T_c, °K.	p_c, atm.	z_c		T_R	P_R	Maximum	Average	Ref.
Argon	39.94	151	48.0	0.291	0	0.56–0.59	(Satd. liq.)	0.66	+ 0.62	*(3)*
Carbon disulfide	76.13	552	78	0.298	0	0.42–0.64	(Satd. liq.) to 25.6	−2.66	−2.39	*(12,20)*
Carbon monoxide	28.01	133	34.5	0.294	0.115	0.53–2.81	(Satd. liq.) to 29.0	−1.59	−1.20 + 0.57	*(3,4)*
Chloroform	119.39	536.6	54	0.293	0.95	0.51–0.61	(Satd. liq.)	−8.65	−8.42	*(20)*
Methane	16.04	191.1	45.8	0.289	0	0.53–1.00	(Satd. liq.)	1.79	−0.74 + 0.52	*(8,10,14)*
Oxygen	32.00	154.8	50.1	0.294	0	0.45–2.41	(Satd. liq.) to 40	−2.36	−0.95 + 0.39	*(1,3)*
Phosgene	98.92	455	56	0.285	1.18	0.40–0.71	(Satd. liq.)	−8.66	−7.58	*(2)*

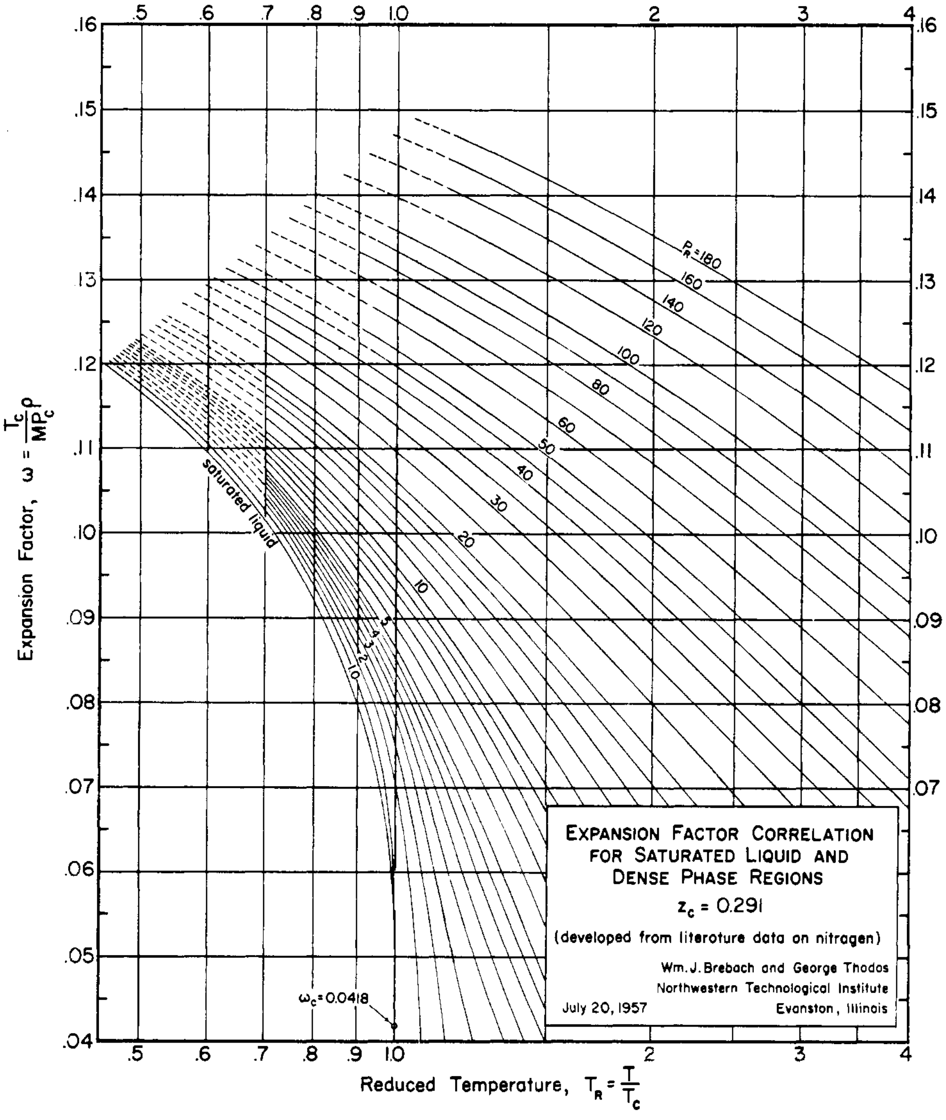

Figure 4. Expansion factor correlation for saturated liquid and dense phase regions (z_c = 0.291)

The excessive negative deviations for chloroform and phosgene cannot be attributed to the fact that their respective critical compressibility factors are not exactly equal to 0.291, but rather may be the result of fundamental differences in molecular structure when compared with nitrogen. Both chloroform and phosgene possess substantial dipole moments *(22)*, whereas the other remaining five substances have negligible or zero dipole moments. The order of magnitude of the respective dipole moments for these substances is presented in Table I.

The resulting deviation of −2.39% for carbon disulfide can be attributed to its value of z_c = 0.298 when compared to that of nitrogen, z_c = 0.291. A density coefficient, α, to be applied to the density values resulting from Figures 3 and 4 has been produced from the above deviation and from the fact that the expected deviation for nitrogen is zero. For this case, α, is assumed to be of the form:

$$\alpha = m z_c \qquad (3)$$

For carbon disulfide, $m = \frac{1.0239}{0.298} = 3.436$ and for nitrogen, $m = \frac{1.00000}{0.291} = 3.436$. Consequently, the recommended expression for the density coefficient, α, becomes

$$\alpha = 3.436 z_c \tag{4}$$

and should be limited in application to the ranges of z_c presented in these comparative studies.

To account for the z_c values of chloroform and phosgene,

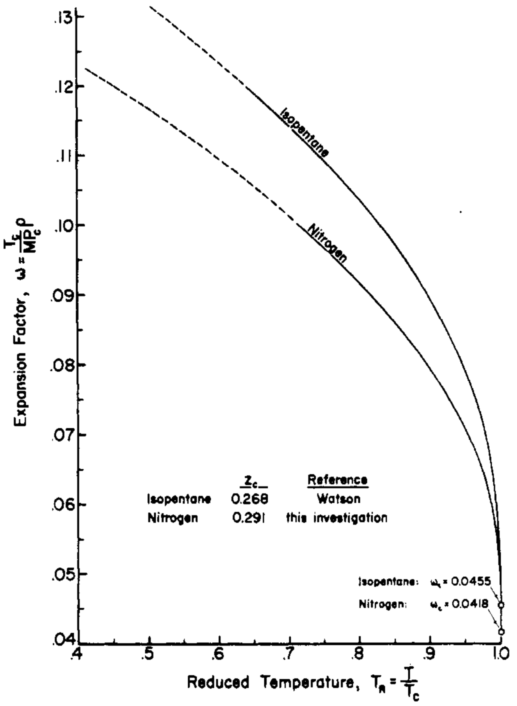

Figure 5. Comparison of expansion factors for nitrogen and isopentane at saturated liquid conditions

Equation 4 has been used to produce the contributions of 1.0068 and 0.9793, respectively. Upon subtracting these values from the respective combined contributions of z_c and the dipole moment, 1.0842 and 1.0758, differences result that represent the dipole moment contributions. These differences are 0.0774 for chloroform and 0.0965 for phosgene. The density coefficient due to the dipole moment contribution is assumed to be of the form:

$$\beta = k\mu \tag{5}$$

where μ represents the dipole moment in Debye units. The value of k in Equation 5 becomes for chloroform, $\frac{0.0774}{0.95} =$ 0.0815 and for phosgene, $\frac{0.0965}{1.18} = 0.0818$. Therefore, the average value of k is taken to be 0.0816 in order to define the dipole moment contribution as:

$$\beta = 0.0816\mu \tag{6}$$

As a result, the combined density coefficient, $\alpha + \beta$, to be applied to the density values resulting from Figures 3 and 4 becomes:

$$\rho_{\text{actual}} = [3.436 z_c + 0.0816\mu]\rho_{\text{chart}} \tag{7}$$

Equation 7 and Figures 3 and 4 make possible the calculation of densities for substances having z_c values from 0.285 to 0.298 and dipole moments as high as 1.18 Debye units. Therefore, Equation 7 should be restricted to the calculation of densities for substances limited to the above ranges of critical compressibility factors and dipole moments. Extensions of these ranges to other substances constitutes a separate study that should provide the necessary background required for a comprehensive evaluation of densities in the liquid and dense phase regions.

NOMENCLATURE

k = constant (Equation 5)
m = constant (Equation 3)
M = molecular weight
P = absolute pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
z_c = critical compressibility factor
α = density coefficient for critical compressibility factor, z_c, dimensionless
β = density coefficient for dipole moment, dimensionless
μ = dipole moment, Debye units
ρ = density, grams/cc.
ω = Watson expansion factor

LITERATURE CITED

(1) Amagat, E. H., *Ann. chim. et phys.* (6) **29**, 68 (1893).
(2) Atkinson, R. H., Heycock, C. T., Pope, W. J., *J. Chem. Soc.* (*London*) **117**, 1410-26 (1920).
(3) Baly, E. C. C., Donnan, F. G., *J. Chem. Soc.* **81**, 907-23 (1902).
(4) Bartlett, E. P., Hetherington, H. C., Kvalnes, H. M., Tremearne, T. H., *J. Am. Chem. Soc.* **52**, 1374-82 (1930).
(5) Benedict, Manson, *Ibid.*, **59**, 2224-33 (1937).
(6) *Ibid.*, pp. 2233-42.
(7) Bird, R. B., private communication.
(8) Bloomer, O. T., Parent, J. D., *Chem. Eng. Progr. Symp. Ser.* No. 6, **49**, 11-24 (1953).
(9) Brock, J. R., Bird, R. B., *A.I.Ch.E. Journal* **1**, 174-7 (1955).
(10) Cardoso, E., *Arch. sci. phys. nat.* **36**, 97 (1913).
(11) Hobson, Merk, Weber, J. H., *A.I.Ch.E. Journal* **2**, 355-9 (1956).
(12) "International Critical Tables," vol. 3, p. 41, McGraw-Hill, New York, 1928.
(13) van Itterbeek, A., de Bock, A., Verhaegen, L., *Physica* **15**, 624-6 (1949).
(14) Keyes, F. G., Taylor, R. S., Smith, L. B., *J. Math. Phys.* **1**, 211 (1922).
(15) Kobe, K. A., Lynn, R. E., Jr., *Chem. Revs.* **52**, 117 (1953).
(16) Lydersen, A. L., Greenkorn, R. A., Hougen, O. A., "Generalized Thermodynamic Properties of Pure Fluids," Rept. 4, Eng. Expt. Station, University of Wisconsin, October 1955.
(17) Mathias, E., Kamerlingh Onnes, H., Crommelin, C. A., *Proc. Acad. Sci. Amsterdam* **17**, 953 (1915).
(18) Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **27**, 48 (1935).
(19) *Ibid.*, **34**, 730 (1942).
(20) Tyrer, Daniel, *J. Chem. Soc.* (*London*) **105**, 2534-53 (1914).
(21) Watson, K. M., *Ind. Eng. Chem.* **35**, 398-406 (1943).
(22) Wesson, L. G., "Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.
(23) Young, Sydney, *Sci. Proc. Roy. Dublin Soc.* **12**, 374 (1909-10).

Received for review October 17, 1957. Accepted March 19, 1958. Figure 3 is available on an 8½ × 11 inch reproduction and can be obtained on request from the Chemical Engineering Department, Northwestern University, Evanston, Ill.