

Generalized Correlations for Gases

Generalized correlations find widespread use. Most popular are correlations of the kind developed by Pitzer and coworkers for the compressibility factor Z and for the second virial coefficient B .

Pitzer Correlations for the Compressibility Factor :

The correlation for Z takes the form:

$$Z = Z^0 + \omega Z^1$$

Where

Z^0 and Z^1 are functions of both T_r and P_r .

$$Z^0 = F^0(T_r, P_r)$$

$$Z^1 = F^1(T_r, P_r)$$

and ω :is the centric factor depend on of (T_c , P_c and V_c).

$$T_r = T / T_c$$

$$P_r = P / P_c$$

Equation of state that represents “ Z ” above is said to be generalized because of their general applicability to all gas.

A disadvantage of the generalized compressibility factor correlation is its graphical nature, thus figures may be used for quick estimates of Z^0 and Z^1 verses P_r and T_r .

Pitzer Correlations for the Second Virial Coefficient

Pitzer correlation provide reliable results for gases which are nonpolar or only slightly polar ; for these errors of no more than 2-3 % are indicated. A disadvantage of generalized compressibility factor correlation is its graphical nature. The simplest form of the Virial equation has validity only at low to moderate pressures where Z is linear in pressure .The generalized Virial-

coefficient correlation is therefore useful only where Z° and Z' are at least approximately linear functions of reduced pressure. The simplest form is:

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_C}{RT_C} \right) \frac{P_r}{T_r}$$

Pitzer proposed a second correlation, which expressed the quantity as BP_C/RT_C

$$\left(\frac{BP_C}{RT_C} \right) = B^\circ + B\omega'$$

Together, these two equations become:

$$Z = 1 + B^\circ \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}$$

Comparison of this equation with generalized compressibility factor :

$$Z = Z^0 + \omega Z^1$$

Provides the following identifications:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r}$$

$$Z^1 = B^1 \frac{P_r}{T_r}$$

Second Virial coefficients are functions of temperature only, and similarly B° and B' are functions of reduced temperature only. They are well represented by the following equations:

$$B^\circ = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B' = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Example 3.9

Determine the molar volume of *n*-butane at 510K and 25bar by each of the following:

- The ideal-gas equation.
- The generalized compressibility-factor correlation.
- The generalized virial-coefficient correlation.

Solution 3.9

(a) By the ideal-gas equation,

$$V = \frac{RT}{P} = \frac{(0.08314)(510)}{25} = 1.691 \text{ m}^3 \text{ kmol}^{-1}$$

(b) Taking values of T_c and P_c from App. B, we find

$$T_r = \frac{510}{425.1} = 1.200 \quad P_r = \frac{25}{37.96} = 0.659$$

Interpolation in Tables E.1 and E.2 then provides

$$Z^0 = 0.865 \quad Z^1 = 0.038$$

Thus, by Eq. (3.54) with $\omega = 0.200$,

$$Z = Z^0 + \omega Z^1 = 0.865 + (0.200)(0.038) = 0.873$$

and

$$V = \frac{ZRT}{P} = \frac{(0.873)(0.08314)(510)}{25} = 1.4807 \text{ m}^3 \text{ kmol}^{-1}$$

If we take $Z = Z^0 = 0.865$, in accord with the two-parameter corresponding states correlation, then $V = 1.4671 \text{ m}^3 \text{ kmol}^{-1}$, which is less than 1 percent lower than the value given by the three-parameter correlation.

(c) Values of B^0 and B^1 are given by Eqs. (3.61) and (3.62):

$$B^0 = -0.232 \quad B^1 = 0.059$$

By Eq. (3.59),

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 = -0.232 + (0.200)(0.059) = -0.220$$

Then by Eq. (3.58),

$$Z = 1 + (-0.220) \frac{0.659}{1.200} = 0.879$$

from which we find $V = 1.4891 \text{ m}^3 \text{ kmol}^{-1}$, a value less than 1 percent higher than that given by the compressibility-factor correlation. For comparison, the experimental value is 1.4807.

Generalized Correlations for Liquids:

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of high accuracy. In addition, generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by Rackett,

$$V^{\text{sat}} = V_c Z_c (1 - T_r)^{0.2857}$$

The only data required are the critical constants, given in App. B. from Smith thermodynamics book.

Lydersen, and Hougen developed a two-parameter corresponding-states correlation for estimation of liquid volumes. It provides a correlation of reduced density ρ_r , as a function of reduced temperature and pressure. By definition,

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

Where

ρ_c : is the density at the critical point.

A better procedure is to make use of a single known liquid volume (state 1) by the identity,

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}}$$

Where

V_2 = required volume

V_1 = known volume

ρ_{r1}, ρ_{r2} = reduced densities read from Fig. 3.17

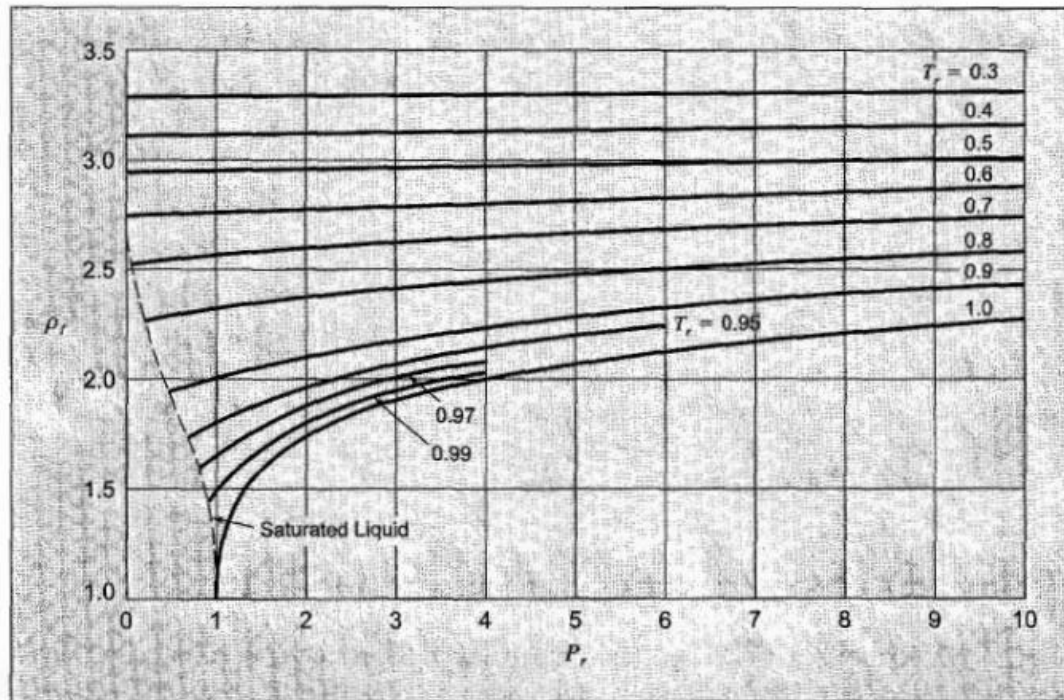


Figure 3.17 Generalized density correlation for liquids

Example 3.12

For ammonia at 310 K (36.85°C), estimate the density of:

- (a) The saturated liquid;
 (b) The liquid at 100 bar.

Solution 3.12

(a) We apply the Rackett equation at the reduced temperature,

$$T_r = \frac{310}{405.7} = 0.7641$$

With $V_c = 0.07247 \text{ m}^3 \text{ kmol}^{-1}$ and $Z_c = 0.242$ (from App. B), we get

$$V^{\text{sat}} = V_c Z_c^{(1 - T_r)^{0.2857}} = (0.07247)(0.242)^{(0.2359)^{0.2857}} = 0.02833 \text{ m}^3 \text{ kmol}^{-1}$$

This compares with the experimental value of $0.02914 \text{ m}^3 \text{ kmol}^{-1}$, and differs by 2.7 percent.

(b) The reduced conditions are

$$T_r = 0.7641 \quad P_r = \frac{100}{112.8} = 0.887$$

From Fig. 3.17, we have $\rho_r = 2.38$. Substituting this value along with V_c into Eq. (3.64) gives

$$V = \frac{V_c}{\rho_r} = \frac{0.07247}{2.38} = 0.03045 \text{ m}^3 \text{ kmol}^{-1}$$

In comparison with the experimental value of $0.0286 \text{ m}^3 \text{ kmol}^{-1}$, this result is in error by 6.5 percent.

If we start with the experimental value of $0.02914 \text{ m}^3 \text{ kmol}^{-1}$ for saturated liquid at 310 K, Eq. (3.65) may be used. For the saturated liquid at $T_r = 0.764$, we find from Fig. 3.17 that $\rho_{r1} = 2.34$. Substitution of known values into Eq. (3.65) gives

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}} = (0.02914) \left(\frac{2.34}{2.38} \right) = 0.02865 \text{ m}^3 \text{ kmol}^{-1}$$

This result is in essential agreement with the experimental value.

Direct application of the Lee/Kesler correlation with values of Z^0 and Z^1 interpolated from Tables E.1 and E.2 leads to a value of $0.03387 \text{ m}^3 \text{ kmol}^{-1}$, which is significantly in error, no doubt owing to the highly polar nature of ammonia.