

6.7 Compressibility Factor and Corresponding States

We have seen that the value of $PV/(nRT)$ deviates significantly from 1.0 at higher pressures. We can define a new variable called compressibility factor (z) as

$$z = \frac{PV_m}{RT}$$

Obviously, z will depend on the pressure and temperature. At very low pressures the ideal gas law is obeyed, hence $z = 1.0$ at very low pressures for all gases. Deviation of z from unity at higher pressures shows the extent of non-ideality.

$z = f(P, T)$ is a general form of equation of state. The PVT relationship for any gas can be written as:

$$PV_m = zRT$$

For a non-ideal gas:

$$P_1 V_1 = n Z_1 R T_1 \text{ and } P_2 V_2 = n Z_2 R T_2, \text{ Or}$$

$$V_2 = V_1 (P_1/P_2) (T_2/T_1) (Z_2/Z_1)$$

If the values of the compressibility factors are known, the volumes measured under one condition can be converted to other conditions. This is important in transportation and sale of natural gas, which is sold by volume at standard conditions. The volumes measured at high pressures and arbitrary temperatures are converted to standard conditions by using compressibility values. The standard condition is chosen to be such that the compressibility factor is equal to 1.0, so that we have to lookup only one compressibility factor for the conversion. If the standard condition is denoted by T_o and P_o then,

$$V_o = (V_1/Z_1) (T_o/T_1)(P_1/P_o)$$

Reduced Conditions

We define "reduced conditions" as dimensionless values of pressure, temperature and molar volume, obtained by dividing the actual values by corresponding critical value.

$$\text{Reduced Pressure, } P_r = P/P_c,$$

$$\text{Reduced Temperature, } T_r = T/T_c,$$

$$\text{Reduced molar volume, } V_r = V_m/V_{cm},$$

Experience shows that all gases behave more or less similarly at the same reduced conditions. That is if for two gases, two of the reduced properties are equal, then the value of the third reduced property would also be approximately equal. --> This important observation is known as the **law of corresponding states**. It was postulated by van der Waals more than 100 years ago.

Mathematically,

$V_r = f(P_r, T_r)$ Where, the function is the same for all gases.

The vdW EOS, for one mole of gas is

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

and at critical conditions

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

We also know that for vdW EOS, $\frac{P_c V_c}{RT_c} = \frac{3}{8}$

Constants a and b can also be related to critical properties as,

$$b = \frac{V_c}{3} = \frac{RT_c}{8P_c}$$

and

$$a = \frac{27R^2T_c^2}{64P_c}$$

Substituting the values of, a and b in terms of the critical properties and using the definition of reduced variables, we get

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

The vdW EOS can also be written in terms of the compressibility factor. The cubic form of vdW EOS is,

$$V_m^3 - \left(b + \frac{RT_c}{P_c} \right) V_m^2 + \frac{a}{P_c} V_m - \frac{ab}{P_c} = 0$$

Replacing V_m by zRT/P , and using the definition of reduced variables, we can get

$$Z^3 - \left[\frac{P_r}{8T_r} + 1 \right] Z^2 + \left[\frac{27P_r}{64T_r^2} \right] Z - \left[\frac{27P_r^2}{512T_r^3} \right] = 0$$

This equation shows that the compressibility factor is a function of P_r and T_r . Charts can be prepared by plotting values of z as a function of P_r , for various values of T_r . According to the van der Waal's equation of state, the same chart should apply to all gases.

Generalised Compressibility Charts

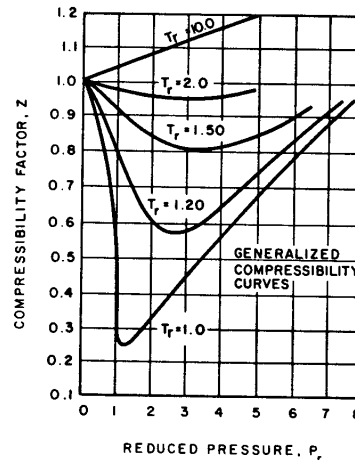


Figure 6-6 A Generalized Compressibility Chart

Figure 6-6 shows values of Z plotted against reduced pressure with T_r as the third variable. In principle, such charts are generalized graphical relationships for P-V-T behaviour of all gases. To use such a chart for calculating molar volume at any pressure and temperature, one would first calculate the values of P_r and T_r . The value of compressibility factor is then read from the chart at the calculated values of the reduced properties. Then the molar volume can be calculated as

$$V_m = \frac{zRT}{P}$$

Difficulty: Need a separate chart for each gas since the values of z are not *exactly* the same at same values of reduced properties. The generalized chart can be used for approximate calculations and would be more accurate than the ideal gas law, but it is still not good enough for precise calculations.

Developing a separate chart for each substance is too cumbersome. A single generalized chart is not accurate enough. An intermediate strategy would be to develop several generalized charts that can be applied to all substances having nearly equal value of a third parameter. Two such parameters have been used.

Use of Z_c as a generalisation parameter (3rd parameter, P_r and T_r are the first two)

$$Z_c = \frac{P_c v_c}{RT_c}$$

z_c varies from 0.22 to 0.31 (Table 6-3)

For most gases: $0.26 < Z_c < 0.29$

Compressibility charts have been prepared for different values of Z_c . Figure C-3 on Page 395, is one such chart for $Z_c = 0.27$ prepared by Lyderson, Greenkorn and Hougen.

Pitzer and Curl Method of Estimating Compressibility using Acentricity (ω) as the Third Parameter

Acentricity is defined as

$$\omega = -\log\left(\frac{P_v}{P_c}\right) - 1$$

Where, P_v is the vapour pressure at $T = 0.7 T_c$. ω is a measure of the deviation of molecules from spherical shape. For noble gases and gases having spherical molecules (such as methane), its value is very close to zero. The compressibility factor for such gases are well correlated by

$$Z = Z^{(o)}(T_r, P_r) \quad \text{Where } Z^{(o)} \text{ is the generalized compressibility for spherical molecules}$$

The compressibility factor of non-spherical gases can be thought of as comprising two parts, one for spherical molecule and the other as a correction factor to account for non-spherical shape.

Pitzer and Curl (1995) found that for many gases, the compressibility can be correlated by Lyderson, Greenkorn and Hougen.

$$Z = Z^{(o)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r)$$

The second term in this equation can be thought of as a correction for acentricity of molecules.

Tables for these functions [$Z^{(o)}$ and $Z^{(1)}$] are given in appendix C.

Example Problem 6-5

Ethyl acetate has a critical temperature of 439.6 K, a critical pressure of 37.8 atm, a critical compressibility of 0.252 and acentricity of 0.369. Find the molar volume of ethyl acetate at 254°C and 53 atm by the

- (a) Lydersen, Greenkorn, Hougen Z chart and
- (b) the Pitzer-Curl tables and acentricity.

Solution

- (a) First, the reduced temperature and pressure are calculated

$$T_r = \frac{254 + 273.15}{439.6} = 1.199 \approx 1.2$$

$$P_r = \frac{53}{37.80} = 1.402 \approx 1.4$$

From the Z chart for these reduced values, Appendix C,

$$Z \approx 0.705$$

This Z is now used in Equation 6.39 to calculate the molar volume.

$$V_m = ZRT/P = \frac{(0.705)(8.314 \text{ kPa m}^3/\text{kmol K})(527 \text{ K})}{(53.0)(101.3) \text{ kPa}} = 0.575 \text{ m}^3/\text{kmol}.$$

- (b) The Pitzer-Curl method requires reading $Z^{(0)}$ and $Z^{(1)}$ from tables in Appendix C. At $T_r = 1.2$ and $P_r = 1.4$,

$$Z^{(0)} = 0.690, \quad Z^{(1)} = 0.13$$

Then,

$$Z = Z^{(0)} + \omega Z^{(1)} = 0.690 + 0.369(0.13) = 0.738$$

and

$$V_m = ZRT/P = 0.602 \text{ m}^3/\text{kmol}.$$

The difference between the calculated molar volumes using these two alternative methods is about 7 per cent. Perhaps the value given by the Pitzer-Curl method is the more accurate. The Lydersen Z chart, strictly speaking, is for substances with $Z_c = 0.27$; ethyl acetate has $Z_c = 0.252$.