

Chapter 3

3.4-2 The Compressibility Factor Equation of State

The dimensionless compressibility factor, Z , for a gaseous species is defined as the ratio

$$Z = \frac{p\bar{v}}{RT} \tag{3.4-1}$$

If the gas behaves ideally $Z = 1$. The extent to which Z differs from 1 is a measure of the extent to which the gas is behaving nonideally. The compressibility can be determined from experimental data where Z is plotted versus a dimensionless *reduced pressure* p_R and *reduced temperature* T_R , defined as

$$p_R = p/p_c \text{ and } T_R = T/T_c$$

In these expressions, p_c and T_c denote the critical pressure and temperature, respectively. A generalized compressibility chart of the form $Z = f(p_R, T_R)$ is shown in Figure 3.4-1 for 10 different gases. The solid lines represent the best curves fitted to the data.

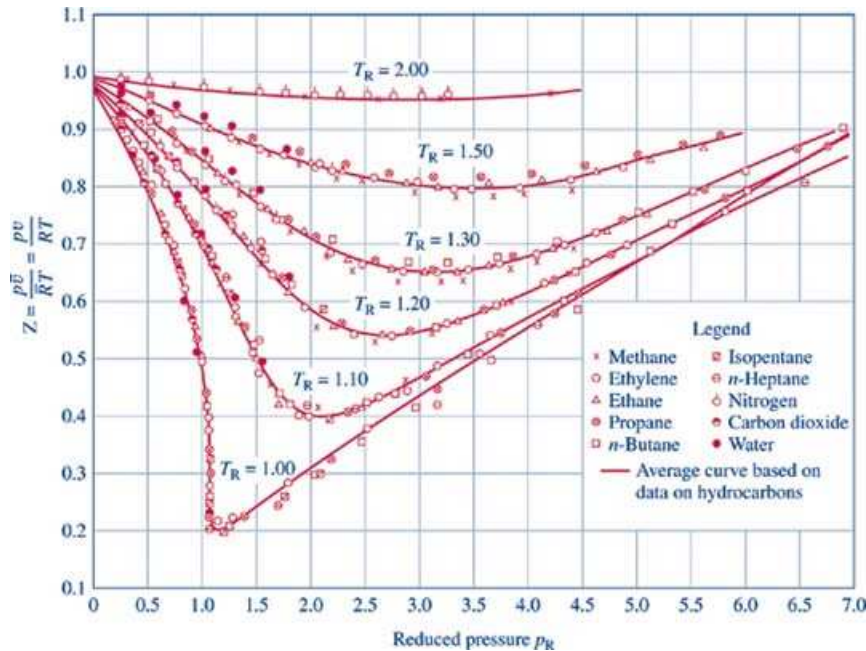


Figure 3.4-1 Generalized compressibility chart for various gases¹⁰.

It can be seen from Figure 3.4-1 that the value of Z tends to unity for all temperatures as pressure approach zero and Z also approaches unity for all pressure at very high temperature. If the p , v , and T data are available in table format or computer software then you should not use the generalized compressibility chart to evaluate p , v , and T since using Z is just another approximation to the real data.

¹⁰ Moran, M. J. and Shapiro H. N., Fundamentals of Engineering Thermodynamics, Wiley, 2008, pg. 112

Example 3.4-2

A closed, rigid tank filled with water vapor, initially at 20 MPa, 520°C, is cooled until its temperature reaches 400°C. Using the compressibility chart, determine
 (a) the specific volume of the water vapor in m³/kg at the initial state.
 (b) the pressure in MPa at the final state.

Compare the results of parts (a) and (b) with values obtained from the thermodynamic table or software¹¹.

Solution

(a) The specific volume of the water vapor in m³/kg at the initial state.

Look up the critical temperature T_c and critical pressure p_c of water:

Substance	Chemical Formula	M (kg/kmol)	T_c (K)	p_c (bar)	$Z_c = \frac{p_c v_c}{RT_c}$
Water	H ₂ O	18.02	647.3	220.9	0.233

Evaluate the *reduce pressured* p_R and *reduce temperature* T_R

$$p_{R1} = 20/22.09 = 0.91, T_{R1} = (520 + 273.15)/647.3 = 1.23$$

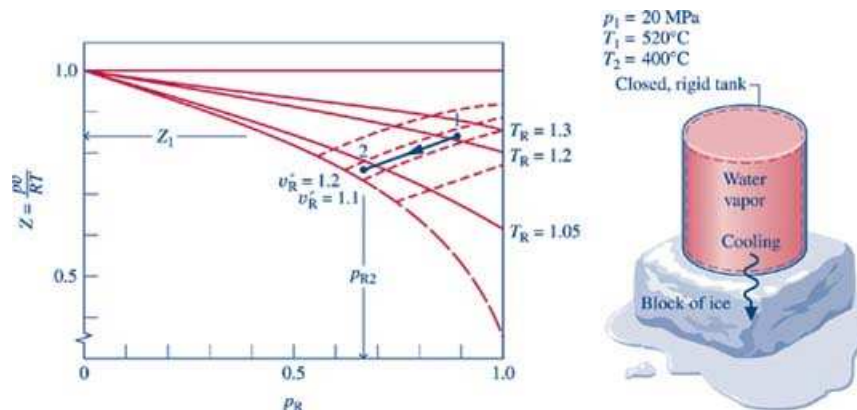


Figure E3.4-2 Generalized Compressibility Chart

With these values for the reduced pressure and reduced temperature, the value of Z from Figure E3.4-2 is approximately 0.83

$$Z = \frac{p\bar{v}}{RT} = \frac{pMv}{RT} \Rightarrow v_1 = Z_1 \frac{\bar{R}T_1}{Mp_1}$$

$$\therefore v_1 = 0.83 \left(\frac{8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K}}{18.02 \text{ kg}/\text{kmol}} \right) \left(\frac{793.15 \text{ K}}{20 \times 10^6 \text{ N}/\text{m}^2} \right) = 0.0152 \text{ m}^3/\text{kg}$$

¹¹ Moran, M. J. and Shapiro H. N., Fundamentals of Engineering Thermodynamics, Wiley, 2008, pg. 113

This value is in good agreement with the specific volume of $0.01551 \text{ m}^3/\text{kg}$ from CATT2 program (Table E3.4-2).

Table E3.4-2 Water properties from CATT2 program

State	Temp C	Pressure MPa	Specific Volume m^3/kg	Internal Energy kJ/kg
1	520	20	0.01551	2992
2	400	15.1	0.01551	2739

(b) The pressure in MPa at the final state.

Since both mass and volume remain constant, the water vapor cools at constant specific volume and thus at reduced specific volume

$$v'_R = \frac{vp_c}{RT_c} = \frac{(0.0152 \text{ m}^3/\text{kg})(22.09 \times 10^6 \text{ N/m}^2)}{\left(\frac{8314 \text{ N} \cdot \text{m}}{18.02 \text{ kg} \cdot \text{K}}\right)(647.3 \text{ K})} = 1.12$$

The reduced temperature at the final state is $T_{R2} = (400 + 273.15)/647.3 = 1.04$

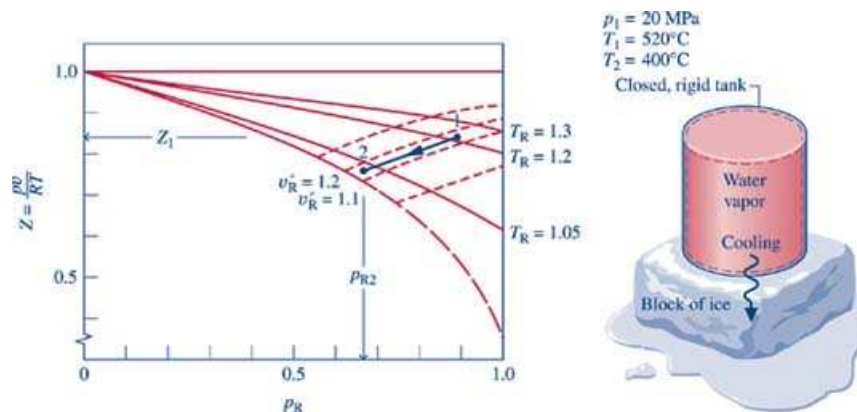


Figure E3.4-2 Generalized Compressibility Chart

Locating the point on the compressibility chart where $v'_R = 1.12$ and $T_R = 1.04$, the corresponding value for p_{R2} is about 0.69. The final pressure is then

$$p_2 = p_c(p_{R2}) = (22.09 \text{ MPa})(0.69) = \mathbf{15.24 \text{ MPa}}$$

This value is in good agreement with the pressure of 15.1 MPa from CATT2 program (Table E3.4-2).

3.4-3 Virial Equation of State

A virial equation of state expresses the quantity $\frac{p\bar{v}}{RT}$ as a power series in the inverse of molar volume \bar{v} .

$$\frac{p\bar{v}}{RT} = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \dots \quad (3.4-8)$$

In this equation, B , C , and D are called *virial coefficient* and are functions of temperature. We will show the use of a truncated virial equation with two terms.

$$\frac{p\bar{v}}{RT} = 1 + \frac{B(T)}{\bar{v}} \quad (3.4-9)$$

In this equation, $B(T)$ can be estimated from the following equations:

$$B(T) = \frac{\bar{R}T_c}{p_c} (B_0 + \omega B_1) \quad (3.4-10)$$

$$B_0 = 0.083 - \frac{0.422}{T_R^{1.6}}, \quad B_1 = 0.139 - \frac{0.172}{T_R^{4.2}}$$

In equation (3.4-10), ω is the Pitzer acentric factor, a parameter that reflects the geometry and polarity of a molecule. The acentric factor for over 1000 compounds can be obtained from comp4.exe program written by T.K. Nguyen. This program is available in the Distribution Folder for CHE302 course.

Physical Properties, Aug. 15, 2003		
1-Eicosyne	Krypton	HBr
Ammonia	Xenon	Iodine
Deuterium-eq	Nitrogen	HI
Hydrogen	Oxygen	NO
H2O	Ozone	NO2
H2O2	Cl2	N2O
D2O	HCl	N2O4
Helium	F2	SO2
Neon	HF	SO3
Argon	Bromine	CO
dH, dG in kJ/mol, Dl = liquid density at 15.5 C		
Nitrogen	N2	Mw = 28.013
Dl,kg/m3 = 806.374	Dipole = 0	Acentric = .0399998
Tb,K = 77.3498	Vc,m3/kmol = .09	Tc,K = 126.194
Pc,bar = 33.9437	dHf = 0	dHc = -32.767

Figure 3.4-2 Acentric factor for nitrogen from comp4.exe program.

Example 3.4-3

A three-liter tank contains two gram-moles of nitrogen at -150.8°C . Estimate the tank pressure using the ideal gas equation of state and then using the virial equation of state truncated after the second term. Taking the second estimate to be correct, calculate the percentage error that results from the use of the ideal gas equation at the system conditions. Data for nitrogen: $T_c = 126.2\text{ K}$, $p_c = 33.5\text{ atm}$, and $\omega = 0.040$ ¹².

Solution

$$\bar{v} = 3.0\text{ L}/2\text{ mol} = 1.5\text{ L/mol}, T = -150.8 + 273.2 = 122.4\text{ K}$$

From the ideal gas law,

$$p_{\text{ideal}} = \frac{\bar{R}T}{\bar{v}} = \frac{(0.08206\text{ L}\cdot\text{atm/mol}\cdot\text{K})(122.4\text{ K})}{1.50\text{ L/mol}} = \mathbf{6.696\text{ atm}}$$

From the truncated virial equation,

$$\frac{p\bar{v}}{\bar{R}T} = 1 + \frac{B(T)}{\bar{v}}$$

$$T_R = 122.4/126.2 = 0.970$$

$$B_0 = 0.083 - \frac{0.422}{T_R^{1.6}} = 0.083 - \frac{0.422}{0.97^{1.6}} = -0.360$$

$$B_1 = 0.139 - \frac{0.172}{T_R^{4.2}} = B_1 = 0.139 - \frac{0.172}{0.97^{4.2}} = -0.0566$$

$$B(T) = \frac{\bar{R}T_c}{p_c} (B_0 + \omega B_1)$$

$$B(T) = \frac{(0.08206\text{ L}\cdot\text{atm/mol}\cdot\text{K})(126.2\text{ K})}{33.5\text{ atm}} [-0.36 + (0.04)(-0.0566)] = -0.112\text{ L/mol}$$

$$p = \frac{\bar{R}T}{\bar{v}} \left(1 - \frac{0.112}{1.5} \right) = \frac{(0.08206\text{ L}\cdot\text{atm/mol}\cdot\text{K})(122.4\text{ K})}{1.50\text{ L/mol}} (0.9253)$$

$$\mathbf{p = 6.196\text{ atm}}$$

Error in using ideal gas law

$$\mathcal{E} = \frac{p_{\text{ideal}} - p}{p} \times 100 = 8.07\%$$

¹² Felder R. M., Rousseau R. W., Elementary Principles of Chemical Processes, Wiley, 2005, pg. 202

3.4-4 Soave-Redlick-Kwong (SRK) Equation

The Soave-Redlick-Kwong (SRK) equation belongs to a class of cubic equations of state because, when expanded, they yield third-degree equations for the specific volume. The SRK equation of state is

$$p = \frac{\bar{R}T}{\bar{v}-b} - \frac{\alpha a}{\bar{v}(\bar{v}+b)} \quad (3.4-11)$$

In this equation, the parameter a , b , and α are empirical functions of the critical temperature and pressure, the Pitzer acentric factor, and the system temperature. The following correlations can be used to estimate these parameters:

$$a = 0.42747 \frac{(\bar{R}T_c)^2}{p_c}$$

$$b = 0.08664 \frac{\bar{R}T_c}{p_c}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2$$

$$\alpha = \left[1 + m(1 - \sqrt{T_R})\right]^2$$

Example 3.4-4

A gas cylinder with a volume of 2.50 m³ contains 1.00 kmol of carbon dioxide at $T = 300$ K. Use the SRK equation of state to estimate the gas pressure in atm. Data for carbon dioxide: $T_c = 304.2$ K, $p_c = 72.9$ atm, and $\omega = 0.225$ ¹³.

Solution

$$T_R = 300/304.2 = 0.9862$$

$$\bar{R}T_c = (0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(304.2 \text{ K}) = 24.96 \text{ L}\cdot\text{atm/mol}$$

$$a = 0.42747 \frac{(\bar{R}T_c)^2}{p_c} = 0.42747 \frac{(24.96 \text{ L}\cdot\text{atm/mol})^2}{72.9 \text{ atm}} = 3.6539 \text{ L}^2\cdot\text{atm/mol}^2$$

$$b = 0.08664 \frac{\bar{R}T_c}{p_c} = 0.08664 \frac{24.96 \text{ L}\cdot\text{atm/mol}}{72.9 \text{ atm}} = 0.0297 \text{ L/mol}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2 = 0.8263$$

¹³ Felder R. M., Rousseau R. W., Elementary Principles of Chemical Processes, Wiley, 2005, pg. 203

$$\alpha = \left[1 + m \left(1 - \sqrt{T_R} \right) \right]^2 = \left[1 + 0.8263 \left(1 - \sqrt{0.9862} \right) \right]^2 = 1.0115$$

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{\alpha a}{\bar{v}(\bar{v} + b)}$$

$$p = \frac{(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(300 \text{ K})}{(2.50 - 0.0297) \text{ L/mol}} - \frac{(1.0115)(3.654 \text{ L}^2 \cdot \text{atm/mol}^2)}{(2.50 \text{ L/mol})(2.50 + 0.0297) \text{ L/mol}}$$

$$p = 9.38 \text{ atm}$$

Example 3.4-5

A stream of propane at temperature $T = 423 \text{ K}$ and pressure $p(\text{atm})$ flows at a rate of 100.0 kmol/hr . Use the SRK equation of state to estimate the volumetric flow rate \dot{V}_{flow} of the stream for $p = 0.7 \text{ atm}$, 7 atm , and 70 atm . In each case, calculate the percentage differences between the predictions of the SRK equation and the ideal gas equation of state. Data for propane: $T_c = 369.9 \text{ K}$, $p_c = 42.0 \text{ atm}$, and $\omega = 0.152^{14}$.

Solution

We first calculate a , b , and α from the following expressions:

$$a = 0.42747 \frac{(\bar{R}T_c)^2}{p_c},$$

$$b = 0.08664 \frac{\bar{R}T_c}{p_c}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2,$$

$$\alpha = \left[1 + m \left(1 - \sqrt{T_R} \right) \right]^2$$

The SRK equation is written in the form

$$f(\bar{v}) = p - \frac{\bar{R}T}{\bar{v} - b} + \frac{\alpha a}{\bar{v}(\bar{v} + b)} = 0$$

\bar{v} is then calculated using Newton's method: $\bar{v} = \bar{v} - \frac{f(\bar{v})}{f'(\bar{v})} = \bar{v} - d\bar{v}$, where

$$f'(\bar{v}) = \frac{\bar{R}T}{(\bar{v} - b)^2} - \frac{\alpha a(2\bar{v} + b)}{[\bar{v}(\bar{v} + b)]^2}$$

The initial value for \bar{v} is obtained from ideal gas law: $\bar{v}_{ideal} = \frac{\bar{R}T}{p}$. The iteration process stops when $\bar{v}/d\bar{v}$ is less than 0.0001. The percentage difference between \bar{v}_{SRK} and \bar{v}_{ideal} is

¹⁴ Felder R. M., Rousseau R. W., Elementary Principles of Chemical Processes, Wiley, 2005, pg. 204

$$\frac{\bar{v}_{ideal} - \bar{v}}{\bar{v}} \times 100\%$$

Once \bar{v} is known for a given p , the volumetric flow rate corresponding to a molar flow rate of 100.0 kmol/hr is obtained as

$$\dot{V}_{flow} \text{ (m}^3\text{/hr)} = \bar{v} \text{ (L/mol)} \frac{10^3 \text{ mol}}{\text{kmol}} \frac{1 \text{ m}^3}{10^3 \text{ L}} (100 \text{ kmol/hr}) = 100 \bar{v} \text{ (L/mol)}$$

The calculations are performed using the following Matlab program:

```
% Example 3.4-5
Tc=369.9; % K
pc=42.0; % atm
w=0.152; % acentric factor
Rg=0.08206; % L*atm/(mol*K)
T=423; % K
p=input('p(atm) = ');
Tr=T/Tc;
a=0.42747*(Rg*Tc)^2/pc;
b=0.08664*(Rg*Tc)/pc;
m = 0.48508 + 1.55171*w - 0.1561*w^2;
alfa=(1+m*(1-Tr^0.5))^2;
videal=Rg*T/p;v=videal;
for i=1:20;
    f=p-Rg*T/(v-b)+alfa*a/(v*(v+b));
    df=Rg*T/(v-b)^2-alfa*a*(2*v+b)/(v*(v+b))^2;
    dv=f/df;
    v=v-dv;
    if abs(dv/v)<1e-4, break, end
end
Di=(videal-v)/v*100;
Flowrate=100*v;
fprintf('videal = %6.2f, v(L/mol) = %6.2f, Percentage Difference = %6.3f\n',videal,v,Di)
fprintf('Flow rate (m3/hr) = %6.1f\n', Flowrate)

>> ex3d4d5
p(atm) = .7
videal = 49.588, v(L/mol) = 49.406, Percentage Difference = 0.37
Flow rate (m3/hr) = 4940.6

>> ex3d4d5
p(atm) = 7
videal = 4.959, v(L/mol) = 4.775, Percentage Difference = 3.86
Flow rate (m3/hr) = 477.5
```


>> ex3d4d5
 p(atm) = 70
 videal = 0.496, v(L/mol) = 0.289, Percentage Difference = 71.57
 Flow rate (m3/hr) = 28.9

The SRK equation of state (and every other equation of state) is itself an approximation. At 423 K and 70 atm, the actual value for \bar{v} is 0.2579 L/mol. The percentage error in the SRK estimate ($\bar{v} = 0.289$ L/mol) is 12%, and that in the ideal gas estimate ($\bar{v} = 0.50$ L/mol) is 92%.

Review: The Newton-Raphson Method

The *Newton-Raphson* method and its modification is probably the most widely used of all root-finding methods. Starting with an initial guess x_1 at the root, the next guess x_2 is the intersection of the tangent from the point $[x_1, f(x_1)]$ to the x -axis. The next guess x_3 is the intersection of the tangent from the point $[x_2, f(x_2)]$ to the x -axis as shown in Figure 5.3-3. The process can be repeated until the desired tolerance is attained.

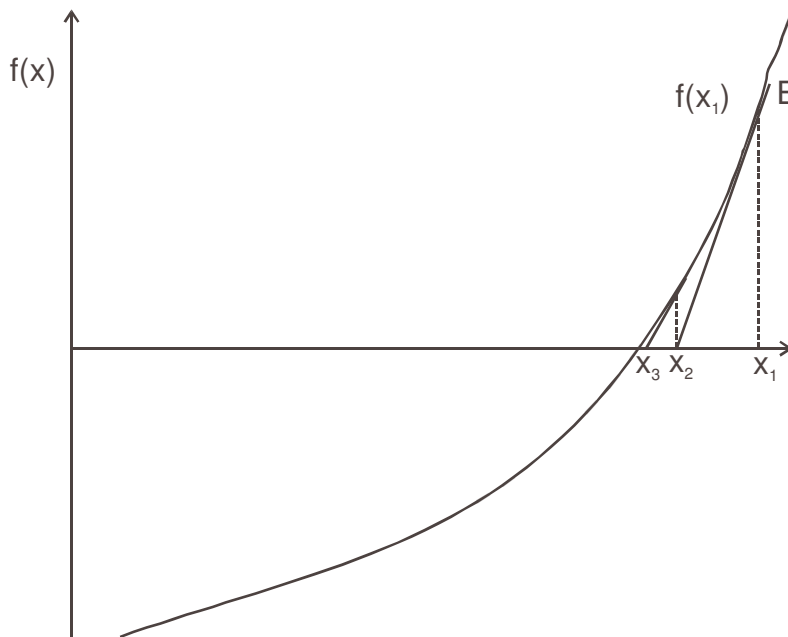


Figure R-1 Graphical depiction of the *Newton-Raphson* method.

The *Newton-Raphson* method can be derived from the definition of a slope

$$f'(x_1) = \frac{f(x_1) - 0}{x_1 - x_2} \Rightarrow x_2 = x_1 - \frac{f(x_1)}{f'(x_1)}$$

In general, from the point $[x_n, f(x_n)]$, the next guess is calculated as

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

The derivative or slope $f'(x_n)$ can be approximated numerically as

$$f'(x_n) = \frac{f(x_n + \Delta x) - f(x_n)}{\Delta x}$$

Example

Solve $f(x) = x^3 + 4x^2 - 10$ using the the *Newton-Raphson* method for a root in the interval [1, 2].

Solution

From the formula $x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$

$$f(x_n) = x_n^3 + 4x_n^2 - 10 \Rightarrow f'(x_n) = 3x_n^2 + 8x_n$$

$$x_{n+1} = x_n - \frac{x_n^3 + 4x_n^2 - 10}{3x_n^2 + 8x_n}$$

Using the initial guess, $x_n = 1.5$, x_{n+1} is estimated as

$$x_{n+1} = 1.5 - \frac{1.5^3 + 4 \times 1.5^2 - 10}{3 \times 1.5^2 + 8 \times 1.5} = 1.3733$$

The next estimate is

$$x_{n+1} = 1.3733 - \frac{1.3733^3 + 4 \times 1.3733^2 - 10}{3 \times 1.3733^2 + 8 \times 1.3733} = 1.3653$$

The next estimate is

$$x_{n+1} = 1.3653 - \frac{1.3653^3 + 4 \times 1.3653^2 - 10}{3 \times 1.3653^2 + 8 \times 1.3653} = 1.3652$$

This value is close to the guessed value of 1.3653, therefore we can accept it as the solution

$$x = 1.3652$$
