5.7 Real Gases and Compressibility

The most accurate way to determine thermodynamic properties is to consult tables or to use appropriate software. Sometimes, however, a table is not available for the substance of interest. If the substance is gaseous, it is tempting to use the ideal gas law, but the ideal gas law does not apply to all gases under all conditions. It is important to have a criterion for when the ideal gas law is inaccurate and an alternative strategy for such cases.

To determine how close to ideal a gas is, a quantity called the compressibility factor is defined as

\[ Z = \frac{v_{act}}{v_{ideal}} \]  

Eq. S5-1

If \( Z \) is equal to unity (\( Z = 1 \)), the actual specific volume, \( v_{act} \), equals the ideal gas specific volume, \( v_{ideal} \), and the gas is perfectly ideal. For real gases, \( Z \) can be either higher or lower than 1, and the extent of the variation from unity indicates the degree of non-ideality.

A more useful version of Eq. S5-1 can be derived by considering the ideal gas law in the form

\[ \frac{v_{ideal}}{RT} = \frac{P}{M} \]

Substituting this into Eq. S5-1 gives

\[ Z = \frac{MP_{act}}{RT} \]  

Eq. S5-2

Figure S5-1 is a plot of the compressibility factor, \( Z \), for hydrogen as a function of pressure and temperature. The horizontal line \( Z = 1 \) is a plot of ideal gas behavior. The plot shows that hydrogen behaves like an ideal gas at high temperatures and low pressures. “High temperature,” in this case, is 200 K and “low pressure” is around 40 atm. At cryogenic temperatures, hydrogen can depart from ideality substantially.

The range of “high temperature” and “low pressure” for which the ideal gas law applies is different for every gas. Hydrogen is still an ideal gas at 200 K because it has such a low boiling point. Water vapor at atmospheric pressure condenses at 373 K (100 °C), so it is definitely not an ideal gas at any temperature below 373 K.

There is a way to compare the behavior of different gases such as water vapor and hydrogen. We can divide the actual temperature of a gas by its temperature at the critical point. Likewise, we divide the actual pressure of the gas by the pressure at the critical point. Experience shows that the difference between real gas behavior and ideal gas behavior depends approximately on how far away the gas is from the critical point.

Recall that the critical point rests at the top of the liquid-vapor dome as shown in Figure 5-5 (see text). At temperatures above the critical temperature or pressures above the critical pressure, the substance cannot exist as a two-phase mixture. When the actual absolute temperature of the gas is divided by the
critical temperature (also expressed in absolute terms), the result is called the reduced temperature as given by

\[ T_R = \frac{T}{T_C} \]

Similarly, the reduced pressure is given by

\[ P_R = \frac{P}{P_C} \]

Figure S5-2 is a plot of compressibility factor for a number of different gases as a function of reduced pressure. The plot contains lines of constant reduced temperature. As can be seen, different gases at the same reduced temperature and pressure tend to have the same compressibility factor. In other words:

\[ Z \approx f(T_R, P_R) \]

This result is called the principle of corresponding states. Figure S5-2 can be used to find any of the three properties \( T, P, \) or \( v \) when the other two are known.

Figure S5-1 The compressibility factor for hydrogen gas  (Moran, M.J.,and H.N. Shapiro, *Fundamentals of Engineering Thermodynamics*, 3rd ed., Wiley, New York, 1995, Fig. 3-10, section 3.4, p. 92, Used with permission)
Example S5-1  Compressibility of a Refrigerant

Find the specific volume of tetrafluoromethane (R-134a) at 140°C and 1.6 MPa by three methods
a) Ideal gas law
b) Compressibility chart
c) Thermodynamic tables

Is R-134a an ideal gas under these conditions?

Approach:

The first part is a routine application of the ideal gas law. For the second part, calculate the reduced temperature and pressure from \( T_R = T/T_C \) and \( P_R = P/P_C \). Values of \( T_C \) and \( P_C \) are available in Table A-1. Then use Figure S5-2 to find \( Z \). Knowing \( Z \), determine \( v \) from Eq. S5-2. For the third part, consult Table A-17 for superheated R-134a.
Solution:

a) To find the specific volume from the ideal gas law use \([A1]\)

\[
v = \frac{RT}{MP}
\]

The value of \(\frac{R}{M}\) for R-134a from Table A-1 is 0.08149 kJ/(kg·K). Substituting this into the ideal gas equation along with given values for pressure and temperature produces

\[
v = \left(\frac{0.08149 \text{ kJ}}{\text{kg} \cdot \text{K}}\right) \left(140 + 273\right) \text{K} \left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{10^6 \text{ Pa}}{1 \text{ MPa}}\right) = 0.02103 \text{ m}^3/\text{kg}
\]

b) To use the compressibility chart, first compute the reduced temperature and pressure. The temperature and pressure at the critical point, \(T_C\) and \(P_C\), can be found in Table A-1. Using these, the reduced quantities are

\[
T_r = \frac{T}{T_C} = \frac{140 + 273}{374.3} = 1.1
\]

\[
P_r = \frac{P}{P_C} = \frac{1.6 \text{ MPa}}{4.067 \text{ MPa}} = 0.3934
\]

Next find the compressibility factor from Figure S5-2. From the point 0.4 along the horizontal axis, move vertically until you reach the isotherm for \(T_r = 1.1\). Then read the value of \(Z\) along the vertical axis. The compressibility \(Z\) has a value of approximately 0.89. Since \(Z = 1\), for an ideal gas, one can expect about 11% error by using the ideal gas law for R-134a at these conditions. Rearranging Eq. S5-2 to isolate \(v\) gives

\[
v = \frac{ZRT}{MP}
\]

Again using values of \(\frac{R}{M}\) from Table A-1 and substituting given values

\[
v = \frac{(0.89) \left(0.08149 \text{ kJ} \cdot \text{kg} \cdot \text{K}^{-1}\right) \left(140 + 273\right) \text{K} \left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{10^6 \text{ Pa}}{1 \text{ MPa}}\right)}{(1.6 \text{ MPa}) \left(\frac{10^6 \text{ Pa}}{1 \text{ MPa}}\right)} = 0.01872 \text{ m}^3/\text{kg}
\]

By comparison, the value from the ideal gas law was 0.02103 m$^3$/kg.

c) The most accurate way to find the specific volume is to consult tables. From Table A-16 for superheated R-134a vapor, the specific volume at 140ºC and 1.6 MPa is

\[
v = 0.01887 \text{ m}^3/\text{kg}
\]

Assumptions:

A1. In part a) assume the gas is ideal.
Comments:

The table value is very close to the value from the compressibility chart and somewhat lower than the ideal gas value. The ideal gas law can only be used to give an estimate at this temperature and pressure.

The compressibility chart can also be used to find $P$ if $T$ and $v$ are known. However, the process requires an iterative approach. A suggested method is as follows:

1) Find reduced temperature, $T_R = T/T_C$.
2) Use the ideal gas law to estimate $P$.
3) Calculate the reduced pressure, $P_R = P/P_C$.
4) Use Figure S5-2 to find $Z$.
5) Calculate $P$ from this value of $Z$.
6) Iterate through steps 3 to 5 until the pressure no longer changes from one iteration to the next.

A similar iterative procedure can be developed to find $T$ if $P$ and $v$ are known.