

6.1 PVT Computations for Non-ideal Gases

Problem Statement

Commercial CO_2 cartridges have a large number of uses including bicycle tire and life jacket inflators, soda dispensers, compressed gas cleaners for electronic devices, and gas powered guns. They can be purchased at low-cost from sports store and on-line.

A popular size of CO_2 cartridge holds 12g in an internal volume of 17.6 cm³. Estimate the pressure inside the cartridge under hot (40°C = 104°F = 313.15 K) conditions.

In [22]:

```
# problem data
n = 12/44          # gram-moles
V = 0.0176/n       # specific volume in liters/gmol
T = 40 + 273.15    # Kelvin

# gas constant
R = 0.08206        # gas constant liter-atm per kelvin-gmol

# critical properties of CO2
Tcritical = 304.25  # Kelvin
Pcritical = 72.9    # atm
acentric_factor = 0.225 # Pitzer acentric factor

print('molar specific volume =', round(V,4), 'liters/gmol')
print('molar density =', round(1/V, 2), 'gmol/liter')

# a dictionary to store results
predictions = {}

molar specific volume = 0.0645 liters/gmol
molar density = 15.5 gmol/liter
```

Estimating Pressure

Ideal Gas Law

Our first attempt at computing the cartridge pressure will use the ideal gas law. Written in terms of molar specific volume

$$\hat{V} = \frac{V}{n}$$

the ideal gas law is given by

$$P\hat{V} = RT$$

Here we solve for P using the problem data. Before going further, decide if the results of this calculation seem realistic to you.

In [3]:

```
P_ideal_gas = R*T/V

predictions['Ideal Gas'] = P_ideal_gas

print('CO2 Pressure (Ideal Gas) =', round(P_ideal_gas, 1), 'atm')
print('CO2 Pressure (Ideal Gas) =', round(14.696*P_ideal_gas, 1), 'psia')
```

```
CO2 Pressure (Ideal Gas) = 398.2 atm
CO2 Pressure (Ideal Gas) = 5851.9 psia
```

Compressibility Charts

Compressibility is defined as

$$z = \frac{P\hat{V}}{RT}$$

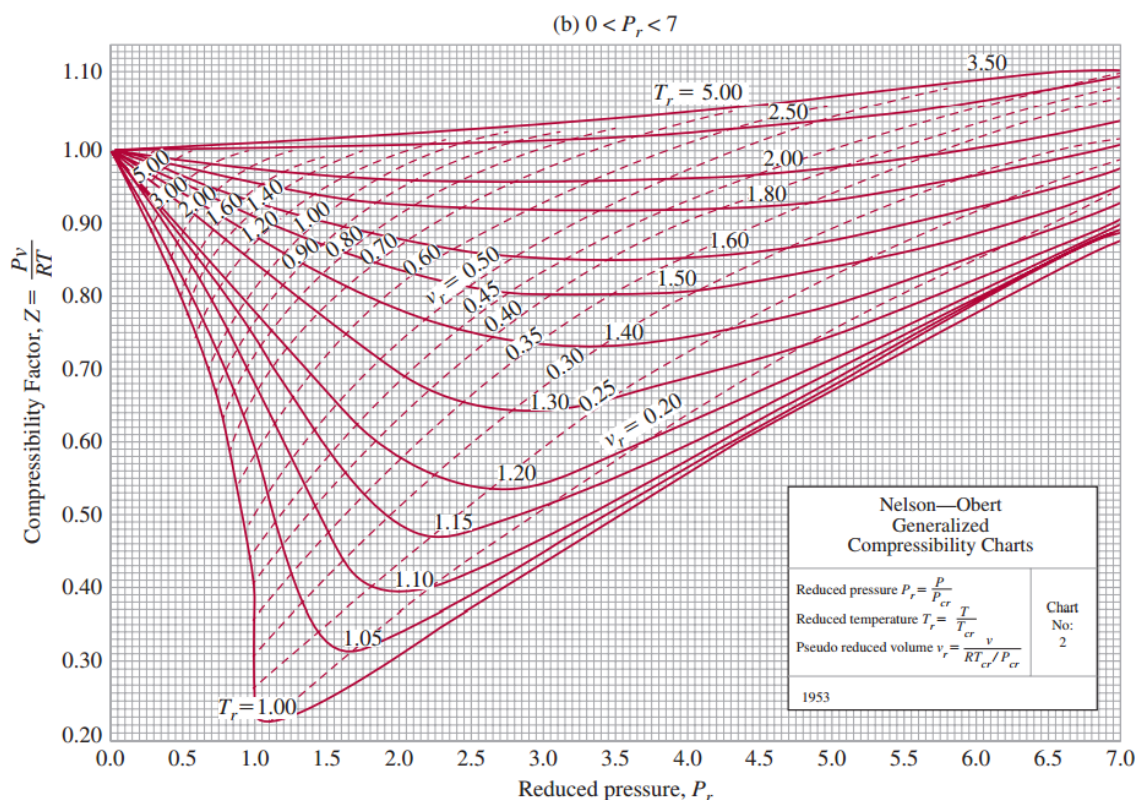
which, by definition, has a value $z = 1$ for an ideal gas. Real gases display a significant deviation from 1, generally increasing with increasing pressure as the gas molecules get closer together, and decreasing with temperature.

The [principle of corresponding states](#), developed by Johannes Diderik van der Waals in 1873, correlates the compressibility of real gases to the critical temperature T_c and critical pressure P_c . For this purpose, the **reduced temperature** T_r and **reduced pressure** P_r are defined as

$$T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c}$$

A [compressibility chart](#) presents the averaged compressibility measured for a number of species. Given values of the reduced temperature and pressure, T_r and P_r , one locates the value of compressibility factor z , then use the above relationship to compute molar volume \hat{V} .



For the case where V is one of the known variables it is convenient to define an **ideal reduced volume**. The first step is to define an ideal critical volume

$$\hat{V}_c^{ideal} = \frac{RT_c}{P_c}$$

The reason for the superscript 'ideal' is because this is a ficti

Then the ideal reduced volume \hat{V}_r^{ideal} is

$$\hat{V}_r^{ideal} = \frac{\hat{V}}{\hat{V}_c} = \frac{P_c \hat{V}}{RT_c}$$

The compressibility chart is augmented with contours of constant \hat{V}_r^{ideal} . Given values for \hat{V}_r^{ideal} and either P_r or T_r , a corresponding value of z is located. The compressibility definition is then used to solve for the unknown variable.

In [23]:

```
Tr = T/Tcritical
Vr = Pcritical*V/(R*Tcritical)

print('reduced temperature =', round(Tr,2))
print('ideal reduced volume =', round(Vr,2))
```

```
reduced temperature = 1.03
ideal reduced volume = 0.19
```

In [5]:

```
# look up values (https://pubs.acs.org/doi/pdf/10.1021/ie50467a036)
z = 0.28

# compute pressure
P_compressibility = z*R*T/V

predictions['Compressibility'] = P_compressibility

print('CO2 Pressure =', round(P_compressibility, 2), 'atm')
print('CO2 Pressure =', round(14.696*P_compressibility, 2), 'psia')
```

```
CO2 Pressure = 111.5 atm
CO2 Pressure = 1638.54 psia
```

While we still can't be sure this estimate is accurate, we can definitely see the estimate based on the ideal gas law is completely off-base. The reason is that the cartridge is filled to a point where the contents are close to the critical point on the phase diagram.

Virial Model

The virial expansion was first proposed by a Kamerlingh Onnes, a physicist who won the Nobel prize in 1911 for his work on superconductivity and liquid helium. (He also coined the word 'enthalpy'). The key idea is to create an infinite series approximation for compressibility in the form

$$\frac{P\hat{V}}{RT} = A + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} \dots$$

where A, B, C are temperature dependent and known as the first, second, and third virial coefficients, respectively. The case $A = 1$ and $B = C = D = \dots = 0$ corresponds to an ideal gas.

A commonly used version of this expansion is to assume $A = 1$, $B(T)$, and $C = D = \dots = 0$, with the further approximation $\hat{V} = \frac{RT}{P}$. Then

$$\frac{P\hat{V}}{RT} = 1 + \frac{BP}{RT}$$

This can be simplified to read

$$P = \frac{RT}{\hat{V} - B}$$

The temperature dependent value of B is estimated by

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

ω is the **Pitzer acentric factor**, values of which are tabulated in standard sources for chemical data.

In [18]:

```
Tr = T/Tcritical
B0 = 0.083 - 0.422/Tr**1.6
B1 = 0.139 - 0.172/Tr**4.2
B = (R*Tcritical/Pcritical)*(B0 + acentric_factor*B1)
print('B =', B)

P_virial = R*T/(V - B)

predictions['Virial'] = P_virial

print('CO2 Pressure =', round(P_virial, 2), 'atm')
print('CO2 Pressure =', round(14.696*P_virial, 2), 'psia')

B = -0.11061596372197276
CO2 Pressure = 146.72 atm
CO2 Pressure = 2156.13 psia
```

van der Waals Equation of State

The **van der Waals** equation of state has the form

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

where values for the coefficients a and b are determined by the critical point temperature and pressure

$$a = \frac{27R^2T_c^2}{64P_c} \quad b = \frac{RT_c}{8P_c}$$

The parameter a accounts for long-range attractive forces acting between molecules, and b for short-range repulsive forces.

In [19]:

```
a = 27*R**2*Tcritical**2/(64*Pcritical)
b = R*Tcritical/(8*Pcritical)
print('a =', a, ' b =', b)

P_vdw = R*T/(V-b) - a/V**2

predictions['van der Waals'] = P_vdw

print('CO2 Pressure =', round(P_vdw, 2), 'atm')
print('CO2 Pressure =', round(14.696*P_vdw, 2), 'psia')

a = 3.6072850418404214    b = 0.042809936556927296
CO2 Pressure = 316.73 atm
CO2 Pressure = 4654.72 psia
```

Soave-Redlich-Kwong Equation of State

The Soave-Redlich-Kwong equation of state is one of most widely used equations of states, and proven to be applicable to a wide variety of systems. The general expression

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)}$$

where the parameters are given by

$$\begin{aligned} a &= 0.42747 \frac{(RT_c)^2}{P_c} \\ b &= 0.08664 \frac{RT_c}{P_c} \\ m &= 0.48508 + 1.55171\omega - 0.1561\omega^2 \\ T_r &= \frac{T}{T_c} \\ \alpha &= [1 + m(1 - \sqrt{T_r})]^2 \end{aligned}$$

In [8]:

```
from math import sqrt

a = 0.42747*(R*Tcritical)**2/Pcritical
b = 0.08664*R*Tcritical/Pcritical
m = 0.48508 + 1.5517*acentric_factor - 0.1561*acentric_factor**2
Tr = T/Tcritical
alpha = (1 + m*(1-sqrt(Tr)))**2

P_srk = R*T/(V-b) - alpha*a/V/(V+b)

predictions['SRK'] = P_srk

print('CO2 Pressure =', round(P_srk, 2), 'atm')
print('CO2 Pressure =', round(14.696*P_srk, 2), 'psia')

CO2 Pressure = 150.24 atm
CO2 Pressure = 2207.97 psia
```

Reference Data from NIST Webbook

The National Institute of Standards and Technology (NIST) maintains a web site devoted to the distribution of standard reference data. The [NIST Chemistry WebBook](#) is an excellent source of carefully curated data on over 7000 organic and small inorganic compounds.

[NIST Fluid Properties Data for CO₂](#)

In [9]:

```
print('density =', 1/V, 'mol/liter')

density = 15.495867768595039 mol/liter
```

In [20]:

```
P_nist = 108.13 # atm

predictions['NIST Webbook'] = P_nist

print('CO2 Pressure =', round(P_nist, 2), 'atm')
print('CO2 Pressure =', round(14.696*P_nist, 2), 'atm')

CO2 Pressure = 108.13 atm
CO2 Pressure = 1589.08 atm
```

Comparison of Estimates

In [21]:

```
print('{0:15s} {1:9s} {2:5s}'.format('EOS', 'Pressure', 'Error'))

for key, val in predictions.items():
    err = 100*(val-P_nist)/P_nist
    print('{0:15s} {1:5.1f} atm {2:5.1f}%'.format(key, val, err))
```

| EOS | Pressure | Error |
|-----------------|-----------|--------|
| Ideal Gas | 398.2 atm | 268.3% |
| Compressibility | 111.5 atm | 3.1% |
| Virial | 146.7 atm | 35.7% |
| van der Waals | 316.7 atm | 192.9% |
| SRK | 150.2 atm | 38.9% |
| NIST | 108.1 atm | 0.0% |
| NIST Webbook | 108.1 atm | 0.0% |

Non-Ideal Behavior

How does the CO_2 pressure depend on temperature in the range from 30C to 50C?

Discussion Points

1. Why is the ideal gas law so wrong?
2. Why do the compressibility charts work so well in this case? Do you expect them to work well in others?
3. How would the calculations change if we were given pressure and temperature, and asked to compute molar volume?