

Compression and condensation of carbon dioxide

Introduction

While the ideal gas equation is a useful starting point in describing the behavior of gases, it fails qualitatively at high pressures and low temperatures. The purpose of this experiment is to examine the behavior of a real gas (CO_2) under conditions where the ideal gas equation fails and to explore a simple equation of state to determine how well it can explain the behavior quantitatively.

The experimental apparatus

The device you will be using, the “SFT Phase Monitor” from Supercritical Fluid Technologies, consists of a chamber containing a movable piston (a “syringe pump”) operated by a precision screw which is turned by four large handles (Fig. 1). As the screw is turned the piston moves in or out, changing the volume of the chamber. The chamber is fitted with a window at one end so that phase transitions can be observed, and the entire device is temperature-controlled.

Pressure is calibrated in pound-force per square inch (PSI). To emphasize that the scale is absolute (referenced to vacuum) the scale is sometimes written PSIA. The conversion to pascals is $1 \text{ PSI} = 6894.76 \text{ Pa}$; to convert to bars, use $1 \text{ PSI} = .0689476 \text{ bar}$. The conversion to atmospheres is $1 \text{ atm} = 14.6959 \text{ PSI}$.

Temperature is read out in $^{\circ}\text{C}$.

The piston is driven at a rate of 14 turns per inch, or 0.36 mL per turn. The total number of turns of the screw is 84.24, so the volume of the chamber may be adjusted by 30.33 mL. The minimum volume of the chamber is about 3 mL, and the maximum volume is a little over 33 mL. The chamber is rated for a total pressure of 10,000 PSI ($1 \text{ atm} \approx 14.70 \text{ PSI}$; $1 \text{ PSI} = 6894.76 \text{ Pa}$). **Be careful not to exceed this pressure.** The most common way of overpressurizing the vessel is to allow it to heat unattended. A schematic of the device showing valves and sensors is shown in Fig. 2.

There is also a small HPLC pump (high pressure liquid chromatography) which can be used to fill the chamber with liquid CO_2 . In order for the pump to work properly, it must pump *liquid* carbon dioxide; this is accomplished in two ways: first, the carbon dioxide tank is equipped with a siphon tube inside so that it draws liquid from the bottom of the tank, and second, the pump

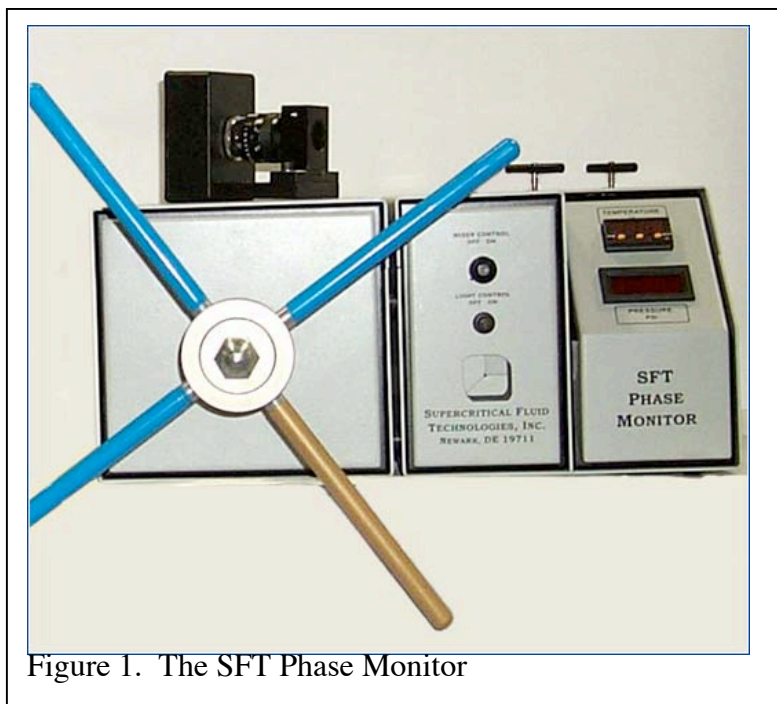


Figure 1. The SFT Phase Monitor

itself is cooled with a small thermoelectric cooler attached to the pump head. Examine the cooling apparatus to make sure you understand it, and ask the teaching assistant about anything you don't understand.

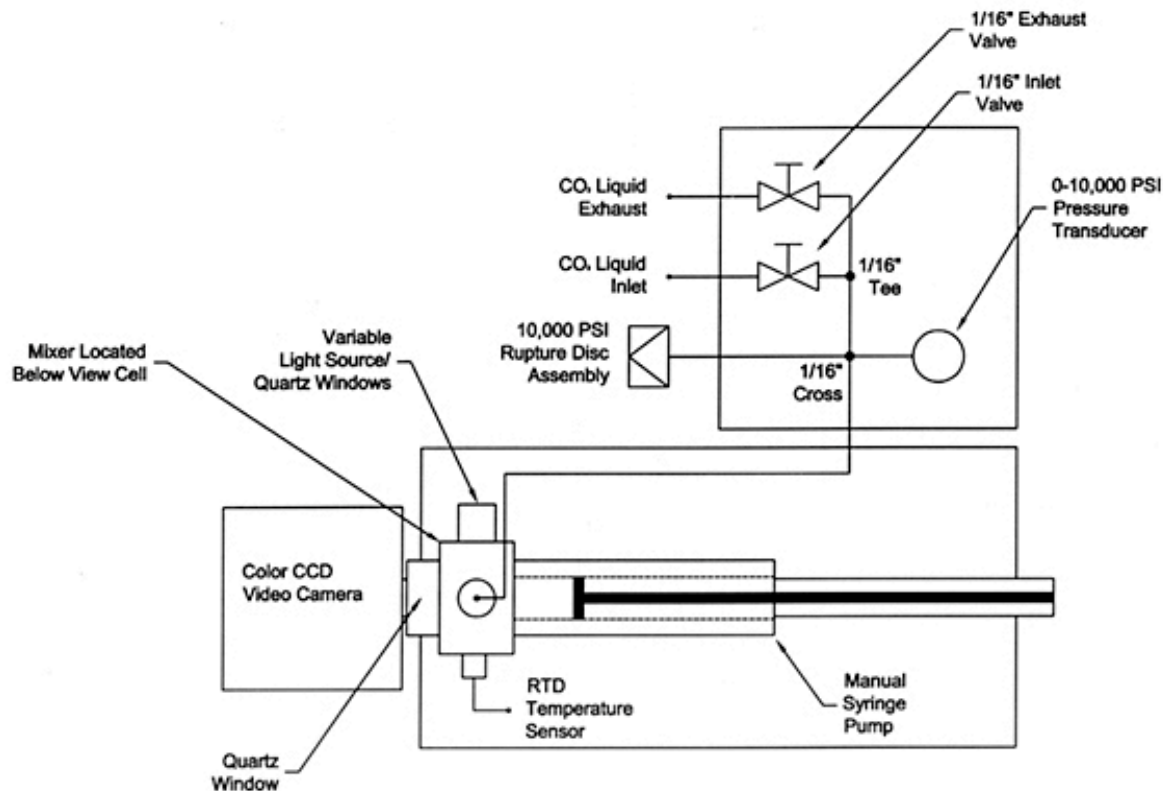


Figure 2. A schematic diagram of the SFT Phase Monitor.

Measuring a PV isotherm of CO₂

The first set of measurements you need to make will be at about 27°C. This temperature is chosen because the compressibility of CO₂ is well known at that temperature. The Phase Monitor should already be at this temperature when you arrive in the laboratory, and the “set point” for the temperature should be set at that temperature. Check to be sure this is the case before proceeding; the teaching assistant will show you how.

Extend the piston to its outermost limit by turning the screw counterclockwise until it stops. Fill the chamber with carbon dioxide until the pressure is about 700 PSI. The pressure and temperature should equilibrate quickly, settling down to a stable value in a minute or less. Record the temperature and pressure.

Now turn the screw inward by 1 turn. The odd-colored handle will help you keep track of whether you have made a full turn; the *number* of full turns is something you will have to count for yourself. Wait about 10-30 seconds for the pressure and temperature to equilibrate, then record (a) the number of turns you have made, (b) the pressure, and (c) the temperature. It might save time later if you also enter these numbers into an Excel spreadsheet at this point. If you do, your data will look something like this:

0	700	27.1
1	703	27.2

Repeat this procedure, recording the pressure and temperature with each turn, until the screw reaches its limit, at all times monitoring the pressure so that you do not exceed a safe limit. If

you take 10 seconds per reading, the procedure will take about 15 minutes. Taking 30 seconds per reading will extend the time to about 45 minutes. The temperature will drift somewhat during the course of the experiment, and the pressure will adjust accordingly. It will not, therefore, yield significantly better results to wait more than 30 seconds for the pressure to stabilize.

As you compress the gas, three things may happen: the pressure may change, the temperature may change (**why?**), and the gas may condense. The first two phenomena will be monitored on the temperature and pressure readouts; condensation may be observed on the video display. Make a note of any indication of condensation in your lab notebook as it occurs.

Measuring the PT curve at the phase boundary

The next part of the experiment will require you to add more CO₂ to the apparatus. Back the piston screw out by 20 – 30 turns, then use the HPLC pump attached to the phase monitor to fill the chamber about half full of liquid CO₂. Wait a minute for the pressure and temperature to equilibrate, then, having made sure the heating jacket is installed around the chamber, set the temperature set point to a temperature of 32°C.

The chamber will slowly heat up, and the pressure will begin to rise as the vapor pressure of CO₂ rises with temperature. Make a note of the temperature and vapor pressure periodically, preferably at 0.1° intervals. You may again want to record your results simultaneously in a spreadsheet. As more and more of the liquid evaporates, you may need to adjust the volume of the chamber to be sure that both liquid and gas are present. Try to keep the meniscus of the liquid about midway up the window. As you pass the critical point, the meniscus will become difficult to observe; pay attention to the behavior of the gas/liquid boundary as the temperature rises from 30° to 31° and try to describe what you see in a concise way.

An isotherm above the critical point

Reduce the chamber volume by tightening the piston screw, **taking great care not to exceed the rated pressure of the equipment**. Once the temperature settles down at its final value you will need to perform one final set of measurements: plot an isotherm for the supercritical fluid.

Release CO₂ from the chamber (if necessary) to bring the pressure down to about 1400 PSI with the screw turned all the way in.

Record the temperature and pressure as you did before, this time expanding the volume of the chamber by one turn of the screw between measurements. At high pressures the chamber may take a bit longer to relax to an equilibrium pressure, but 30 seconds or so should be ample time to allow this to happen. Record pressure and temperature as a function of number of turns of the screw until the chamber has reached its maximum volume (that is, the screw is completely extended). Once again, recording your measurements simultaneously in your notebook and an Excel spreadsheet may save time later. You are now ready to analyze your data.

Shutting down the Phase monitor

Once you are done with the experiment, reset the temperature to 27°C and leave the instrument on. In that way it will be ready for the next group that needs to use it. If there has been a problem with the Phase Monitor, be sure the teaching assistant knows about it.

Analysis of the data

Analysis of your data will go most smoothly if you use a spreadsheet program such as Excel (which is provided on the laboratory computers). You *can* do these calculations on a hand calculator, but there is a much greater opportunity for making a mistake.

Changing to real-world units

Look at the spreadsheet where you recorded the first set of data. You will need to convert the number of screw turns to a volume measurement; the formula is shown below in Fig. 3.

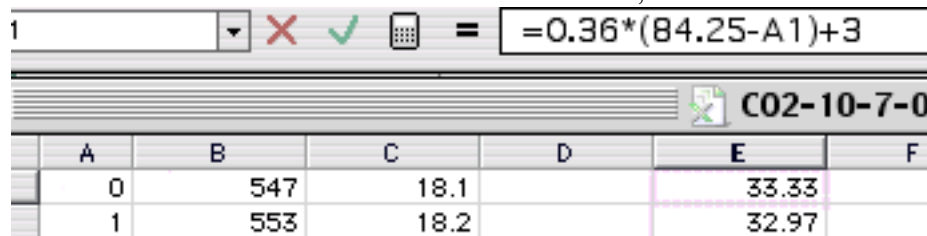


Figure 3. Part of the spreadsheet for the CO₂ isotherm.

You will also need to convert the pressure from PSI to some other unit. The system of choice is SI units if there is no compelling reason to use anything else. The SI unit of pressure is the pascal (Pa); dividing by 10⁶ gives the pressure in megapascal, which is a bit easier to read (see Fig.4).

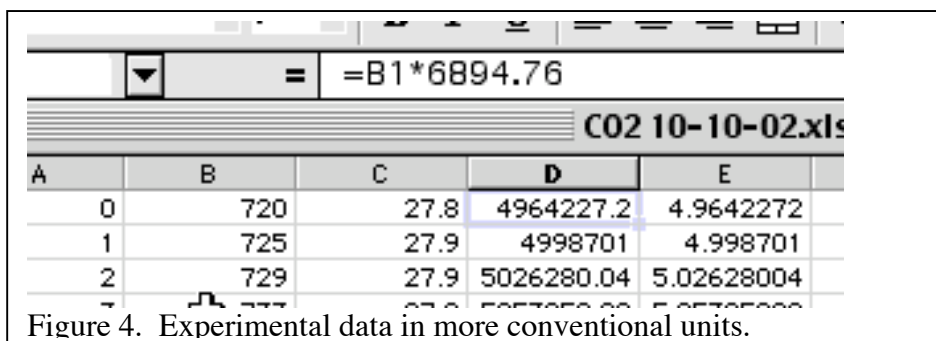


Figure 4. Experimental data in more conventional units.

If you are to compare the measurements with an equation of state, you need one more piece of information: the number of moles of gas in the system. If you had a way of *measuring* the absolute number of moles of gas in the chamber, that would be ideal. As it is, you will need to rely on a previously determined compressibility of CO₂ to calibrate the amount of material present. This can be

Table 1. Molar volume and compressibility factor of CO₂ at 300.15 K.

P/MPa	V _m /m ³	Z
4.00	0.00047924	0.768
5.00	0.00034358	0.688
6.00	0.00024254	0.583

computed from any point on the curve; for a variety of reasons, a low pressure is best for this purpose. Examine Table 1, which lists the compressibility factor $Z=PV/nRT$ as a function of pressure in megapascals (it also lists the molar volume in m³ for your convenience). Find a pressure in Table 1 that falls within the range of pressures you measured. Select the data point from among your measurements with the pressure that falls closest to the tabulated point, and perform a linear interpolation of the tabulated data to find the compressibility Z at your measured pressure. Use this compressibility to compute the number of moles of gas in the chamber, given your experimental volume, pressure, and temperature.

Now compute the following quantities for each data point:

- P , the pressure (in Pa)
- V_m , the molar volume (in m^3)
- T , the absolute temperature (in K)

From these and the ideal gas constant R in JK^{-1} you will then be able to compute the

- Compressibility factor, $Z = PV_m/RT$ (dimensionless).

We want to plot this and, ultimately, compare the compression curve with a PV isotherm of a van der Waals gas. The plot will look something like the one in Fig. 5.

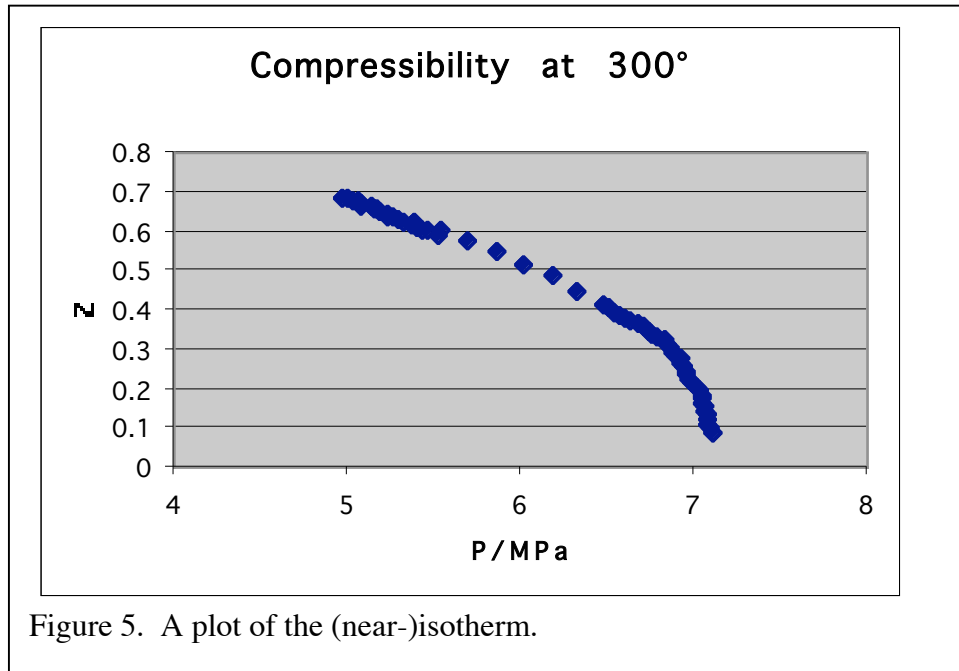


Figure 5. A plot of the (near-)isotherm.

The sloping part of the graph at low pressures represents a single phase where the sample is behaving as a gas. The nearly vertical part on the right is a region where condensation occurs. The pressure there is simply the vapor pressure of the liquid.

Repeat this calculation for the high temperature isotherm you measured, this time using the compressibility factors from Table 2 to calibrate the number of moles of CO_2 in your sample.

Table 2. Compressibility at $T=305.15\text{K}$

P/MPa	V_m/m^3	Z
4	0.000498	0.785
5	0.000362	0.714
6	0.000266	0.628
7	0.000182	0.503

You are now ready to compare your data with a model equation of state.

Comparison with a model

The ideal gas equation is usually the starting point for any discussion of numerical models of gases. Pressure (P), volume (V), moles of gas (n) and absolute temperature (T) are related through the ideal gas constant R (which is just the Boltzmann constant in molar units):

$$PV = nRT$$

While this equation is always a good limiting equation for very low pressure, it becomes a poor approximation at high pressures, especially at low temperatures. Exactly *how* high a pressure (or

how low a temperature) will depend, of course, on the accuracy of the measurement to be performed; as a simple rule, pressures and temperatures that allow the gas to condense into a liquid will cause the ideal gas equation to fail spectacularly.

It seems likely, therefore, that the ideal gas law will not be good enough. The equation of state that is most often introduced as a refinement to the ideal gas law is the van der Waals equation of state, which is discussed in detail in most physical chemistry textbooks:

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

P , R , and T have the meaning given above; a and b are constants chosen to describe the behavior of a particular gas (more on this later), and V_m is the molar volume, given by V/n . Another way of expressing this relationship is in terms of the dimensionless compressibility factor, $Z = PV_m/RT$.

$$Z = \frac{PV_m}{RT} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}$$

You need to decide on values of a and b , and the most common way of assigning these values is based on the critical constants of the gas in question. As is described in many places, the three critical constants P_c , T_c , and V_c are related to the two van der Waals constants a and b by the equations

$$V_c = 3b$$

$$T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{a}{27b^2}$$

The critical constants for CO_2 are presented in Table 3.

Critical (molar) volume	V_c	2.137 dm ³ /kg
Critical pressure	P_c	73.815 bar
Critical temperature	T_c	31.04°C

Table 3. Critical constants of CO_2 (taken from the Matheson Gas Data Book).

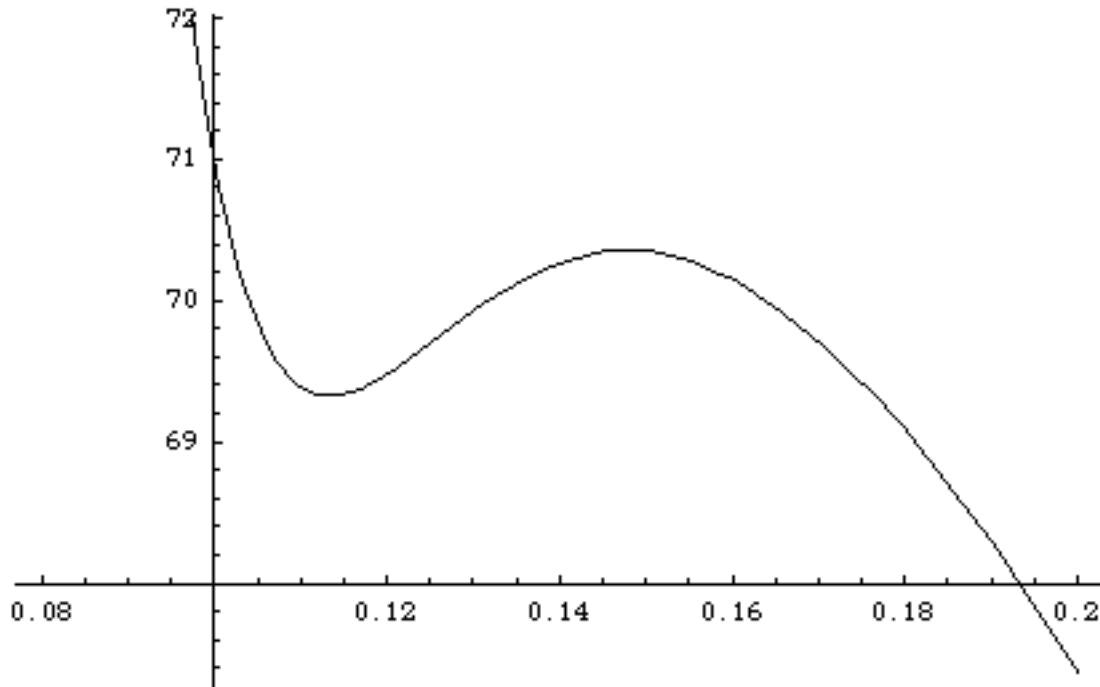
Calculate a and b from P_c and T_c , then make two checks to be sure you did it right: compare the values of a and b with those in your textbook (they should be similar though not identical), and compute V_c from b to get some idea of how good the model is at the critical point.

Once you have decided on values of a and b , compute the compressibility factor for each of your data points using the van der Waals equation of state and plot the predicted values of Z for a van der Waals gas on the same plot as your experimental data. Describe how well the model predicts the experimental data. Where is the behavior qualitatively different? Where does the model fit the data reasonably well? Under what circumstances is the van der Waals model good enough?

Repeat the exercise for your high temperature isotherm, this time choosing a value from Table 2.

Finding the Equilibrium Vapor Pressure for a van der Waals Fluid

If you plot the isotherm for a van der Waals gas below the critical point, the curve looks like this:



A moment's reflection will convince you that this curve is not physically reasonable. If there are three allowed values of the molar volume for $P=70$, for instance, how does the gas know which one to choose?

Within the pressure region for which the van der Waals equation has three real roots (three solutions for volume), the experimental state of affairs is that liquid and vapor coexist. The "outside" roots correspond to the molar volumes of the coexisting liquid and vapor phases; the "middle" root has no physical significance. At the selected temperature, the pressure of the system is constant, and variation of the volume merely shifts the relative amounts of liquid and vapor which coexist in the closed system. The question arises: within the region of three real van der Waals roots for some specified temperature and substance, can we find the equilibrium vapor pressure (accepting the van der Waals function as the equation of state)?

J. C. Maxwell applied some principles of thermodynamics to present a solution to the problem. The relationship among the Helmholtz free energy, temperature, entropy, pressure, and volume can be written as:

$$dA = -PdV - SdT$$

At constant temperature (corresponding to problem posed), the statement simplifies to

$$dA = -PdV; \quad \Delta A = A_2 - A_1 = -\int_1^2 PdV$$

Selecting some particular pressure (within the region of three real roots) on a P vs. V plot for a van der Waals fluid, we see that there are two isothermal paths between the two "outside" roots: one along the van der Waals function, and the other along the path of constant pressure. The free energy A is a state function, that is, the difference in its values at two different states of the system is independent of the path taken between the two states. It therefore follows that the free energy change for any path which finally returns to the initial condition of the system is zero. In the present case, this means that if we move out from the first root along the van der Waals isotherm to the "far" root, and then return along the constant pressure path, the total free energy

change for the expedition will be zero. The free energy change is the integral along the path, which here has two distinct parts:

$$\int_{V_1}^{V_2} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) dV - \int_{V_1}^{V_2} P' dV = \int_{V_1}^{V_2} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2} - P' \right) dV$$

The value of the integral depends upon the choice of pressure P' ; we seek the unique pressure (for the stated temperature and fluid) which makes the value of the integral zero. Graphically, this occurs when the area under the constant pressure path is equal to the area under the van der Waals isotherm.

An outline of a solution using *Mathematica*:

- Define $P(V,T,a,b)$ for the van der Waals equation for 1 mol of CO_2 at 300 K;

```
In[3]:= r := 8.314472145136097`
```

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In[4]:= pvdW[v_m_, t_, a_, b_] :=  $\frac{r t}{v_m - b} - \frac{a}{v_m^2}$ 
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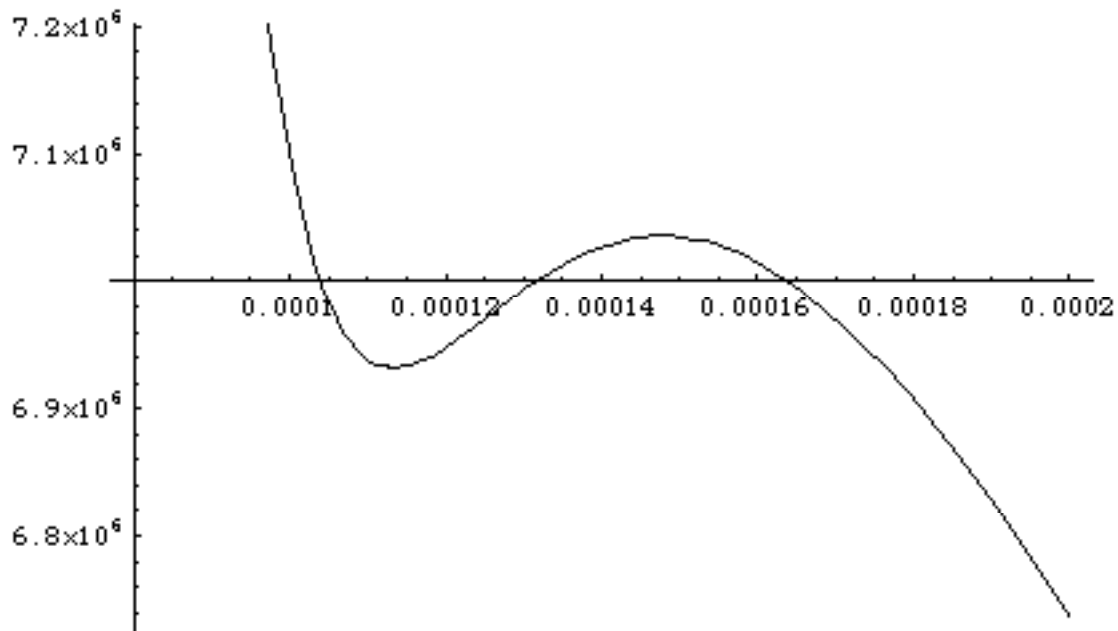
- Define the ideal gas and van der Waals constants for CO_2 :

```
In[8]:= aCO2 := 3.658 × 10-1
```

```
In[10]:= bCO2 := .04286 × 10-3
```

- Plot the function as an aid in finding approximate roots.

```
In[11]:= Plot [pvdW[v_m, (273.15 + 27), aCO2, bCO2],
{v_m, .00008, .0002}]
```



```
Out[11]= - Graphics -
```


- Find the "outside" roots using the *Mathematica* "Solve" routine. Repeat for several values of pressure.

In[12]:= **pTest = 6.99 10⁶**

Out[12]= 6.99 × 10⁶

In[13]:= **temp = 273.15 + 27**

Out[13]= 300.15

In[15]:= **Solve[pTest == pvdW[v, temp, aCO2, bCO2], v]**

Out[15]= {{v → 0.000104444}, {v → 0.000129121}, {v → 0.000166318}}

In[16]:= **pTest = 7.00 10⁶**

Out[16]= 7. × 10⁶

In[17]:= **Solve[pTest == pvdW[v, temp, aCO2, bCO2], v]**

Out[17]= {{v → 0.000103848}, {v → 0.000131446}, {v → 0.000164078}}

In[18]:= **pTest = 7.01 10⁶**

Out[18]= 7.01 × 10⁶

In[19]:= **Solve[pTest == pvdW[v, temp, aCO2, bCO2], v]**

Out[19]= {{v → 0.000103309}, {v → 0.000134026}, {v → 0.000161529}}

- Find the value of the closed path integral for each choice of constant pressure. This and the two preceding steps are interactive, since we are trying to bracket the zero value of the integral.

In[20]:= **pTest = 6.99 10⁶**

Out[20]= 6.99 × 10⁶

In[22]:=
$$\int_{0.00010444393400798764}^{0.00016631792726668618} \left(\frac{r \text{ temp}}{v - bCO2} - \frac{aCO2}{v^2} - pTest \right) dv$$

Out[22]= 0.225885 + 0. i

In[23]:= **pTest = 7.00 10⁶**

Out[23]= 7. × 10⁶

In[25]:= $\int_{0.00010384794801082502}^{0.00016407840201561251} \left(\frac{r \text{ temp}}{v - b_{\text{CO2}}} - \frac{a_{\text{CO2}}}{v^2} - p_{\text{Test}} \right) dv$

Out[25]= -0.384898 + 0. i

Out[26]= 7.01 × 10⁶

In[28]:= $\int_{0.00010330893772527824}^{0.00016152930180292777} \left(\frac{r \text{ temp}}{v - b_{\text{CO2}}} - \frac{a_{\text{CO2}}}{v^2} - p_{\text{Test}} \right) dv$

Out[28]= -0.977514 + 0. i

From the above examples we can see that, for a van der Waals gas with the a and b constants given earlier at 27.00°C (300.15 K), the predicted vapor pressure is between 6.99 and 7.00 MPa. Once you have the vapor pressure bracketed to within your experimental uncertainty (three or four significant figures) you can quit.

Repeat the calculation for several temperatures in your experimental range. Plot the predicted vapor pressures of a van der Waals fluid as a function of temperature on a graph along with your experimentally observed vapor pressures. Does the van der Waals equation of state predict the vapor pressure curve qualitatively? Within experimental error?

Note that the above calculation is not restricted to a van der Waals equation of state. There are several superior equations of state whose parameters are reasonably well documented for CO₂, so the accuracy of your model can be far more accurate if you have the time, patience, and energy to pursue the issue further.

References

1. J. C. Holste, K. R. Hall, P. T. Eubank, G. Esper, M. Q. Watson, W. Warowny, D. M. Baily, J. G. Young, and M. T. Bellomy, "Experimental (p, V_m, T) for pure CO₂ between 220 and 450K," *J. Chem. Thermodynamics* **19**, 1233-1250 (1987).
2. *SFT Phase Monitor Users Manual, 1st Edition*, Supercritical Fluid Technologies, Inc., Newark, DE (2002).
3. D. A. Chapman, private communication. The section "Finding the Equilibrium Vapor Pressure for a van der Waals Fluid" above is adapted from this communication.
4. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, Oxford: Clarendon Press (1980).

