Data analysis of heat capacity measurements of argon, nitrogen and carbon dioxide

Step 1. Determine the calibration between voltage and volume using linear regression. Note that the diameter of the piston is 4.09 cm. Therefore, the area of the piston is

$$A = \pi \left(\frac{d}{2}\right)^2$$

The area is 13.14 cm². We convert the height to volume in liters and then conduct a linear regression on the volume versus the voltage. The linear regression gives a line

$$Volume = 0.07314 + 0.027959\ voltage$$

The linear regression is shown in the Figure.
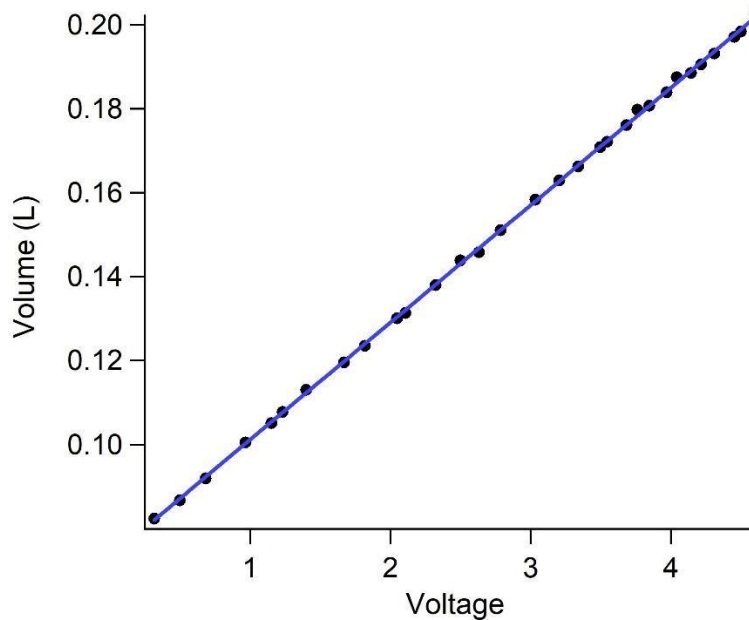
The midpoint of the volume is 0.151 L. Next calculate the upper and lower 95% confidence limits, using the formula:

$$\sigma_e = \frac{RMSE}{slope} \sqrt{\frac{Nx^2 + \sum_i x_i^2 - 2x \sum_i x_i}{DD}}$$

Where DD is

$$= N \sum_i x_i^2 - \left(\sum_i x_i \right)^2$$

The regression gives

$$slope = 0.02796$$

And

$$RMSE = 7.71 \ x \ 10^{-5}$$
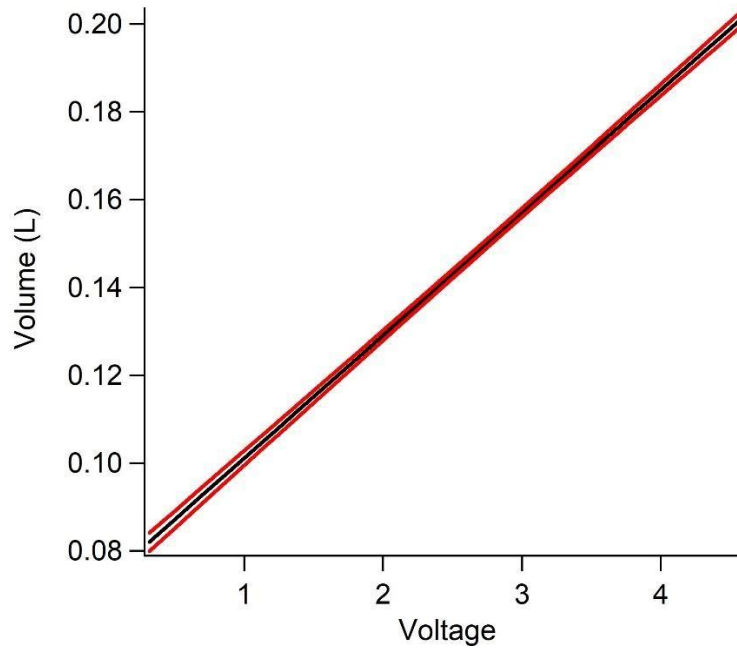
The ratio is

$$\frac{RMSE}{|slope|} = 0.00276$$

$$\sum_i x_i^2 = 9.432$$

$$\sum_i x_i = 2.783$$

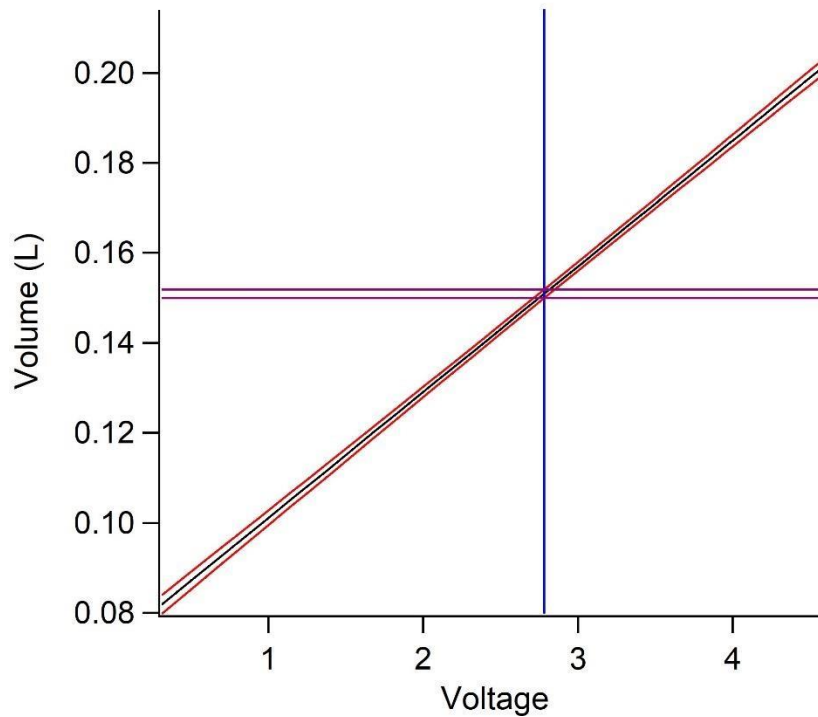Using Igor the formula is

0.002796*sqrt((voltage*voltage+9.432-2*voltage*2.783)/(9.432-2.783*2.783)/33)

The 95% confidence limit is represented by upper and lower bounds shown in the Figure.

The practical extraction of the 95% confidence limit of the volume can be obtained graphically.


We find $\sigma_V = 0.0019$ L at the midpoint (or average)..The maximum and minimum volumes are 0.2024 and 0.0824 L, respectively. Given that the calculated volume at the midpoint is 0.150 L, the relative error is approximately 1.3%.

Analysis of Ar compression data

Our hypothesis is that Ar behaves as a monatomic ideal gas. Thus, we expect that the molar heat capacity at constant volume is $C_v = \frac{3}{2}R$. Since $C_p = C_v + R$ for an ideal gas we also expect $C_p = \frac{5}{2}R$. Therefore, we expect that

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67$$

We begin the analysis by selection a region of the compression that has little curvature.
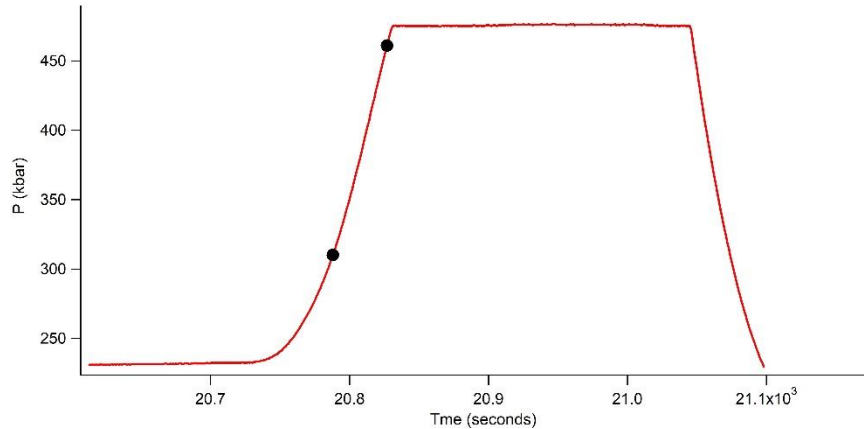
This is shown between the black dots for one of the cycles of compression and expansion. Extract both the pressure and the volume points from 20788 to 20826. Then we use those points to calculate a value of gamma at each point. Analysis of several of the argon data sets was carried out by calculating

$$\gamma = -\frac{ln\left(\frac{P}{P_o}\right)}{ln\left(\frac{V}{V_o}\right)}$$

This implies that we will obtain a series of gamma measurements from a single compression. Right here we could do statistics and determine the standard error. It is interesting to compare this to the error obtained starting with volume and pressure and then using propagation of error, which you should do! According to this formula, all of the data involved in the compression should give the same value. We must observe that the application of this formula has an artifact on the first point, $P = P_o$ and also for $V = V_o$. On this initial point value of the function is zero since the logarithm of one is equal to zero. We will throw away this point and even a few other points since the data appears to improve in quality near the end of the compression. This is shown in the Figure.

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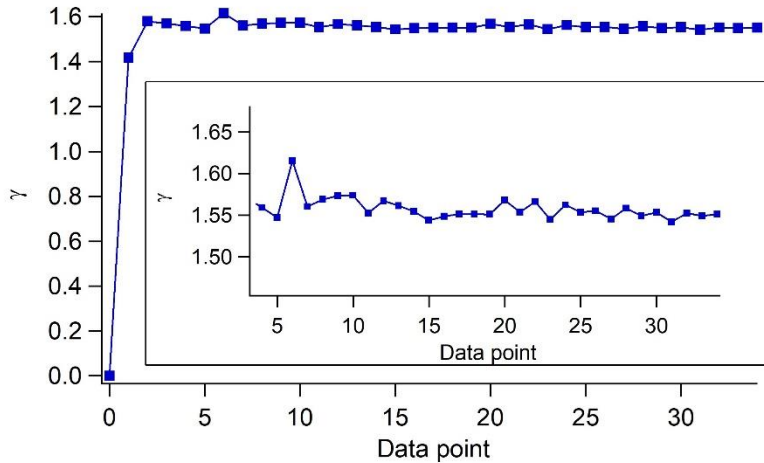
The initial points are an artifact of the approach used of taking the logarithm. To find gamma we can average the points after point 5. Indeed, this is arbitrary. However, we know from the formula that the result should be a constant and the data after point 5 are pretty constant. We can also estimate the error in gamma from these data and from comparison of a number of data sets. How many should we use? I gave you lots of data so you could see if there is any variation. I would use some data from each data set and perhaps check a few. Somewhere from 6-10 data sets would be appropriate. Once you have done this the first time it begins a production line for the remaining data sets.

For ten data sets we obtain the following γ shown with the 95% confidence limit. The latter was obtained by multiplying by the appropriate t-value, which ranged from 2.05-2.2 depending on the number of data points.
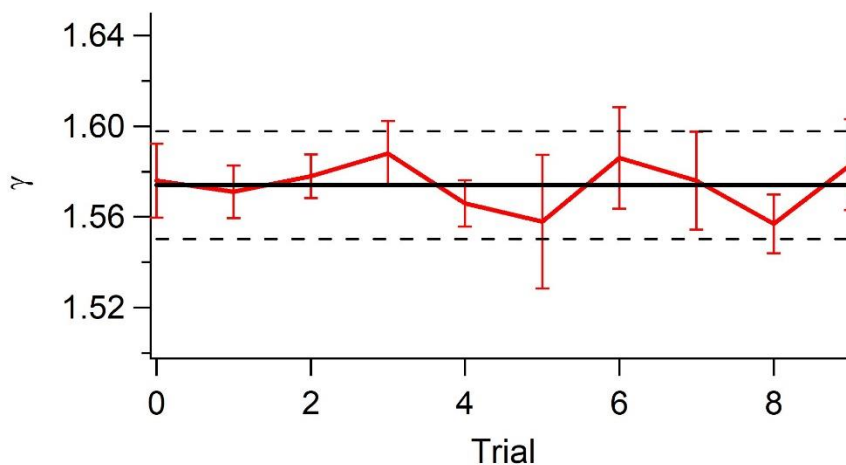
For Ar we obtained an average of $\gamma = 1.57$, which corresponds to $C_v = \frac{7}{4}R$. Given the 95% confidence limit, it was appropriate to round to three significant figures.

This value of γ obtained from these experiments leads to an overestimation of the heat capacity of Ar by 16%. One reason we can suspect is that possible presence of trace water vapor in the gas. As the Ar gas was compressed we observed formation of a cloud, which could be from condensation as water vapor is compressed. Although the temperature increases by 20% during the compression the pressure increases by a factor of 2.7. The partial pressure of water increases in parallel. Thus, if water is present it surpasses the dew point during the compression. The experiment obtained the value.

$$C_v = \frac{7}{4} R = 14.5 \, J/molK$$

The experimental value is

$$C_v = 12.2 \, J/molK$$

The theoretical value is

$$C_v = \frac{3}{2} R = 12.5 \, J/molK$$

Aside from the possibility of contamination by water vapor, one should also bear in mind that the assumption of ideality of the gas begins break down for pressures above atmospheric pressure.

No matter which gas we use for the measurement, this method gives us an overestimate of approximately 20%. There is a systematic error that may have arisen due to experimental design. There is a number of factors we have ignored in our treatment.

1. The heat capacity of some of the gasses is temperature dependent and the experiment results in a significant increase in temperature during the compression. We are trying to measure a quantity that is changing under our experimental conditions (a moving target).
2. We have assumed ideal gas behavior. While that is normally a good assumption at 1 bar of pressure, the pressure in this experiment can be nearly 5 bars in some data sets. Note that 1 bar = 1.0132 atm, and therefore we can assume that they are approximately equal. Are there deviations from ideality that may affect the results?
3. There could be impurities. Particularly in the argon experiment we observed interesting behavior that appeared to be condensation. We cannot be sure, but it could be that there is trace water vapor. This seems a little unlikely except for the fact that the argon tank in particular is very old. This explanation could not apply to all three gases. There cannot be trace water in the CO_2 tank (why?).
4. The may be deviations from adiabatic behavior.

The temperature dependent heat capacity of carbon dioxide

Unlike At and N_2, the heat capacity of CO_2 is temperature dependent. The experimental temperature dependence is shown in the Figure.
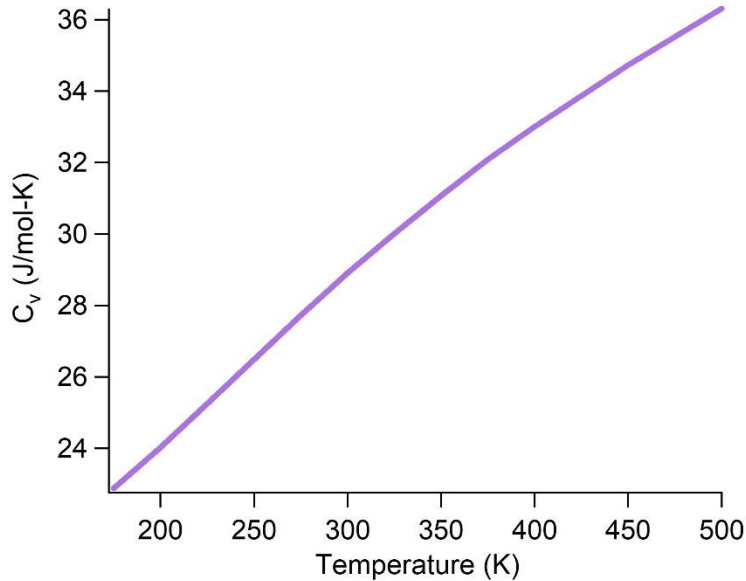
The average energy of a harmonic oscillator is

$$\langle E \rangle = \frac{hc\tilde{v}}{e^{hc\tilde{v}\beta} - 1}$$

The statistical mechanical heat capacity is

$$\langle C_v \rangle = -k\beta^2 \frac{\partial}{\partial \beta}\left(\frac{hc\tilde{v}}{e^{hc\tilde{v}\beta} - 1}\right)$$

$$\langle C_v \rangle = ke^{hc\tilde{v}\beta}\left(\frac{hc\tilde{v}\beta}{e^{hc\tilde{v}\beta} - 1}\right)^2$$

We can write this as a molar heat capacity with a vibrational temperature

$$\theta_v = \frac{hc\tilde{v}}{k}$$

$$\langle C_v \rangle = Re^{\theta_v/T}\left(\frac{\theta_v/T}{e^{\theta_v/T} - 1}\right)^2$$

If we use the fact that there are two vibrational modes in CO_2, the bending and symmetric stretching mode (ignoring the high-energy asymmetric stretch), we can calculate a theoretical heat capacity. We must recall that the bending mode is doubly degenerate so its contribution will be twice as large. The comparison of experiment and calculation is given in the Figure.
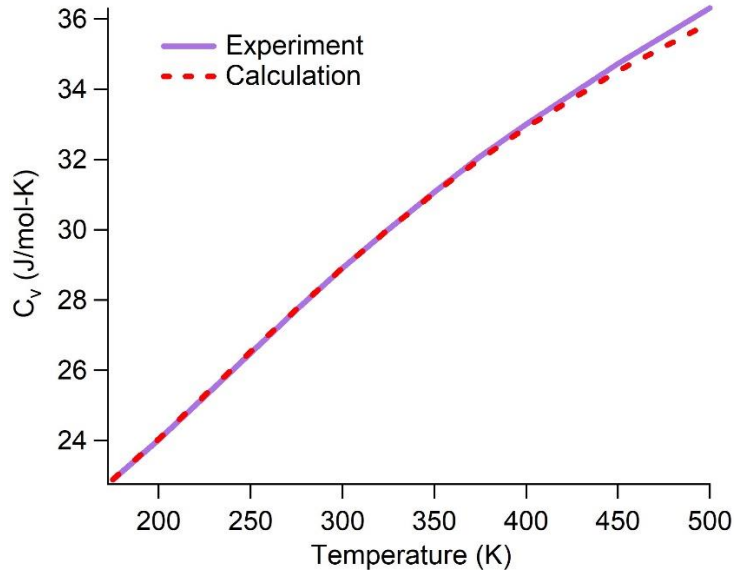
Considering the discrepancies between data and experiment

There appears to be a systematic error in the experiment. We have suggested an impurity of water as one possibility. However, we also should consider that the pressures in this experiment may cause increases in the deviation from ideality that would invalidate the assumption of $C_p = C_v + R$ and result in corrections to the pressure. One way to estimate such effects is to use a non-ideal equation of state, such as the van der Waal's gas. The van der Waal's equation of state includes the hard-sphere equation of state with an excluded volume nb, and an attractive term n^2a^2.

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a^2}{V^2}$$

We often use the molar form

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

Calculation of corrections to the pressure of a van der Waal's gas

We have seen that the derivatives of P, V and T are related by a cyclic permutation and are also related to the expansion coefficient and isothermal compressibility. We have the following relations

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \alpha V_m \; ; \; \left(\frac{\partial V_m}{\partial P}\right)_T = -\kappa V_m \; ; \; \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

To calculate these for a van der Waal's gas we can use implicit differentiation. There are several ways to write the van der Waal's gas equation. Starting with the form based on molar volume:

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

We can solve for RT to compare the equation more conveniently with the ideal gas law:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

To understand the deviation from ideality with more depth we define the "real" pressure and molar volume as:

$$P_{vdw}V_{m,vdw} = RT$$

The real pressure (or van der Waal's pressure if you like) includes the internal pressure:

$$P_{vdw} = P + \frac{a}{V_m^2} = P + \pi_T$$

Note that this van der Waal's pressure is larger than the measured pressure because of the cohesive forces in the gas. In an adiabatic compression V_m decreases substantially as the pressure increases. Thus, π_T increases during the compression. One could correct each pressure in the compression using this term. For argon it is approximately a correction of approximately one percent.

$$\frac{a}{V_m^2} = \frac{1.355}{6.15^2} = 0.035 \, bar$$

The pressure corresponding to this molar volume is

$$P = \frac{RT}{V_m} = \frac{(0.0831)(360)}{6.15} = 4.8 \, bar$$

Calculation of C$_p$ – C$_v$ for a van der Waal's gas

The real molar volume includes the excluded molar volume term, b:

$$V_{m,vdw} = V_m - b$$

We can obtain the derivatives needed using implicit differentiation. Starting with the temperature differentiate both sides by T:

$$\frac{\partial}{\partial T}\left[\left(P + \frac{a}{V_m^2}\right)(V_m - b)\right] = \frac{\partial}{\partial T} RT$$

Treating P as a constant but Vm as a function of T, using the product rule we obtain:

$$-2\frac{a}{V_m^3}\left(\frac{\partial V_m}{\partial T}\right)(V_m - b) + \left(P + \frac{a}{V_m^2}\right)\left(\frac{\partial V_m}{\partial T}\right) = R$$

$$\left(\frac{\partial V_m}{\partial T}\right) = \frac{R}{P - \frac{a}{V_m^2} + 2\frac{ab}{V_m^3}}$$

We use the same method to obtain the derivative with respect to P:

$$\frac{\partial}{\partial P}\left[\left(P + \frac{a}{V_m^2}\right)(V_m - b)\right] = \frac{\partial}{\partial P} RT$$

Now holding T constant we have:

$$\left(1 - 2\frac{a}{V_m^3}\left(\frac{\partial V_m}{\partial P}\right)\right)(V_m - b) + \left(P + \frac{a}{V_m^2}\right)\left(\frac{\partial V_m}{\partial P}\right) = 0$$

First, moving the term that does not depend on the derivative to the right hand side:

$$\left(-2\frac{a}{V_m^3}\right)(V_m - b)\left(\frac{\partial V_m}{\partial P}\right) + \left(P + \frac{a}{V_m^2}\right)\left(\frac{\partial V_m}{\partial P}\right) = -(V_m - b)$$

And collecting terms on the left hand side we obtain:

$$\left(P - \frac{a}{V_m^2} + 2\frac{ab}{V_m^3}\right)\left(\frac{\partial V_m}{\partial P}\right) = -(V_m - b)$$

so that:

$$\left(\frac{\partial V_m}{\partial P}\right) = \frac{-(V_m - b)}{P - \frac{a}{V_m^2} + 2\frac{ab}{V_m^3}}$$

To check these derivatives let's calculated $\partial P/\partial T$ and see if it is true that

$$\left(\frac{\partial P}{\partial T}\right)_{V_m}\left(\frac{\partial T}{\partial V_m}\right)_P\left(\frac{\partial V_m}{\partial P}\right)_T = -1$$

This implies that

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = -\frac{\left(\frac{\partial V_m}{\partial T}\right)_P}{\left(\frac{\partial V_m}{\partial P}\right)_T} = \frac{\alpha}{\kappa}$$

The derivative is:

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{V_m - b}$$

and

$$\alpha = \frac{1}{V_m}\left(\frac{R}{P - \frac{a}{V_m^2} + 2\frac{ab}{V_m^3}}\right) = \frac{R}{PV_m - \frac{a}{V_m} + 2\frac{ab}{V_m^2}}$$

$$\kappa = -\frac{1}{V_m}\left(\frac{V_m - b}{P - \frac{a}{V_m^2} + 2\frac{ab}{V_m^3}}\right) = -\frac{V_m - b}{PV_m - \frac{a}{V_m} + 2\frac{ab}{V_m^2}}$$

Indeed, we see that it is true that:

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{\alpha}{\kappa} = \frac{R}{V_m - b}$$

Since the denominators in α and κ are identical and therefore cancel.

$$C_P - C_V = \frac{\alpha^2 T V_m}{\kappa}$$

$$C_P - C_V = \left(\frac{R}{V_m - b}\right) \frac{R T V_m}{\left(P V_m - \frac{a}{V_m} + 2\frac{ab}{V_m^2}\right)}$$

$$C_P - C_V = \frac{R^2 T V_m}{(V_m - b)\left(P V_m - \frac{a}{V_m} + 2\frac{ab}{V_m^2}\right)}$$

Another way to write this expression that eliminates the temperature and clarifies the meaning of the ratio is:

$$C_P - C_V = \left[\frac{P V_m^2}{(V_m - b)\left(P V_m - \frac{a}{V_m} + 2\frac{ab}{V_m^2}\right)}\right] R$$

Obviously, if a = b = 0, the ration in the square brackets is 1 as expected for an ideal gas.

For argon the maximum pressure is 4.8 bars. The molar volume is 6.15 L/mol. The van der Waals parameters for argon are

$$a = 1.355 \; L^2 bar/mol^2$$

$$b = 0.032 \; L/mol$$

Thus, the ratio for argon is

$$ratio = \left[\frac{(4.8)(6.15)^2}{(6.118)\left((4.8)(6.15) - \frac{1.355}{6.15} + 2\frac{(1.355)(0.032)}{(6.15)^2}\right)}\right]$$

$$ratio = \left[\frac{(6.15)(29.5)}{(6.118)(29.3)}\right] = 1.01$$

The van der Waals parameters for CO_2 are

$$a = 3.640 \; L^2 \, bar/mol^2$$

$$b = 0.0426 \; L/mol$$

Thus, the ratio for CO_2 is

$$ratio = \left[\frac{(4.8)(6.15)^2}{(6.107)\left((4.8)(6.15) - \frac{3.64}{6.15} + 2\frac{(3.64)(0.0426)}{(6.15)^2}\right)} \right]$$

$$ratio = \left[\frac{(6.15)(29.5)}{(6.107)(28.94)} \right] = 1.027$$

If C_v = 30 J/mol-K, then

$$\gamma = \frac{30 + (1.027)(8.31)}{30} = 1.284$$

Compared to 1.277 for an ideal gas. For CO_2 the difference is not negligible given the experimental accuracy, however, including the deviation from ideality only increases the theoretical value of γ. This result does not help to explain the smaller value of γ obtained by experiment.

Losses as the origin of the experimental discrepancy

The fatal flaw of this experiment is that the plexiglass cylinder is a poor insulator. We can be sure that there is some heat loss. The problem is that we do not know how much. We do know that as the volume is mechanically decreased the measured pressure would be decreased by any thermal losses. That is because for a fixed mechanical volume, the pressure would be lower than expected according to the formula if the temperature were lower than expected because of losses. We should measure the temperature!

Since we do not have a good temperature sensor at present we can model the effect and see if it is reasonable. If we assume that the losses due to heat transfer grow as the temperature increases (i.e. the thermal gradient with respect to the ambient temperature increases), then we can calculate what the pressure would be in the absence of these losses. Let's assume that the losses are 1% at the maximum temperature of 360 K. Then the pressure is actually less by approximately

$$P_{corrected} = P_{exmpt} \left(\frac{T_{corrected}}{T_{exmpt}} \right)^{C_p/R}$$

In this equation, we assume that the loss due to heat transfer leads to an experimental temperature that is 1% smaller than it would be in a truly adiabatic cylinder. The effect on the pressure is substantial.

$$4.97 \ bar = (4.80 \ bar) \left(\frac{1.0}{0.99}\right)^{7/2}$$

This type of correction has the same effect as the van der Waal's internal pressure correction, but is significantly larger. The effect of a 1% loss is a nearly 3% reduction in the pressure compared to expectation. This correction tends to increase γ because the true pressure is increased by taking losses into account. This model is still not ideal, but it does suggest that very small thermal losses are the most likely origin for the discrepancy with experiment.