Physical Chemistry Experiments

Adiabatic Compression

NC State University

Adiabatic compression
Application: measuring heat capacity

Adiabatic Expansion-Compression Experiment

The laboratory experiment can simultaneously measure pressure, volume and temperature since all three of these are coupled in an adiabatic expansion or compression.

Don’t lose sight of the fact that the goal of the lab is to measure a heat capacity.

Adiabatic Processes

Using the form on the previous page we can derive the relationship between the volume change and temperature.

$$dU = \delta w$$

$$C_V dT = -PdV$$

$$C_V dT = -\frac{nRT}{V} dV$$

$$C_V \frac{dT}{T} = -nR\frac{dV}{V}$$

$$C_V \int_{T1}^{T2} \frac{dT}{T} = -nR\int_{V1}^{V2} \frac{dV}{V}$$

$$C_V \ln\left(\frac{T_2}{T_1}\right) = -nR\ln\left(\frac{V_2}{V_1}\right)$$

Adiabatic Processes

Using the form on the previous page we can derive the relationship between the volume change and temperature.

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{nR}{C_V}\ln\left(\frac{V_1}{V_2}\right)$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{nR/C_V}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{2/3} \quad \textit{for an ideal monatomic gas}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{2/5} \quad \textit{for an ideal diatomic gas}$$

This expression is great practical value since you can predict the temperature of air as it rises. This phenomenon leads to rain over mountains and cooling that affects ecosystems at high elevation.

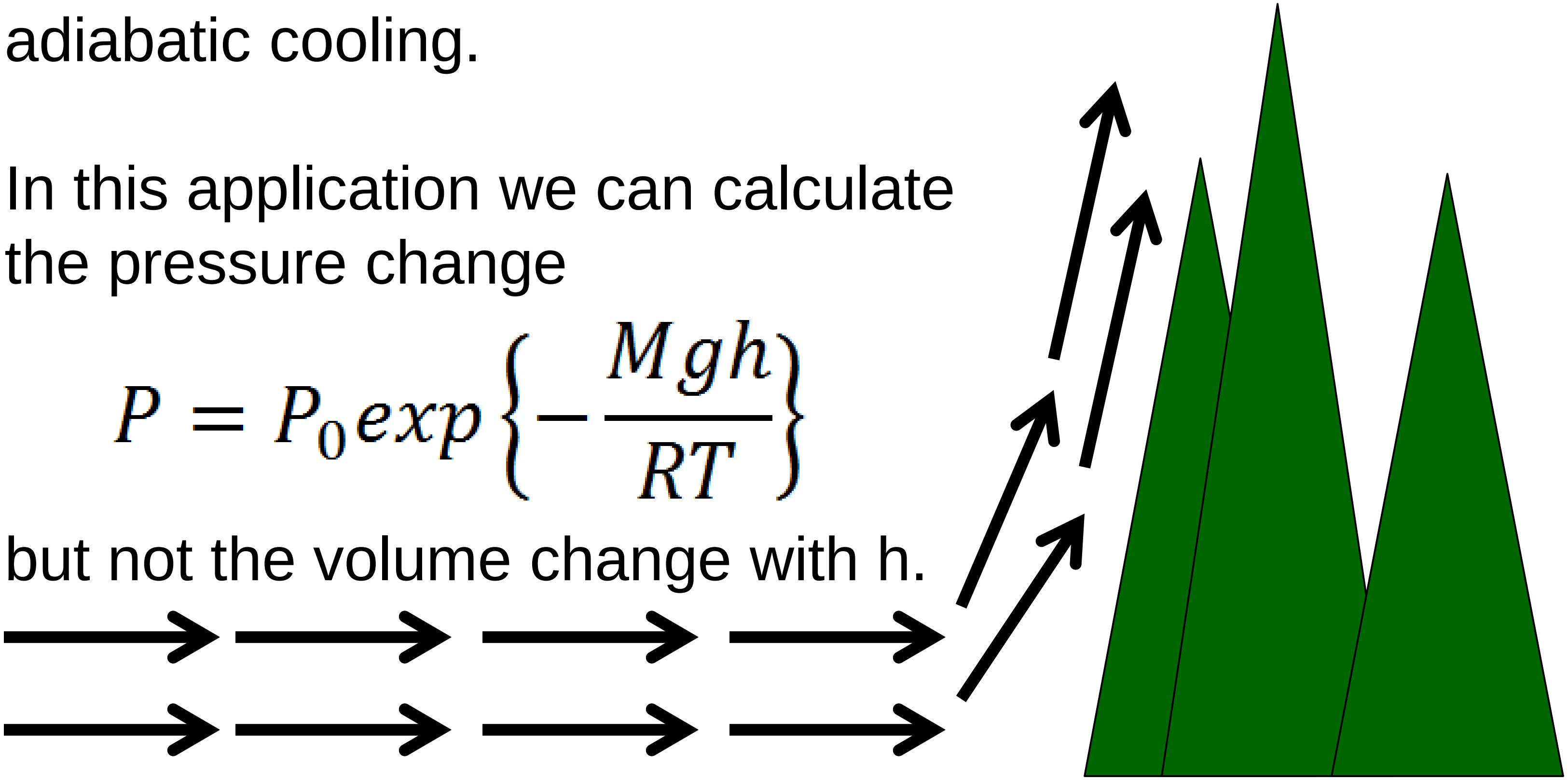
Application to meterology

Elevation increases the average rainfall. This occurs because air masses rise as the encounter mountains, and as they rise they cool. Because the lateral heat transfer in the atmosphere is poor, we can treat this as an adiabatic cooling.

In this application we can calculate the pressure change

$$P = P_0 exp\left\{-\frac{Mgh}{RT}\right\}$$

but not the volume change with h.



Example: Temperature on Mt. Mitchell on a summer day

Assuming that the temperature in Raleigh is nice warm 310 K. What is the temperature on the top of Mt. Mitchell at 2000 m?

Solution:

Atmosphere is a diatomic gas so $C_p = 7/2nR$.

Using the barometric pressure formula to find P = 0.80 atm.

$$T_2 = (310\,K)\left(\frac{0.8}{1}\right)^{\frac{2}{7}} = 290\,K$$

Pressure dependence of adiabatic expansion

$$PV = nRT$$

In an adiabatic expansion all of the variable, P, V and T can change.

$$\frac{P_2V_2}{P_1V_1} = \frac{nRT_2}{nRT_1}$$

Therefore,

$$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1} \longrightarrow \left(\frac{V_1}{V_2}\right)^{nR/C_v} = \frac{T_2}{T_1}$$

Pressure dependence of adiabatic expansion

Solve for V_1/V_2 and substitute into the formula

$$\frac{P_2 T_1}{P_1 T_2} = \frac{V_1}{V_2} \quad \longrightarrow \quad \left(\frac{V_1}{V_2}\right)^{nR/C_v} = \frac{T_2}{T_1}$$

$$\left(\frac{P_2 T_1}{P_1 T_2}\right)^{nR/C_v} = \frac{T_2}{T_1}$$

$$\left(\frac{P_2}{P_1}\right)^{nR/C_v} = \left(\frac{T_2}{T_1}\right)^{1+nR/C_v}$$

Pressure dependence of adiabatic expansion

Rearrange the exponent to write it in a compact form:

$$\left(\frac{P_2}{P_1}\right)^{\frac{nR/C_v}{1+nR/C_v}} = \frac{T_2}{T_1}$$

$$\frac{nR/C_v}{1+nR/C_v} = \frac{nR}{C_v+nR} = \frac{nR}{C_p}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{nR}{C_p}}$$

The "other" PV relation

From the T,P and T,V correlations we can derive a P,V correlation

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\bar{C}_p}$$

and

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/\bar{C}_v}$$

Gives

$$\left(\frac{P_2}{P_1}\right)^{R/\bar{C}_p} = \left(\frac{V_1}{V_2}\right)^{R/\bar{C}_v}$$

The “other” PV relation

Gives

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\bar{C}_p/\bar{C}_v}$$

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

Where

$$\gamma = \frac{\bar{C}_p}{\bar{C}_v}$$

This equation suggests a method for measuring heat capacity based only on an adiabatic change. The other information we need is the well-known thermodynamic equation

$$\bar{C}_p = \bar{C}_v + R$$

Comparison with isothermal processes

An isothermal process is a constant temperature process. Therefore

$$\frac{P_2 V_2}{P_1 V_1} = \frac{nRT}{nRT}$$

And we have

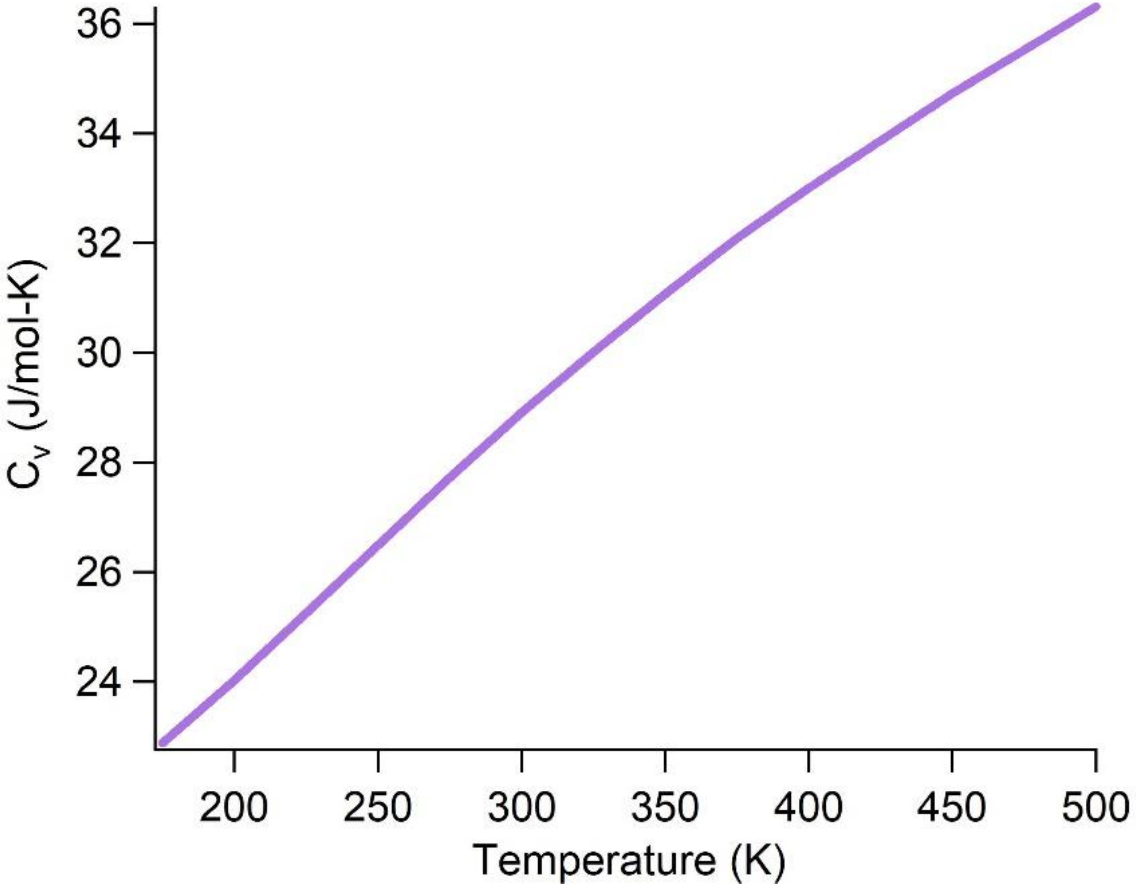
$$P_1 V_1 = P_2 V_2$$

Don’t confuse these two. The assumptions are quite different (the path is different!). Keep in mind that for an adiabatic process the temperature is not constant, so

$$\frac{P_2 V_2}{P_1 V_1} = \frac{nRT_2}{nRT_1}$$

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

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

The statistical mechanical heat capacity is

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

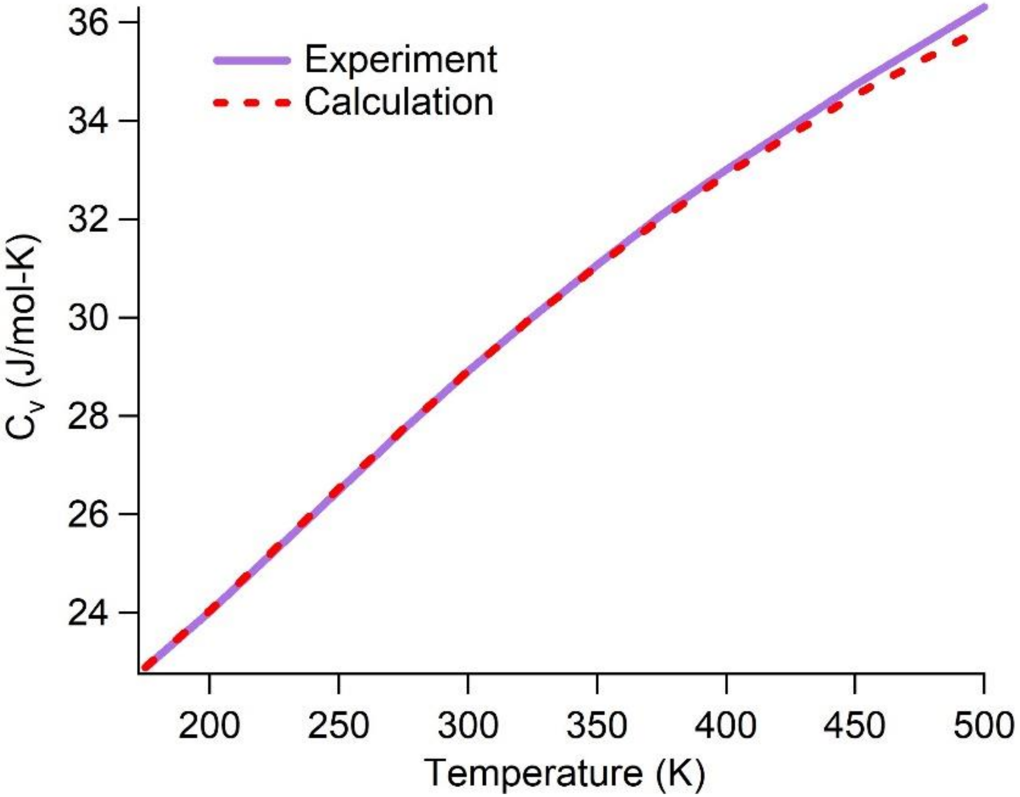
$$\langle C_v\rangle = ke^{hc\tilde{\nu}\beta}\left(\frac{hc\tilde{\nu}\beta}{e^{hc\tilde{\nu}\beta} - 1}\right)^2$$

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

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

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

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 shown in the Figure



Analysis of Ar compression data

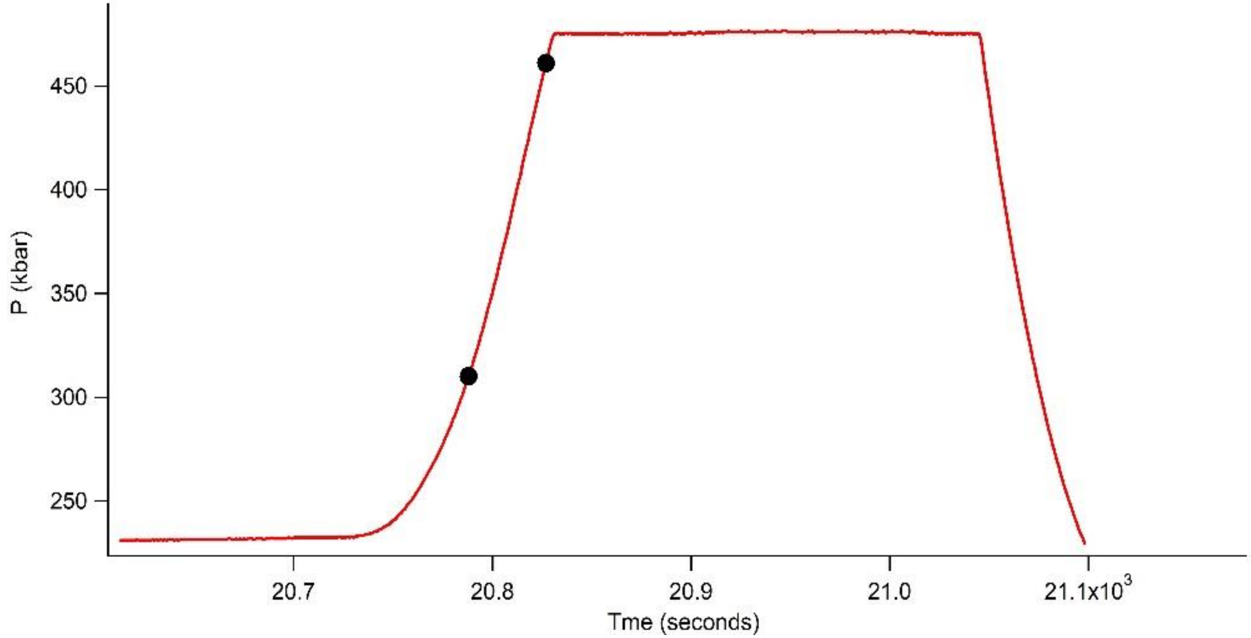
Our hypothesis is that Ar behaves as a monatomic ideal gas. The molar heat capacity at constant volume is $C_v = \frac{3}{2}R$. Since $C_p = C_v + R$ for an ideal gas, $C_p = \frac{5}{2}R$. We expect that

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

Analysis of several of the argon data sets was carried out by calculating

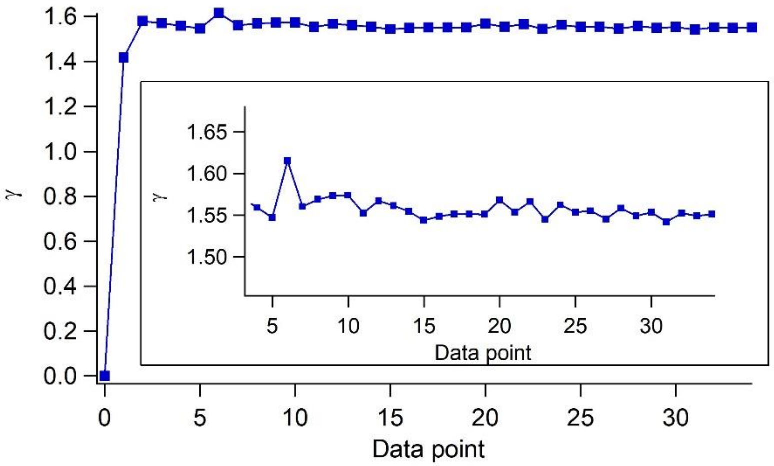
$$\gamma = -\frac{ln\left(\frac{P}{P_o}\right)}{ln\left(\frac{V}{V_o}\right)}$$

We begin the analysis by selection a region of the compression that has little curvature.



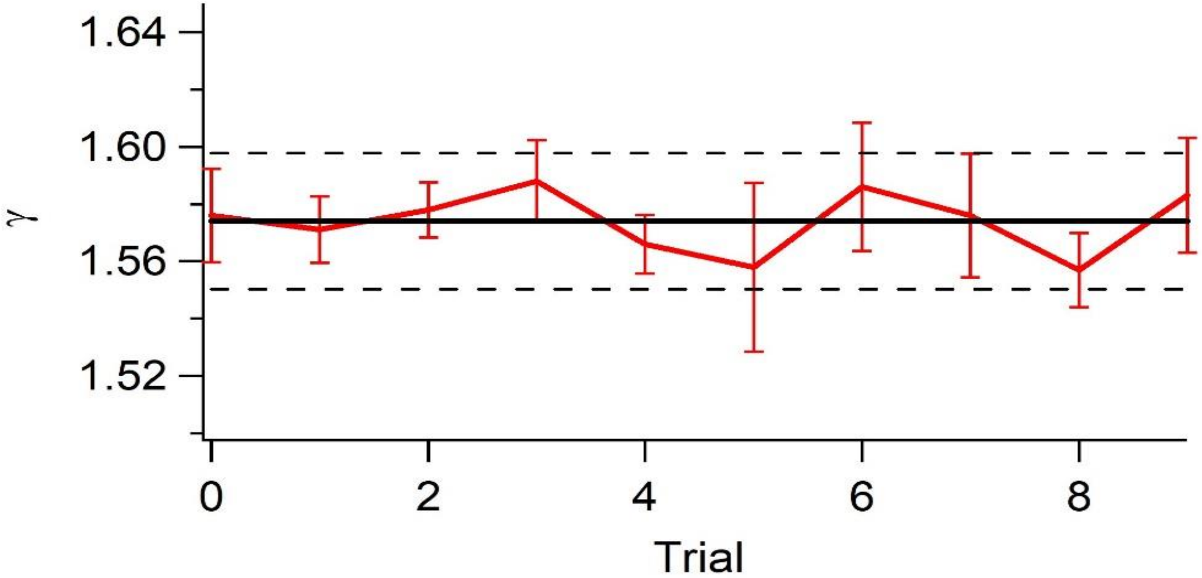
This is shown between the black dots for one of the cycles of compression and expansion. Extract both the pressure and the volume points from 20788 to 20826. Then we use those points to calculate a value of gamma at each point. This implies that we will obtain a series of gamma measurements from a single 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.



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. 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? 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. We used 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. The value of γ obtained from these experiments leads to an overestimation of the heat capacity of Ar by 16%.

The experiment obtained the value.

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

The theoretical value is

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

You will find that this type of discrepancy is not unique to Argon. All the gases have a similar percent discrepancy. Unfortunately, it is not that small 14-20%. If we can understand the reason then the method may still be of quantitative value. We could calibrate for example. Three possible reasons for deviation are suggested for you to think about and research for your lab report.

1. Contamination by water vapor. During a compression water could condense if the conditions in the cylinder are below the dew point.
2. Deviation from ideality. You could treat the gases as van der Waal’s gases (the parameters are in Atkins and DePaula or online). You could estimate how large the deviation from ideality is at the maximum compression.
3. Perhaps the device is not ideal. After all it is just a Plexiglas cylinder. We are counting on speed to make the compression adiabatic. You can see strong deviations it you do not pull down fast enough. Perhaps even the maximum speed is not enough to completely maintain adiabatic conditions.

Adiabatic compression laboratory example

Starting with the ideal gas law

$$P = \frac{nRT}{V}$$

We can propagate the error in the volume to the error in the pressure as follows:

$$\sigma_P = \sqrt{\left(\frac{\partial P}{\partial V}\right)^2 (\sigma)^2} = \left|\frac{\partial P}{\partial V}\right| \sigma_V$$

In this case the derivative is simply solved. Note that the absolute value is used here.

$$\sigma_P = \left|\frac{nRT}{V^2}\right| \sigma_V$$

Propagation of error in calculation of γ

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$ln\left(\frac{P_2}{P_1}\right) = -\gamma\ ln\left(\frac{V_2}{V_1}\right)$$

$$\gamma = -\frac{ln(P)}{ln(V)}$$

$$\sigma_{\gamma} = \sqrt{\left(\frac{\partial\gamma}{\partial V}\right)^2 \sigma_V^2 + \left(\frac{\partial\gamma}{\partial P}\right)^2 \sigma_P^2}$$

$$\left(\frac{\partial\gamma}{\partial V}\right) = \frac{ln(P)}{ln(V)^2}\frac{1}{V} = -\frac{\gamma}{V\,ln(V)}$$

$$\left(\frac{\partial\gamma}{\partial P}\right) = -\frac{1}{ln(V)}\frac{1}{P} = \frac{ln(P)}{P}\gamma$$

Propagation of error in calculation of γ and C_p

The relative error is given by

$$\frac{\sigma_\gamma}{\gamma} = \sqrt{\left(\frac{1}{ln(V)}\frac{\sigma_V}{V}\right)^2 + \left(ln(P)\frac{\sigma_P}{P}\right)^2}$$

Note that this differs from the relative error of a product or quotient because of the logarithmic terms. To use this equation choose a value of γ, V and P near the center of the adiabatic path. Then use the definition of γ, solve for C_p and continue the propataion of error into C_p.

$$\gamma = \frac{C_p}{C_v} = \frac{C_p}{C_p - nR}$$