

The Calculation of Heat Capacity Ratios of Nitrogen and Argon Using Adiabatic Expansion

Introduction:

The heat capacity C of a substance tells us how much heat q must be put into a system to get a certain amount of change in the temperature T : $C = \partial q / \partial T$. Holding volume V and pressure P constant we get $C_V \stackrel{\text{def}}{=} \left(\frac{\partial q}{\partial T} \right)_V$ and $C_P \stackrel{\text{def}}{=} \left(\frac{\partial q}{\partial T} \right)_P$ respectively. For ideal gasses and gas constant R :

$$C_{P,m} - C_{V,m} = R \quad (1)$$

For ideal monoatomic gasses $\overline{C_V} = 3/2R$ and $\overline{C_V} = 5/2R$ for ideal diatomic gasses. This can be intuitively explained with molecular degrees of freedom. Temperature increases proportionally with translational energy of molecules, but due to symmetry, monoatomic gasses have only translational energy to store. Diatomic gasses can store energy in the vibration of two molecules as well as rotational energy. So, diatomic gasses have more ways of storing heat before changing temperature resulting in a higher heat capacity.

$$\gamma = \frac{C_{P,m}}{C_{V,m}} \quad (2)$$

We can imply $\gamma = (C_{V,m} - R)/C_{V,m}$ using equation 1 and substitute $C_{V,m}$ to get $\gamma = 5/3$ for ideal monoatomic gasses and $\gamma = 7/5$ for ideal diatomic gasses.

In this experiment, we are not concerned with calculating heat capacity (although it can be easily derived). The purpose is to calculate the ratio of heat capacities gamma defined in equation 2. We do this using adiabatic expansion, first taking a system at pressure P_1 allowing to adiabatically expand to atmospheric pressure P_2 resulting in a temperature drop from ambient T_1 to T_2 which after closing the system equilibrates to P_3 . The ratio of heat capacities can be calculated using only those pressures:

$$\gamma = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{P_1}{P_3}\right)} \quad (3)$$

The temperature drop $T_2 - T_1$ can be calculated using the combined gas law:

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 \quad (4)$$

Argon and nitrogen are the monoatomic and diatomic gasses of choice as they have very small intermolecular interactions and take up relatively little space. The gamma values will be calculated for each, compared to literature and expected values using statistical analysis.

Experimental Methods:

The apparatus consists of a 5-gallon jug connected to a pressure gauge and gas cylinder. The 5-gallon glass jug was used as a vessel to contain argon and nitrogen for the process. This was defined as the system. Before beginning the experiment, the vessel was filled with either argon or nitrogen. The procedure for both was identical: the vessel was lowered upside down into a water bath with a tube allowing air in the vessel to be displaced by the water. The same tube was plugged into a regulator on the gas cylinder and the gas was allowed to displace the water in vessel until gas flowed freely out the surface of the water. The vessel was quickly raised out of the water bath and capped with the 3-holed rubber stopper. All tubes were connected as shown

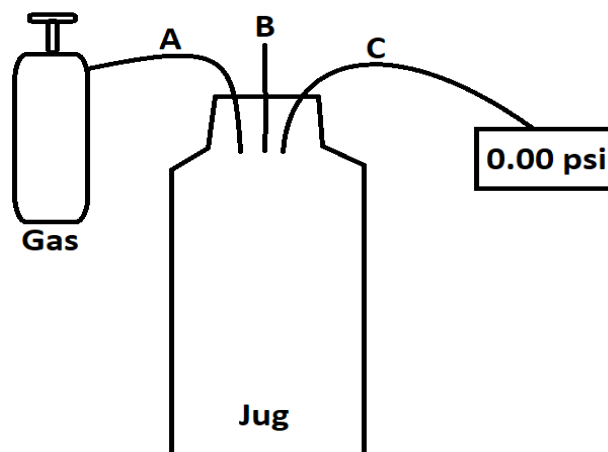


Figure 1. Vessel with a gas canister to the left and pressure gauge to the right. The system is closed by a rubber stopper.

in figure 1. Tube C was attached to a digital pressure gauge to determine the difference between ambient atmospheric pressure and the pressure in the vessel P_{gauge} . Tube A was attached to the gas canister and tube B was clamped closed.

The vessel was pressurized to around 1.6 psi above atmospheric and allowed to return to room temperature. The pressure was checked again to ensure 1.6 psi after thermal contraction and to ensure there were no leaks in the system. The pressure P_1 was recorded. The gas was allowed to adiabatically expand by quickly unclamping tube C and reclamping it. After thermal equilibrium was achieved, the pressure P_3 was measured. Two trials of nitrogen and two of Argon were completed. Between trials 2 and 3, the atmospheric pressure P_2 was gathered using some trustworthy information source for later calculations.

Data and Results:

Table 1. Data and calculations for gamma with uncertainties. P_3 for argon is higher on average which corresponds to the difference in gamma values for nitrogen and argon. The argon trial 1 seems to be a statistical error though as it has a lower P_3 than either nitrogen trial. The temperature drop for each is similar.

	$P_{1, \text{ gauge (psi)}}$	$P_{3, \text{ gauge (psi)}}$	$P_1 \text{ (psi)}$	$P_3 \text{ (psi)}$	$\Delta T(K)$	γ
N ₂ trial 1	1.66±0.01	0.45±0.01	16.409±0.006	15.20±0.02	-29.8±.2	1.39±0.08
N ₂ trial 2	1.64±0.01	0.43±0.01	16.389±0.006	15.18±0.02	-29.5±.2	1.37±0.08
Ar trial 1	1.63±0.01	0.41±0.01	16.379±0.006	15.16±0.02	-29.4±.2	1.35±0.08
Ar trial 2	1.71±0.01	0.58±0.01	16.459±0.006	15.33±0.02	-30.7±.2	1.54±0.10

Table 2. 95% confidence intervals for gamma values of nitrogen and argon. Argon has a large uncertainty but the theoretical values for each fall within the confidence intervals.

	γ
Nitrogen	1.38 ± 0.11
Argon	1.49 ± 0.95

Our pressure gauge only measures pressure difference, so we have to add atmospheric pressure to our gauge measurements to get the absolute pressure. In other words, the calculation of P_1 and P_3 are relative to the measurement of P_2 . This value was 30.03±0.01inHg as acquired from IBM's Weather Data API at 2:00 PM, August 31, 2022.^[1] The conversion from inHg to psi went as follows:

$$30.03 \pm 0.01 \text{ inHg} \left(\frac{1 \text{ psi}}{2.03602 \text{ inHg}} \right) = 14.749 \pm 0.005 \text{ psi}$$

Therefore, $P_2 = 14.749 \pm 0.005 \text{ psi}$ for all trials. P_1 and P_3 are calculated with uncertainty. For example:

$$P_1 = 1.66 \pm 0.01 \text{ psi} + 14.749 \pm 0.005 \text{ psi} = 16.41 \pm \sqrt{\left(\frac{0.01}{1.66}\right)^2 + \left(\frac{0.005}{14.749}\right)^2} = 16.409 \pm 0.006$$

Now we can calculate gamma using equation 3 while formally propagating errors:

$$\gamma = \frac{\ln\left(\frac{16.409 \pm 0.006}{14.749 \pm 0.005}\right)}{\ln\left(\frac{16.409 \pm 0.006}{15.20 \pm 0.02}\right)} = 15.20 \pm \sqrt{\left(\frac{\partial \gamma}{\partial P_1}\right)_{P_2, P_3}^2 \Delta^2(P_1) + \left(\frac{\partial \gamma}{\partial P_2}\right)_{P_1, P_3}^2 \Delta^2(P_2) + \left(\frac{\partial \gamma}{\partial P_3}\right)_{P_1, P_2}^2 \Delta^2(P_3)}$$

Partial derivatives of gamma with respect to various pressures are calculated using Mathematica.

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In[1]:= gamma[{p1_, p2_, p3_}] := Log[p1 / p2] / Log[p1 / p3];
      atm = 14.749;
      (* trials {N2 1, N2 2, Ar 1, Ar 2} *)
      data = {{1.66+atm, atm, 0.45+atm}, {1.64+atm, atm, 0.43+atm}, {1.63+atm, atm, 0.41+
      atm}, {1.71+atm, atm, 0.58+atm}};

In[4]:= Map[gamma, data]
Out[4]= {1.39235, 1.37469, 1.35423, 1.54229}

In[5]:= D[Log[p1 / p2] / Log[p1 / p3], p1] // Simplify
Out[5]= 
$$\frac{-\text{Log}\left[\frac{p1}{p2}\right] + \text{Log}\left[\frac{p1}{p3}\right]}{p1 \text{Log}\left[\frac{p1}{p3}\right]^2}$$


In[6]:= gammadp1[{p1_, p2_, p3_}] := (-Log[p1 / p2] + Log[p1 / p3]) / (p1 * Log[p1 / p3]^2)
      gammadp2[{p1_, p2_, p3_}] := -1 / (p2 Log[p1 / p3])
      gammadp3[{p1_, p2_, p3_}] := Log[p1 / p2] / (p3 Log[p1 / p3]^2)

In[9]:= Sqrt[gammadp1[data[[trial]]]^2 * 0.006 + gammadp2[data[[trial]]]^2 * 0.005 +
      gammadp3[data[[trial]]]^2 * 0.002] /. trial -> 1
Out[9]= 0.0858042

In[10]:= Map[PlusMinus[gamma[#1], Sqrt[gammadp1[data[[Position[data, #1][[1, 1]]]]]^2 * 0.006 +
      gammadp2[data[[Position[data, #1][[1, 1]]]]]^2 * 0.005 +
      gammadp3[data[[Position[data, #1][[1, 1]]]]]^2 * 0.002] ] &, data]
Out[10]= {1.39235 ± 0.0858042, 1.37469 ± 0.0850241, 1.35423 ± 0.0834777, 1.54229 ± 0.0991616}

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Figure 2. Calculation of the uncertainty of gamma values using Mathematica. In[1] shows the definition of the gamma function followed by the data points. In[4] shows the calculation of gammas for each trial. In[5] shows an example calculation of the partial derivative of gamma. In[6-8] is the partial derivatives with respect to P₁, P₂ and P₃ respectively. In[9] is an example calculation of the uncertainty of gamma for trial 1. In[10] is all gamma values and uncertainties

Gamma values and uncertainties are listed in table 1 along with measurements and pressures. Measured values contain uncertainties of half the incremental value on the instrument. Uncertainties in P₁ and P₃ are propagated from P₂. Gamma values and uncertainties are formally propagated.

Now, we can calculate the mean gamma value of each gas and apply the student-t distribution. With 95% confidence and 1 degree of freedom using a two tailed distribution, the critical value is 12.71.

$$s^2 = \frac{1}{n-1} \sum (x_i - \bar{x})^2 \quad (5)$$

$$\bar{x} \pm \frac{ts}{\sqrt{n}} \quad (6)$$

Equation 5 gives the squared variance of a set x with n elements. Using equation 5 we calculate the variance of our nitrogen data:

$$s = \sqrt{(1.39 - 1.38)^2 + (1.37 - 1.38)^2} = 0.0125$$

Using equation 6 we can find the 95% confidence interval for our nitrogen data with critical value t :

$$1.38 \pm \frac{12.71 \times 0.0125}{\sqrt{2}} = 1.38 \pm 0.11$$

All Gamma values with 95% confidence are listed in table 2.

Checking the literature, we find $\gamma = 1.44 \pm 0.07$ for nitrogen and $\gamma = 1.7 \pm 0.1$ for argon both with two standard deviations of uncertainty.^[2] We can now compare our gamma values with 95% confidence from table 2 with literature values. We determine if zero falls within the range of the difference of the values \pm the uncertainties added in quadrature. For nitrogen we find zero within said range:

$$1.44 - 1.38 \pm \sqrt{0.11^2 + 0.07^2} = 0.06 \pm 0.13$$

Thus, our experimental nitrogen value agrees with the literature value. For argon we find 0 inside the range as well, so our values also agree. Unfortunately, there was a relatively large variance of 0.95 within our set of data for argon, compared to 0.0125 for nitrogen. More experimental data is needed to get a more precise value of gamma for argon.

There were two main differences during the trials of argon. The jug was capped more quickly in the second trial, and the capping and uncapping process was faster in the second trial. We originally thought the low gamma value was due to air entering the system during the first trial. This is likely not the case because the calculated gamma value would not have been lower than the gamma of the atmosphere (1.44 ^[2] compared to 1.35 for the first argon trial). If the air theory is true, the entire volume of argon would have had to been displaced within a few seconds, which likely did not happen.

Comparing values: the measurement for P_3 is consistent within 0.5% between the two trials, but P_3 is larger in trial 2 by 1.1%. When we look at the actual gauge values, the difference becomes 5% for P_1 and 41% for P_3 . With a smaller P_1 we expect a smaller P_3 , although the difference here seems significant. There are multiple possibilities for such a low value: there may have been a leak after capping and before measuring P_3 which could have been sealed before the measurement. It is also possible the uncapping and capping procedure took too long and the gas was allowed to escape during thermal expansion. Pressure differentials do not take long to equilibrate in the absence of a barrier, so both answers seem reasonable. If we find what P_3 of the first trial should have been to achieve the same gamma value in the second, we rearrange the equation of gamma to get:

$$P_3 = \frac{16.379}{\exp\left(\frac{\ln\left(\frac{16.379}{14.749}\right)}{1.5}\right)} = 15.27$$

Which means $P_{3,\text{gauge}}$ should be 0.52psi compared to the measured value of 0.41psi to achieve a gamma of 1.5. Such a difference in pressure results in a volume of gas small enough to have escaped through a small leak. This same small volume of gas could have also escaped before the thermal expansion.

The temperature drop values are calculated using equation 5. $T_1 = (295.09 \pm 0.01)K$ for all trials. Uncertainty arises from half the increment on the digital instrument used to measure temperature in the lab. For example:

$$T_2 = 295.09K * \frac{14.749psi}{16.409psi} = 265.24K$$

Uncertainties are calculated using worst case scenario:

$$T_2 = 295.10K * \frac{14.754psi}{16.403psi} = 265.47K$$

$$265.47K - 265.24K = 0.23K$$

Since the temperature drop for each is similar this shows the heat energy transferred to the molecules will be affected only by heat capacity.

Conclusion:

In this experiment, the heat capacity ratio is calculated from the pressures before adiabatic expansion and after thermal expansion of nitrogen and argon. Our ratios were calculated to be $\gamma_{N_2} = 1.38 \pm 0.11$ and $\gamma_{Ar} = 1.49 \pm 0.95$ with 95% confidence. These values agree with the literature values, and even the theoretical $\gamma_{N_2} = 1.40$ and $\gamma_{Ar} = 1.67$ from equation 1, although our values are not very precise. This is due to both a small sample size ($N = 2$) resulting in a large variance and discrepancies in the argon trials. We concluded that $P_{3,\text{gauge}}$ for argon trial 1 should be 27% larger to produce the same gamma value in argon trial 2. This lower pressure was likely caused by gas escaping before the measurement of P_3 , either before the capping process during thermal expansion, or through a leak after capping. In the future, we should include more trials and ensure consistent capping and uncapping to get better data.

Regardless of the error, the trend in heat capacity ratios for both gasses is clear. Nitrogen has a lower heat capacity ratio than argon which corresponds to argon having the lower heat capacity from the relation described in

equation 1. This is consistent with the molecular degrees of freedom explanation to heat capacity of monoatomic and diatomic molecules.

Safety:

Despite being quite abundant in our atmosphere, argon and nitrogen pose risks within a lab environment and safety measures must still be taken. When working around high pressure gas cylinders it is always necessary to ensure they will not tip over. When using regulators, close the main valve when not in use and always open it slowly to begin. Experiments should be done in a well-ventilated area as not to displace a large amount of oxygen in the room. ^[3,4] Argon has a specific vapor density of 1.66: greater than that of air, increasing risk of asphyxiation. ^[4] When left in the lungs, argon may settle to the bottom, replacing oxygen.

References:

1. *Site-Based Observations - v1*; The Weather Company: Atlanta, GA, 2022. <https://ibm.co/v1cSBO> (accessed August 31, 2022)
2. Branca M.; Soletta I., “C_P / C_V Ratios Measured by the Sound Velocity Method W Using Calculator-Based Laboratory Technology”, *J. Chem. Educ.* **84**, 3, 462 (2007). doi: 10.1021/ed084p462
3. *Nitrogen*; MSDS No. 001040; Airgas: Radnor, PA, August, 31, 2021. <https://www.airgas.com/msds/001040.pdf> (accessed 9/27/22)
4. *Argon*; MSDS No. 001004; Airgas: Radnor, PA, January, 5, 2021. <https://www.airgas.com/msds/001004.pdf> (accessed 9/27/22)

Calculations:

To propagate errors for P₁ and P₃:

```
atm = 14.749;
(* trials {N2 1, N2 2, Ar 1, Ar 2} *)
(* For each trial: {P1gauge, P2, P3gauge} *)
data = {{1.66, atm, 0.45}, {1.64, atm, 0.43}, {1.63, atm, 0.41}, {1.71, atm, 0.58}};
In[62]:=
(* For P1 *)
Map[PlusMinus[#1[[1]] + atm, Sqrt[(0.01 / #1[[1]])^2 + (0.005 / atm)^2]] &, data]
(* P3 *)
Map[PlusMinus[#1[[3]] + atm, Sqrt[(0.01 / #1[[3]])^2 + (0.005 / atm)^2]] &, data]
Out[62]=
{16.409 ± 0.00603363, 16.389 ± 0.00610698, 16.379 ± 0.00614433, 16.459 ± 0.00585777}
Out[63]=
{15.199 ± 0.0222248, 15.179 ± 0.0232583, 15.159 ± 0.0243926, 15.329 ± 0.0172447}
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Comparing literature values with experimental values for argon:

$$1.73 - 1.49 \pm \sqrt{0.10^2 + .95^2} = 0.24 \pm 0.95$$