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

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Note: Highlighting needs revision

Introduction:

The heat capacity C of a substance tells us how much heat must be put into a system to get a certain amount of change in the temperature: $C = \frac{\partial Q}{\partial T}$. There are 4 main variables that affect heat capacity: number of moles of substance n, pressure P, volume V and temperature T. Number of moles can be easily normalized for by diving by n to get the molar heat capacity C_m or $\overline{C}$. Although heat capacity is a function of T, we can neglect this variable as it is unlikely to change much for small (<10K) temperature changes. Now we are still left with two variables to control, which results in two ways of defining heat capacity: constant volume $C_{V,m}$ and constant pressure $C_{P,m}$, put mathematically: $C_{V,m} \stackrel{\text{def}}{=} \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_V$ and $C_{P,m} \stackrel{\text{def}}{=} \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_P$.

$$\boldsymbol{\Delta U = q + w} \tag{1}$$

Equation 1: The first law of thermodynamics where q is the heat added to the system and w is the work done on the system.

There are different attributes a system may have which yield large simplifications. Adiabatic means no heat transfer between the system and the surroundings ($q = 0$ and using equation 1: $\Delta U = w$). Alternatively, a system may be isochoric, where the volume is held constant ($w = 0$ and $\Delta U = q_v = C_v \Delta T$).

$$\boldsymbol{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}} \tag{2}$$

Equation 2: the combined gas law

$$\boldsymbol{P_i {V_i}^{\gamma} = P_f {V_f}^{\gamma}} \tag{3}$$

Equation 3: During adiabatic expansion this equation can be derived using the following definition for gamma

$$\boldsymbol{\gamma \stackrel{\text{def}}{=} \frac{C_{P,m}}{C_{V,m}} = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{P_1}{P_3}\right)}} \tag{4}$$

Equation 4: The definition of gamma and a derived equivalence using only measurable variables

Statistics are important:

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

Equation 5: The variance of a set x with n elements

$$\bar{x} \pm \frac{ts}{\sqrt{n}} \tag{6}$$

Equation 6: The student-t confidence interval for critical value t and set x with n elements

Experimental Methods:

A 5-gallon glass jug was used as a vessel. This was eventually closed by a three-holed rubber stopper with outlet tubes A, B and C. 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 rubber stopper. Tube C was attached to a digital pressure gauge to determine the difference between ambient atmospheric pressure and the pressure in the vessel. Tube A was attached to the gas canister and tube B was clamped closed. Temperature T_1 was recorded.

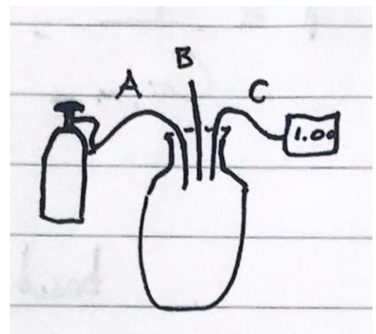

Figure 1: The vessel with a gas canister to the left

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 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 measured along with ambient room temperature T_1 for later calculations.

Results and Discussion:

The calculation of P_1 and P_3 are relative to the measurement of P_2. This value was acquired from IBM's Weather Data API on August 31, 2022 as 30.03±0.01inHg. [?] The conversion from inHg to psi went as follows:

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

Next, the uncertainty must be propagated to P_1 and P_3. For example:

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

Now we can calculate gamma using equation 4:

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

Oh no! This is getting complicated. Let's use Mathematica to calculate the partial derivates.

```
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]= (-Log[p1/p2] + Log[p1/p3]) / (p1 Log[p1/p3]^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}
```

Figure 2: The 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 P_1, P_2 and P_3 respectively. In[9] is an example calculation of the uncertainty of gamma for trial 1. In[10] is all gamma values and uncertainties

Yikes! That didn't get any simpler. Oh well, here's all the data.

	N_2 trial 1	N_2 trial 2	Ar trial 1	Ar trial 2
$P_{1,\ gauge}$ (psi)	1.66±0.01	1.64±0.01	1.63±0.01	1.71±0.01
$P_{3,\ gauge}$ (psi)	0.45±0.01	0.43±0.01	0.41±0.01	0.58±0.01
P_1 (psi)	16.409±0.006	16.389±0.006	16.379±0.006	16.459±0.006

P_3 (psi)	15.20±0.02	15.18±0.02	15.16±0.02	15.33±0.02
γ	1.39±0.08	1.37±0.08	1.35±0.08	1.5±0.1

Table 1: Wow! Look at all that data.

$P_2 = 14.749 \pm 0.005\, psi$ and $T_1 = 21.94 \pm 0.01°C$ for all trials.

Now we can calculate the mean of each gas using the student-t distribution. With 95% confidence and 1 degree of freedom using a two tailed distribution, the critical value is 12.71[source?]. Using equation 5 we can calculate the variance of the two gamma values for nitrogen:

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

Using equation 6 we can find the 95% confidence interval:

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

	Nitrogen	Argon
γ	1.38 ± 0.11	1.49 ± 0.13

Table 2: 95% confidence intervals for gamma values of nitrogen and argon

When compared to the literature values we find …

Conclusion:

Safety:

There is no important safety information for nitrogen or argon as they are already abundant in our atmosphere. However, 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.

References:

Calculations:

To propagate errors for P_1 and P_3:

```
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}

Chemistry 451 Lab Report Grading Sheet

Name:________________________________ Lab Partners:________________________________

Experiment: ____

Introduction: 15 points

____/3 Name, title, date, lab partners names, grading sheet are included and correct.

____/2 Clear statement of the objective of the experiment is presented.

____/10 most important ideas and equations (define all symbols!) for the lab are concisely summarized.

Methods: 10 points

____/5 Instrumental apparatus is explained and diagramed as necessary.

____/5 Experimental description allows another 451 student to reproduce your work.

Results and Discussion: 50 points

____/15 All data is clearly presented in a table or graph that is referenced and described in the text.

____/5 All data has units and experimental uncertainty clearly identified.

____/10 Calculations and derived information are discussed briefly in narrative, and appendices referenced.

____/10 Final results and all additional information requested in handout is presented clearly in narrative.

____/5 Literature/ theoretical values are listed; appropriate comparisons are made, including error propagation.

____/5 Major sources of error given (includes magnitude and direction that they would impact final result).

Conclusions: 10 points

____/4 Quantitative summary of results (and uncertainty) reflects the objective statement from the introduction.

____/4 Discussion of errors suggests ways to improve or fatal flaws (goes beyond what is in the discussion).

____/2 Results are placed into the context of the broader scientific picture, with future applications noted.

Safety/References: 5 points

____/3 Major safety issues are addressed, MSDS are cited.

____/2 Citations for introduction, safety and literature or theoretical values are correct and complete.

General Writing: 10 points

____/5 Scientific writing style is used, including proper tenses and voices.

____/5 Organization, sentence structure, and flow make the report easy to follow and understand.

____/100 Total Score