Laboratory 1. Adiabatic and reversible compression of a gas

Introduction

The initial and final states of an adiabatic and reversible volume change of an ideal gas can be determined by the First Law of Thermodynamics and this will be discussed extensively in CH433. The resulting equation for such a change relates volume and pressure:

An ***adiabatic*** change is a change for which heat is prevented to exchange with the surroundings.

A ***reversible*** change is a change that follows path consisting of states of rest.

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \tag{1}$$

Where the exponent:

$$\gamma = \frac{\overline{C_p}}{\overline{C_v}} \tag{2}$$

That means that γ is the ratio of the ***heat capacities*** at constant pressure and constant volume. In addition, there is an expression

$$\overline{C_p} = \overline{C_v} + R \tag{3}$$

Form these, the molar heat capacity $\overline{C}_p$ can be determined from a measurement of γ.

Heat capacity is related to the number of ***accessible degrees of freedom*** system, such as rotations, vibrations and translations, because if the system has more degrees available we must spend more heat to make it go up one degree.

- Monatomic gases like Argon have only translational degrees of freedom. Statistical thermodynamics shows that $\overline{C}_v$ = 3/2R for such a gas.
- Diatomic gases have 2 degenerate rotational degrees and one vibrational one. The latter is not active at room temperature, but the rotational ones add a term R to the $\overline{C}_v$. For a rigid diatomic molecule $\overline{C}_v$ = 5/2R.
- Triatomic molecules have an even greater heat capacity that is also somewhat temperature dependent. This is because of vibrational states that are partially occupied at room temperature. It can be calculated from the knowledge of the frequencies and with the vibrational partition function. A linear triatomic such as CO_2 will have $\overline{C}_v$ = 5/2R + vibrational contribution.

All gases in this experiment are sufficiently dilute that we can consider them ***ideal***

EXPERIMENT

The Pasco TD 8565 Adiabatic Gas Law Apparatus allows the rapid and simultaneous measurement of P, V and T for a gas sample confined in the cylinder of the apparatus. Two hundred data points can be stored on a computer for a compression lasting 200 milliseconds, fast enough to assume that the process is adiabatic, but slow enough that we can assume that the conditions are uniform throughout the gas sample, i.e. that the compression is also reversible.

It is advisable to first do a dummy run using whatever gas happens to be in the cylinder (air probably) to familiarize yourself with the PASCO TD 8565

Make sure the cylinder device is powered
- Start DataStudio
- Create experiment: the interface should be visible and active.
- On the picture of the interface on the "experiment setup" window there are three smaller yellow rings on the right
- Click on the left most of the 3 smaller rings
- Scroll pop up to bottom and opt for "voltage sensor"
- Click on the middle one
- Opt for "pressure sensor (absolute)"
- On the experiment setup window set the sample frequency to 500 Hz

NOTE: We will not use the temperature sensor

Calibration run

- On the left bottom window "Displays" click on graphs and make a graph for the voltage and one for the pressure.
- Open one of the gas taps and push the piston all the way down
- Click "start" on the computer panel
- Read off the position of the bottom of the piston on the centimeter scale on the cylinder. Bring the piston up stepwise 1 cm at the time. Write down how far the bottom of the piston is each time. The voltage curve should look like a stair case.
- Under file go to export data and export the voltage staircase to a suitable location and filename (create a directory for yourself).

- The exported files can be opened in excel.

Measurement run

- Click "sampling options" and then "delayed start" opt for data measurement = voltage and set the value to 4V. This means you will have to lift the boom of the instrument to the top to trigger a measurement
- Make sure your cylinder is filled with the right gas with both taps closed
- Have one partner at the cylinder, have the other click Start on the left top of the main panel
- Lift the boom to the top and quickly press it down. Let the other partner press stop
- Go to file (top left) and export the three data sets to disc. Make a separate directory for your data and decide upon sensible file names like argon-p1, e.g.
- The files can be opened in excel. They are tab delimited and you need to the combine the v,p and t files for the same experiment into one sheet.

Data collection

We will examine three gases: Ar, N_2 and CO_2. Use the valves to flush the cylinder five times with the gas. It is useful to have two people operate them (Open exit valve, move piston down, close exit valve, open entry valve to fill with gas, close entry valve, open exit valve, etc.) Close both valves at the end, but briefly open the exit valve to make sure the pressure in the cylinder with the piston up is equal to ambient. Make sure the piston is up, such that it is beyond the reset sensor point, otherwise the data collection is not triggered. Collect data for 10 consecutive runs. Repeat for each of the three gases.

Calculations and Reporting

For regression purposes ***derive*** a suitable formula involving $\ln(P/P_0)$ versus $\ln(V/V_0)$ by taking a logarithm of Eq 1.($\rightarrow$ introduction). (What is the relationship between the slope of an $\ln(P/P_0)$ versus $\ln(V/V_0)$ plot to γ?)

The data files can be opened directly into Excel. The "text import wizard" menu will popup, select 'Next' and in the second popup tick the 'comma option', then select 'Finish'.

The report need *not* contain all raw data in hard copy. Just list the file names ($\rightarrow$ Data).

Calibration data

The output voltage from the sliding resistor on the side of the cylinder is a linear measure for the volume, but zero voltage does not correspond to zero volume. Take an average of the measured voltage for each plateau of the staircase and plot the height position against the voltage and determine the best regression line. Assume that the diameter of the cylinder is 4.45 cm to convert the height to volume.

Plot the data as Volume vs. Voltage. Perform a linear regression, including 95% confidence interval. You may use this to determine the error estimate for voltage $\sigma(V)$. Find the other errors $\sigma(V)$, $\sigma(\gamma)$ and $\sigma(C_p)$ by propagation of error. Use the linear coefficients to convert voltage vs. time data into volume vs. time data.

Measurement runs

For each of the data sets do the following:

First you need to determine what the valid P and V data are. There are a lot of bad data at the beginning of the set and the point the piston hit bottom marks the end of the valid data. First inspect a plot of V against time. Use the intercept and the slope of the calibration line to convert the voltage to volume. (Include one such graph in Data section).

Note the *kink* in the graph; this roughly marks the end of the valid data. Put the cursor on the kink in the graph to find out up to which point the data is valid → Data).

Version 1: Using the RLS worksheet prepare two columns with lnP and lnV data. Prepare a graph. (lnP on Y-axis). Apply the RLS module to the data up to the 'kink'-point to refine the valid data range. Somewhere between data point 20 and 100 or so there should be a range where the studentized residuals remain between the rejection limits (say –3 and +3), this is the valid data range. Inspect the plots of studentized residuals to see if they are indeed (more or less) random and show one of these plots (under Results). For this one set of residuals do the following:

Collect the γ values for each gas and determine average, standard deviation and the standard error over three sets of at least 5 replicates (i.e. std. error of replication, *not* by propagation). (In table →results) Why can the standard error of replication be bigger than the standard errors of the individual slopes?. This error estimate will be compared with propagation of error starting with the calibration of volume vs. voltage.

Alternative to RLS worksheet: Fit the ln V vs ln P data and determine the slopes and standard deviations for each data set using linear least squares fitting. As above use the central region of the change in V and P for your linear fit. Once you have made the fits for data sets use the t-test to determine what value to multiply calculate a 95% confident limit for your data. Determine the heat capacity based with appropriate errors based on the slope and the known relationships between the parameters (see below for the math to complete this).

Use propagation of error to determine appropriate error estimates. Consider the fact that your calibration line for the volume contains a measurement error that is significantly larger than the pressure since you must convert from voltage (measured) to volume.

Complete the report as follows: Derive an expression that allows you to express the molar heat capacity at constant pressure $\overline{C}_p$ in γ and R (from Eqn 2 and 3). (→Introduction). Calculate $\overline{C}_p$ (using your formula) and its uncertainty (by propagation from γ, using your formula and its derivative). (Results in table please, together with literature values,→Results. Literature source →Reference. Sample calculation →Calculation).

DISCUSSION

1. What values for $\overline{C}_p$ and γ would you theoretically expect for monatomic and diatomic ideal gases? Why is the $\overline{C}_p$ different for CO_2 relative to these gases (i.e. relative to a rigid rotator model of a linear triatomic?
2. Compare your measured $\overline{C}_p$ and γ values with theoretical and literature values. Provide references and discuss different methods used to measure heat capacity.
3. Discuss the systematic error in this method and the possible causes. What would happen to the slope value for Ar if the flushing would not be entirely successful and your gas sample contains a small amount of either air or CO_2? How would the result be affected if a small amount of H_2O were present in the line or the cylinder. Why is the cylinder made of a thick polymeric material rather than e.g. copper? Is the cylinder thick enough to prevent heat loss? Why is the intercept of the calibration curve more important than the slope? What would be the consequences of deviation from ideality_ How might you check these various contributions using control experiments or calculations?
4. Discuss the comparison of the random error using two methods. The first is the measurement of five or more values of γ, averaging and determining the 95% CO. Compare this method to propagation of error starting with the 95% CI in the volume calibration to voltage. Calling that σ_V you will need to propagate that into pressure, σ_P, then using both of those you will propagate into gamma, σ_γ. Finally, both methods will have a final step of propagation into $\overline{C}_p$. Since we will assume that the gases are ideal (at 1 atm of pressure), there is a fixed relation between $\overline{C}_p$ and $\overline{C}_V + R$. Therefore, when you make a table and compare values and errors you only need to report $\overline{C}_p$.

Checklist for your report

1. Do all your measurements have a sign, a magnitude, a precision and a dimension (units!)?
2. Did you check for systematic error? If observed, did you discuss?
3. Did you compare random error using two different methods? Which is larger? Discuss.
4. Do all your tables and all your figures have captions? Axis labels? Units? Is their scaling and size appropriate? (Can the reader see what you want to show?)
5. Do you have appropriate references and a discussion of alternative methods of measurement of heat capacity for comparison.

REFERENCES

MacQuarrie & Simon, Physical Chemistry, University Science Books, Sausalito CA, 1997, pp754-756, 797-799
P.W. Atkins, Physical Chemistry, Freeman, New York, pp. 604-605
Pasco Manual.

* (=NORMDIST(x,μ,σ,false)) calculates the theoretical value of the probability density of normal curve $N(\mu,\sigma^2)$ at the point x. Because the bin-width is ½ we must scale this with N/2, to make sure the integral will sum up to N).