Heat Capacity Ratio for Gases

Preparation
The basic theory and a description of the experimental procedure are given in your lab text as experiment 3, method B (sound velocity).

Do a literature search for experimental values, including uncertainty estimates, for the sound speed near room temperature for helium, argon, nitrogen, and carbon dioxide. Determine how you will adjust these values for comparison to your data if the actual lab temperature is not the same as for the literature values.

Background
The speed of sound \( c_s \) in a medium is related to the oscillation frequency \( f \) and the length of the longitudinal waves \( \lambda \).

\[
c_s = f \cdot \lambda \quad (1)
\]

In our modified version of the well known Kundt’s tube apparatus, the tube length \( L \) is fixed and an audio oscillator generates a series of certain frequencies where standing waves satisfy resonance conditions indexed by positive integers \( n \).

\[
L = n \lambda / 2 \quad n = 1, 2, 3, ... \quad (2)
\]

The set of resonant frequencies thus appear as multiples of \( n \)

\[
f_n = n \cdot \frac{c_s}{2L} \quad (3).
\]

The sound speed can be found from the slope of a plot of \( f_n \) vs. \( n \).

In an ideal gas of molar mass \( M \), the sound speed is related to the heat capacity ratio \( \gamma \) through

\[
c_s^2 = \frac{\gamma \cdot RT}{M} \quad (4)
\]

and

\[
\gamma = \frac{C_p}{C_v} = 1 + \frac{R}{C_v} \quad (5).
\]

For gases having simple molecular structures, the molar heat capacity at constant volume can be calculated from spectroscopic data using the statistical thermodynamic relationship

\[
\tilde{C}_v = \frac{R}{2} \left[ 3 + i_g + 2 i_r \right] \quad (6),
\]

where the number of active translational modes is 3 for any gas molecule and \( i_g \) and \( i_r \) are the number of active (fully excited) rotational and vibrational degrees of freedom (modes). For linear molecules \( i_g = 2 \) and for non-linear molecules \( i_g = 3 \). For an N-atom molecule the maximum number of vibrational modes is \( 3N-5 \) or \( 3N-6 \), but most molecular vibration frequencies are high enough that these modes are only slightly active \( (i_v = 0) \) at ordinary temperatures, and the small vibrational contribution to the molar heat capacity is better represented as

\[
\tilde{C}_v(vib) = R \sum_j \frac{u_j^2 e^{-u_j}}{1-e^{-u_j}} \quad (7)
\]

with

\[
u_j = \frac{\hbar \nu_j}{k_B T} = \frac{\hbar \tilde{\nu}_j}{k_B T} = 1.4388 \cdot \frac{\tilde{\nu}_j}{T} \quad (8).
\]

for the wavenumbers \( \tilde{\nu}_j \) (in cm\(^{-1}\)) of each vibrational normal mode \( j \).
This spectroscopic - statistical approach does not account for intermolecular forces in non-ideal gases, but such effects may be estimated in a van der Waals gas where the heat capacity ratio is given by

$$\gamma = 1 + \frac{R}{C_v} \left( 1 + \frac{2a}{PV^2} \right) \quad \tilde{V} = \frac{RT}{P}$$  \hspace{1cm} (9).

**Additions to and deviations from written procedure**

Sketch the apparatus in your notebook along with other observations, and attach duplicates to your report. Measure the length of the tube, its temperature, and the pressure in the lab, including estimates of uncertainty. Use L and the literature values for $c_s$ to predict the resonant frequencies for each gas.

We are studying three different gases: He, N$_2$, and CO$_2$. Connect the supply hose for N$_2$ to the needle inlet of the tube and open the valve on the regulator to start the gas flow. To purge the previous contents, flush the tube for several minutes at a flow rate high enough to feel or hear gas leaking from the exit port at the other end. Then set the supply valve nearly closed to maintain a small flow rate during your measurements.

Apply a white noise source (e.g. ToneGen software) to the speaker and increase the amplitude until audible. Acquire data using a Vernier sound pressure sensor and LoggerPro set with a sampling rate of 10,000 samples/second for a data range of 0.5 or 1 second in repeat mode. Insert another graph window to show the fast Fourier transform (FFT) of the signal over a range of 0 to 2000 Hz. Adjust the sound bandwidth (pink noise, blue noise, etc.) and the sound intensity as needed to optimize the signals. Avoid using a high intensity as the sensor will saturate and degrade the data. Examine one prominent frequency for a minute or so to make sure that the gas sample composition is not still changing. Switch to single sweep acquisition (or pause) to measure and tabulate resonant frequencies with corresponding estimated uncertainties.

After completing data collection for your first sample, close the supply valve and disconnect the hose. Switch to another gas sample and repeat the measurement procedure. You may need to adjust the electronics and the FFT graph range if the sound speed is significantly different. Measure frequencies again for the third gas. Note that CO$_2$ gas becomes cold when rapidly expanding from the cylinder, so you should keep it at lower flow rate to avoid freezing the regulator on the cylinder. Graph each of your data sets and do preliminary fits to verify that each set of measurements is reasonable. Switch off all electronics and close gas supplies when finished.

**Reports**

Preliminary reports should state clearly how $\gamma$ will be determined 1) from your observations, 2) from statistical calculations using spectroscopic constants given below with equations 5 to 8 above, and 3) from van der Waals constants given below with equation 9 above.

Plot the observed resonant frequencies (with error bars) vs. n for each gas sample. These may be shown together on one graph. From the slope of a weighted, linear fit determine the sound speed for each gas with an uncertainty estimate using equation 3. Then compute the experimental heat capacity ratio for each gas from equation 4 and propagate errors to estimate the uncertainties. Discuss possible systematic errors due to incomplete replacement of air from the tube.

Calculate the heat capacity ratio for He or Ar from equation 6. Given the following molecular spectroscopic data, calculate the statistical heat capacities for N$_2$ ($v = 2331$ cm$^{-1}$) and CO$_2$ ($v_1 = 1388$ cm$^{-1}$, $v_2a = 667$ cm$^{-1}$, $v_2b = 667$ cm$^{-1}$, $v_3 = 2349$ cm$^{-1}$) using equations 6 – 8.

Search for literature values for van der Waals coefficients, and use these with equation 9 to estimate effects of non-ideality for each gas.

Address the discussion questions described in your lab text, especially the validity of the statistical calculations of heat capacity and whether non-ideality is important.
References


2. The power spectrum of white noise is independent of frequency. Digital filtering enables other spectral response functions. For example, pink noise power decreases by 3 dB/octave as frequency increases whereas blue noise increases by 3 dB per octave. Audio filtering may improve resonant frequency signals when the speaker or microphone have limited response for some frequencies.

SAFETY ISSUES

- Cylinders containing pressurized gases must be secured at all times. Do not move a cylinder unless the regulator has been disconnected and it is capped. Do not open the main cylinder valve suddenly if the diaphragm is tightened.

- Wear safety glasses when using pressurized gases.
**Chem 3421: "Heat-capacity ratios for gases" Lab**

**TA's Instructions:**

1) Locate a plastic tube, 50 to 60 mm in diameter and ~ 100 cm in length, with a hole near one end. Mount a Vernier sound pressure sensor in one end using a stopper that also has a small hole to let gas escape.

2) Mount a small speaker (e.g. from an old computer) to the other end of the tube using vinyl tape.

3) Attach the speaker to a computer-driven sound system. Check that the computer also has audio generation software such as **ToneGen**.

4) Mount (He or Ar), N₂, and CO₂ cylinders to the bench securely using clamps. Attach regulators to each. Connect 6 ft of 1/4” OD polyethylene tubing to each output.

5) Attach the tubing to the sound tube using a #0 1-hole rubber stopper (hole enlarged to accept the tubing).

6) Tape a K-type thermocouple (for DMM readout) to the side of the tube.

7) Provide a tape measure for students to determine the length of the tube.

8) Have a barometer or pressure gauge (Vernier) in the lab to take a daily reading.