Heat-Capacity Ratio for Gases

Abstract

The heat-capacity ratio of a gas is defined as the heat-capacity at constant pressure divided by the heat-capacity at constant volume [1]. The heat-capacity ratios of carbon dioxide, argon, and nitrogen gas were determined experimentally by adiabatic expansion and sound velocity methods. The ratios for nitrogen gas, determined via adiabatic expansion and sound velocity method, coincided with each other and were found to be within each others error (1.40 ±0.10 and 1.41 ±0.06 for adiabatic and sound method, respectively). The experimental heat-capacity ratios of all three gasses agreed well with their literature values: 1.33 ±0.05 with a 2.33% difference for CO_2, 1.64 ±0.06 with a 1.78% difference for Ar, and 1.41 ±0.06 with a 0.243% difference for N_2. The theoretical heat-capacity ratios of the three gasses were calculated using the equipartition theorem [2] to be 1.15, 1.67, and 1.29 for carbon dioxide, argon, and nitrogen, respectively. The difference between the theoretical value and the experimental value of the gases increased with the number of atoms of the gas, due to the ideal gas assumption of the theorem. The theoretical heat-capacity ratio for nitrogen was found to be closer to the experimental value when the vibrational contribution is excluded

Experimental

Adiabatic Expansion Method

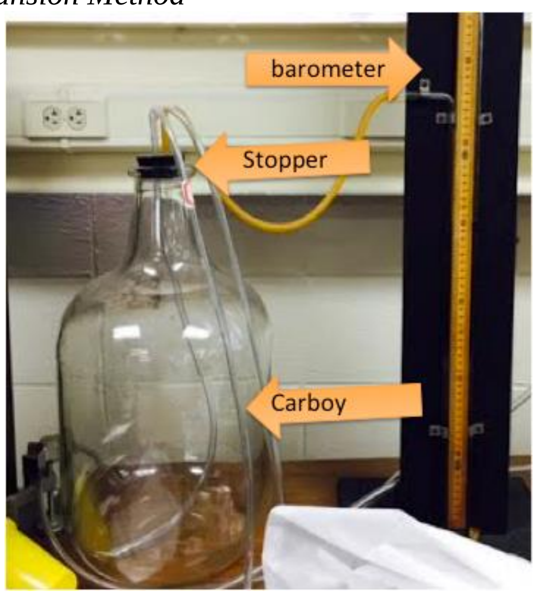

Figure 1. *Adiabatic expansion method apparatus. The rubber stopper was easily removable to cause adiabatic expansion. Pressure measurement were made using the barometer and ruler.*

The carboy was firmly sealed using the rubber stopper. A steady flow of N_2 gas from a gas cylinder was allowed to flow through the carboy, purging the carboy for ~10 minutes. After waiting several minutes for the gas of to reach room temperature, the pressure was recorded. Following the filling, a screw clamp was attached to the inlet tube of the carboy to reduce the gas flow until the manometer's liquid reached an appropriate height for measurement, and then the clamp was tightened fully to seal the system. After fifteen minutes (allowing thermal equilibration) the adiabatic expansion was initiated by dropping the pressure to atmospheric pressure by quickly removing the stopper (causing a popping sound from the released pressure) and then replacing it. The gas then returned to room temperature after several minutes and the third pressure reading was taken. This process was repeated two more times for nitrogen gas.

Sound Velocity Method

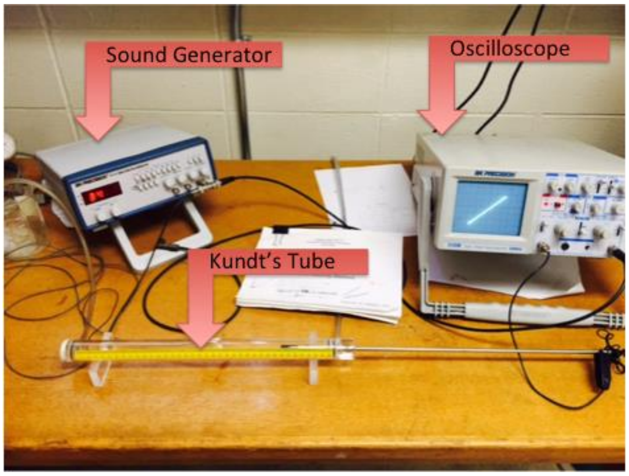

Figure 2*. Sound velocity method set-up. The sound generator produced a signal of the desired frequency for the gas. The Kundt's tube microphone piston could be moved along the length of the tube, with the signal being recorded on the oscilloscope.*

The Kunt's tube was purged with the analyte gas for several minutes before taking measurements. The sound generator was set to the appropriate frequency (Ar: 3200 ± 50 Hz, CO_2: 2650 ± 50 Hz, N_2: 3450 ± 50 Hz) and the microphone was moved to an initial position at which the Lissajous figure was displayed on the oscilloscope, with a positively sloped 45° straight line (as seen in Fig. 2). The microphone piston was then moved towards the speaker until the increasing slope appeared on the screen again, the position was recorded. Three of these positions were recorded, with the distance between them corresponding to the wavelength of the measured sound. The temperature was also recorded by an external Omega thermocouple device. This process was repeated three times for each gas, with a different frequency being used for each.

Results

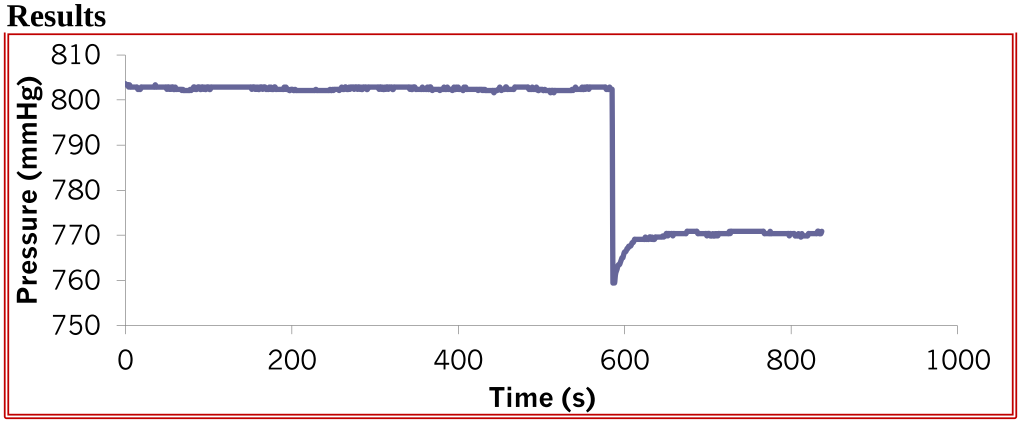

Figure 3. *Adiabatic expansion of nitrogen gas barometer recording. The carboy sustained an initial pressure of ~802 mmHg, followed by a drop to atmospheric pressure at ~758 mmHg after the stopper was removed. The gas preformed work against the atmosphere by using internal energy when the stopper was removed. The pressure then equilibrated with a slow rose ~770 mmHg.*

Table 1. *Manometer height and temperature readings for adiabatic expansion method of N_2 gas.*

Trail #	Temp (°C)	P_1: delta *h* (cm)	P_2: delta *h* (cm)	P_3: delta *h* (cm)	Height uncertainty (cm)
1	22.5	12.44	0	4.20	±0.01
2	22.5	56.50	0	14.46	±0.01
3	22.5	56.32	0	13.88	±0.01

Table 2. *Calculated pressures (see appendix) of each stage of the adiabatic expansion method of N_2 gas.*

Trail #	P_1 (mmHg)	P_2 (mmHg)	P_3 (mmHg)	Uncertainty of pressure (mmHg)
1	768.56	758.95	762.19	±0.08
2	802.57	758.95	770.11	
3	802.43	758.95	769.67	

Table 3*. Calculated heat capacity ratios of N_2 gas from adiabatic expansion method and theoretical value difference.*

Trail #	C_p/C_v	Uncertainty of heat capacity ratio	Equipartition theorem Theoretical γ	Percent Difference (%)
1	1.51	±0.10		
2	1.35			
3	1.34			
Average	1.40	±0.10	1.29	8.60

Table 4. *Wavelength measurements of CO_2, Ar, and N_2 gas using sound velocity method.*

Species	Trial #	Frequency (Hz)	Temp (°C)	Average Wavelength (m)	Uncertainty in wavelength (m)
CO_2	1	2647	23.10	0.1025	±0.0001
	2	2642	23.24	0.1037	
	3	2645	23.26	0.1033	
Ar	1	3162	23.10	0.0992	
	2	3156	23.11	0.1017	
	3	3167	23.11	0.1009	
N_2	1	3450	23.26	0.1017	
	2	3447	23.33	0.1030	
	3	3460	23.33	0.1011	

Table 5. *Calculated sound velocities and heat capacity ratios of CO_2, Ar, and N_2 gas using sound velocity method.*

Species	Trial #	Sound Velocity (m Hz)	Uncertainty in sound velocity (m Hz)	Heat Capacity Ratio, γ	Uncertainty in heat capacity ratio
CO_2	1	271.32		1.32	
	2	274.06	±0.26	1.34	±0.05
	3	273.32		1.33	
	1	313.78	±0.32	1.60	
Ar	2	320.97		1.67	±0.06
	3	319.44		1.65	
	1	350.98		1.40	
N_2	2	355.04	±0.35	1.43	±0.06
	3	349.92		1.39	

Table 6. *Sound velocity experimental, theoretical, and literature comparison of heat-capacity ratios for CO_2, Ar, and N_2 gas.*

Species	Experimental Average, γ	Equipartition theorem Theoretical γ	Percent Difference (%)	Lit. Value of γ [3]	Percent Difference (%)
CO_2	1.33 ±0.05	1.15	15.7	1.30	2.33
Ar	1.64 ±0.06	1.67	1.75	1.67	1.78
N_2	1.41 ±0.06	1.29	9.10	1.40	0.243

Conclusion

The heat capacity ratios of several gases (i.e. CO_2, Ar, and N_2) were determined theoretically and experimentally, using the adiabatic expansion method and sound velocity method. The theoretically heat capacity ratios of the gases were derived from the equipartition theorem. The heat capacity ratio of N_2 gas was determined to be 1.40 ±0.10 via the adiabatic expansion method and 1.41 ±0.06 via the sound velocity method; although the ratios were not in agreement with the theoretical ratio of 1.29 (8-9% difference), they correspond well with the literature value for N_2 gas (<0.5% difference). Similar results were obtained by the sound velocity method determination of the heat capacity ratio CO_2 gas, with the experimental value of 1.33 ±0.05 differing 15.7% from the theoretical value, but only 2.33% from the literature value. However, argon gas was found to have a ratio of 1.64 ±0.06 that agreed well with both the theoretical and literature ratio values (1.75% and 1.78% difference for theor. and lit., respectively). The experimental heat-capacity ratio results of both methods coincided well with the literature values, while the theoretical value became less accurate as the gas became more complex (monatomic, diatomic, polyatomic). The inaccuracy of the theoretical value can be attributed to the equipartition theorem's assumption that the gas is ideal.

References

1. Wrolstad, Ronald E., Terry E. Acree, Haejung An, Eric A. Decker, Michael H. Penner, David S. Reid, Steven J. Schwartz, Charles F. Shoemaker, and Peter Sporns. *Preface*. John Wiley & Sons, Inc., 2001.
2. Atkins, P. W. "Physical Chemistry. 6th." (1998).

3. White, Frank M.: Fluid Mechanics 4th ed. McGraw Hill

Sample Calculations

Degrees of freedom for N_2 gas using equipartition theorem

$$DF_s = 3N = DF_{trans} + DF_{rot} + DF_{vib}$$
$$DF_s = 3(2) = (3)_{trans} + (2)_{rot} + (1)_{vib}$$

N being the number of atoms in the system, DF_s, DF_{trans}, DF_{rot}, and DF_{vib} being the system, translational, rotational, and vibrational degrees of freedom, respectively.

Internal energy for N_2 gas

$$U = \langle E_{trans} \rangle + \langle E_{rot} \rangle + \langle E_{vib\text{-}kinetic} \rangle + \langle E_{vib\text{-}potential} \rangle$$

$$U = \underbrace{3 * \frac{1}{2}RT}_{translational} + \underbrace{2 * \frac{1}{2}RT}_{rotational} + \underbrace{1 * \frac{1}{2}RT}_{vibration\text{-}kinetic} + \underbrace{1 * \frac{1}{2}RT}_{vibrational\text{-}potential}$$

$$U = \frac{7}{2}RT$$

Heat capacity at constant volume, C_v, for N_2 gas

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{\partial}{\partial T}\left(\frac{7}{2}RT\right)_V = \frac{7}{2}R$$

Heat capacity at constant pressure, C_p, for N_2 gas

$$C_p = C_V + R = \frac{9}{2}R$$

Heat capacity ratio for ideal N_2 gas

$$\gamma \equiv \frac{C_p}{C_v} = \frac{\frac{9}{2}R}{\frac{7}{2}R} = \frac{9}{7} \approx 1.29$$

$$\gamma \equiv \frac{C_p}{C_v} = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{P_1}{P_3}\right)} = \frac{\ln\left(\frac{768.56\text{ mmHg}}{758.95\text{ mmHg}}\right)}{\ln\left(\frac{768.56\text{ mmHg}}{762.19\text{ mmHg}}\right)} \approx 1.51$$

Heat capacity ratio, γ, of argon gas using sound velocity method

$$\gamma = \frac{Mv_s^2}{RT} = \frac{\left(0.03995\frac{\text{kg}}{\text{mol}}\right)\left(313.78\frac{\text{m}}{\text{s}}\right)^2}{\left(8.314\frac{\text{kg m}^2}{\text{s}^2\text{ mol K}}\right)(295.83\text{ K})} = 1.60$$