# T17a: Introduction to Thermodynamics

## Introduction:

Thermodynamics is a branch of physics that describes processes involved thermal changes, heat, and heat transfer. It is applicable to "macroscopic systems" which are systems containing a very large number of particles. Thermodynamics is mostly based on two fundamental laws. The First Law of thermodynamics is essentially the principle of conservation of energy. The Second Law describes behavior of macro systems in reversible and irreversible processes and allows us to determine a theoretical efficiency of heat engines. In this experiment, you will investigate different thermodynamic processes, learn about work done by a gas, and apply the First and the Second laws of thermodynamics to an ideal gas. You will also learn about the Otto Cycle, which is the basis for operation of an internal combustion engine.

## Apparatus:

- Adiabatic Gas Law Apparatus Pasco TD-8565
- Computer Interface Pasco 850
- Computer with Interface Software Pasco Capstone

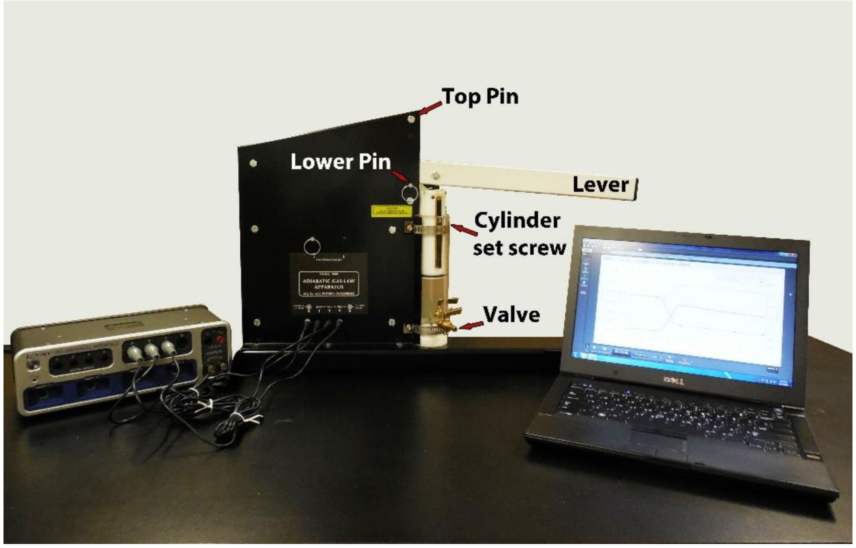

Figure 1 Experimental Setup

## Theoretical Background:

When the number of particles in a system is very large, analyzing and describing the system via the microscopic interaction of each pair of these particles becomes a challenge. Being able to use macroscopic quantities *temperature, pressure*, *volume*, *internal energy,* and *entropy* to describe the state of the system is a more efficient approach. These quantities, namely *pressure*, *volume* and *temperature* are measureable macroscopic parameters. They can be used to establish an equation of state for a system, thus providing a connection between the microscopic behavior and the macroscopic observables. An example of the equation of state is the ideal gas law, which relates the pressure $P$, volume $V$, temperature $T$, and number of moles $n$, in the gas:

$$PV = nRT , \qquad (1)$$

where $R=8.31(J/mole \cdot K)$ is the ideal gas constant. One mole is the amount of a substance which contains the Avogadro number, $N_A=6.02 \times 10^{23}$, molecules of the substance. Thermodynamics deals with a very large number of molecules, and moles represent a convenient measure of this amount. The *system* in this experiment is the air in a cylinder, which can be described as a gas of *ideal,* non-interacting molecules, under the range of pressures and temperatures in consideration.
Using the ideal gas law, one can determine the molar density (mass per unit volume of one mole of the gas) if the molar mass of each of the constituent gasses are known using

$$\rho = \frac{M_{molarmass} P_{initial}}{RT_{initial}} , \qquad (2)$$

and the number of moles of gas can be determined using

$$n = \frac{\rho V_{initial}}{M_{molarmass}} . \qquad (3)$$

A thermodynamic process is the passage of a thermodynamic system from an initial state, characterized by initial state parameters ($P, V, T$), to a final state of thermodynamic equilibrium, characterized by final state parameters. There are four special thermodynamic processes:

- *Isothermal* – constant temperature
- *Isobaric* – constant pressure
- *Isochoric* – constant volume
- *Adiabatic* – no transfer of heat or matter

Earlier in the course you learned about work, $W$. Work is a physics quantity related to force $F$ and displacement $s$ by, $W = \int \vec{F} \cdot d\vec{s}$ . Work done by a conservative force changes potential energy into kinetic energy and vice versa. Work done by a non-conservative force changes internal energy of the system. Work done by a thermodynamic system can be expressed in terms of pressure $P$ and volume $V$ as:

$$W = \int PdV . \qquad (4)$$

Internal energy of a thermodynamic system $U$, is the sum of kinetic and potential energies of all particles of the system.

The **First Law of Thermodynamics** relates the change in internal energy $U$ of a system with work $W$ and heat $Q$. It states that a system's change in total internal energy is equal to the heat transferred to the system minus the work done by the system

$$dU = dQ - dW . \qquad (5)$$

Thus, the first law of thermodynamics is merely a statement of the fact that the total energy in the environment and system is conserved.

In a cyclic process, a thermodynamic system undergoes a series of steps, returning to its initial state. While heat flows in and out of the system and work is done by the system and on the system, the overall change of internal energy of a system in a cyclic process is zero.

While the ***Second Law of Thermodynamics*** has many equivalent definitions, one that is the most applicable to this experiment describes the maximum attainable efficiency of a thermodynamic cycle:

> *It is impossible to extract heat from a hot reservoir and convert the entirety of that energy into work, thus some of that heat must be transferred to a cold reservoir thereby raising its temperature.*

This means that the efficiency of any thermodynamic cycle is *always* less than 100%. The efficiency is defined as

$$e = \frac{W}{Q} = \frac{Q_H - Q_C}{Q_H} . \qquad (6)$$

This statement also implies that it is not possible for heat to flow from a colder body to a warmer body without preforming work on the system.

An ideal gas is a substance where molecules do not interact with each other, and collisions between molecules are assumed elastic. Therefore, internal energy of an ideal gas is strictly kinetic energy of its molecules. In case of a monoatomic ideal gas, kinetic energy includes only translational energy. Combining laws of classical mechanics with the ideal gas law allows establishing a relationship between the average internal energy of a molecule of an ideal monoatomic gas $U_m$, and absolute temperature

$$U_m = \tfrac{3}{2} k_B T , \qquad (7)$$

where $k_B = 1.38 \times 10^{-23} (J/K)$ is one of the fundamental constants of nature called the Boltzmann's constant. The ideal gas constant $R$, is related to the Boltzmann's constant through Avogadro's number as $R = k_B N_A$.

Molecules of diatomic gas, in addition to translational kinetic energy, also have rotational and vibrational kinetic energy. This yields the following expression for the average internal energy of one molecule of a diatomic ideal gas $U_{D}$,

$$U_D = \tfrac{5}{2} k_B T \,. \qquad (8)$$

The kinetic theory predicts that in general, the average internal energy of an ideal gas molecule should depend on the number of degrees of freedom *f*, the molecules have, $U = \tfrac{f}{2} k_B T$ . The internal energy of *n* moles of an ideal diatomic gas can be expressed as

$$U = \tfrac{5}{2} nRT \,. \qquad (9)$$

The specific heat is defined as the amount of energy (heat) *dQ* required to raise the temperature *T* of a quantity of the material by *dT*:

$$c \equiv \frac{dQ}{dT} \,. \qquad (10)$$

If the quantity of the substance is one *mole*, *C* is called the *molar* specific heat capacity.

When a system undergoing an isochoric (constant volume) process, the work done by the system is zero, *W=0*, and according to the First Law of thermodynamics, molar specific heat at constant volume is,

$$C_V \equiv \frac{dQ}{dT} = \frac{dU}{dT} = \tfrac{f}{2} R\Delta T \,. \qquad (11)$$

When an ideal gas undergoes an isobaric (constant pressure) process, work, $dW = PdV = nRdT$, and the First Law yields that the molar specific heat at constant pressure is,

$$C_P \equiv \frac{dQ}{dT} = \frac{dU}{dT} + \frac{dW}{dT} = C_V + R \,. \qquad (12)$$

The ratio of specific heat capacities plays an important role in a number of physical processes and is given by

$$\gamma = \frac{C_P}{C_V} \,. \qquad (13)$$

By combining equations (11) and (12), it can be shown that the ratio of specific heat capacities is 1.4 for an ideal diatomic gas. It can also be shown that for an ideal gas undergoing an adiabatic process,

$$PV^{\gamma} = \text{constant} \,. \qquad (14)$$

## The Otto Cycle

The Otto cycle describes an idealized case of an internal-combustion engine. A fuel mixture enclosed within a cylinder is compressed quickly in an adiabatic process. Once compressed, the fuel is ignited which adds heat into the system. The added heat increases the pressure and the volume is allowed to expand quickly, also in an adiabatic process. Once expanded, the excess heat is allowed to escape.

This experiment will use a reverse Otto cycle. Beginning at *state* (1), the cylinder volume will be compressed in an adiabatic process reaching *state* (2). From *state* (2) to *state* (3), heat will be allowed to escape from the cylinder until the temperature is again stable. Now at *state* (3), the volume will be expanded in an adiabatic process until reaching *state* (4). Finally, from *state* (4) to *state* (1) heat will be allowed to enter the cylinder until the temperature is stable again.

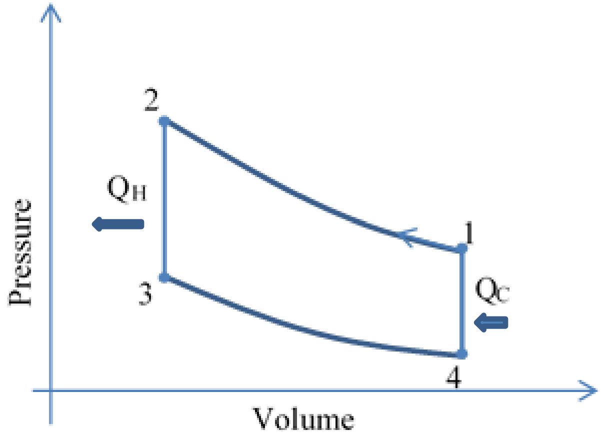

Figure 2 Reverse Otto Cycle

Returning to the concept of efficiency but now in the context of the Otto cycle, the heat is transferred only during the isochoric steps (the remaining steps are adiabatic). The efficiency is given by

$$e = \frac{Q_H - Q_C}{Q_H}, \tag{15}$$

and since

$$Q = nC_V \Delta T\ , \tag{16}$$

it can then be shown that

$$e = 1 - \left(\frac{V_{\max}}{V_{\min}}\right)^{1-\gamma}. \tag{17}$$

Equations (15) and (17) allows calculating the *ideal* efficiency of the reverse Otto cycle. One would expect that the experimentally determined efficiency would *always* be less than this ideal efficiency.

*More detailed description can be found in the Appendix at the end of this lab handout. Please also read the relevant material in your textbook for this experiment.*

| | |
|---|---|
| Quantity of Heat, | Sears & Zemansky, **University Physics**, *Chapter* **17** *section* **5.** |
| Equation of State, | Sears & Zemansky. **University Physics**, *Chapter* **18** *section* **1.** |
| Heat Capacity, | Sears & Zemansky. **University Physics**, *Chapter* **18** *section* **4.** |
| 1st Law of Thermodynamics, | Sears & Zemansky, **University Physics**, *Chapter* **19** *all sections***.** |
| Heat Engines, | Sears & Zemansky. **University Physics**, *Chapter* **20** *section* **2.** |
| Internal-Combustion Engines, | Sears & Zemansky. **University Physics**, *Chapter* **20** *section* **3.** |

| Data Determined from NIST Database | | | | | |
|---|---|---|---|---|---|
| Element | Atomic Molar Mass | Form of Molecule in Air | Percent in Air | Molar Heat Capacity Constant Pressure, $C_P$ | Molar Heat Capacity Constant Volume, $C_V$ |
| | (kg/mol) | | (%) | (J/mol K) | (J/mol K) |
| Oxygen | $1.59994 \times 10^{-2}$ | $O_2$ | 21 | 29.3605 | 21.0460 |
| Nitrogen | $1.40067 \times 10^{-2}$ | $N_2$ | 78 | 29.1215 | 20.8071 |
| Argon | $3.99480 \times 10^{-2}$ | Ar | 1 | 20.7860 | 12.4715 |
| | | | | | |
| Ideal Gas Constant $R$ | | | | 8.3144598 | (J/mol K) |
| Boltzmann Constant $k_B$ | | | | $1.380648 \times 10^{-23}$ | (J/K) |
| Avogadro’s Number | | | | $6.022140 \times 10^{23}$ | (constituents/mol) |

## Procedures:

Each Adiabatic Gas Law Apparatus has a unique set of calibration constants. The equipment has been labeled with Device 1 thru 4. Open the Capstone software startup routine that corresponds to your Device number. Notice that there are six labeled tabs along the top. The first tab, labeled PVT-time graph, is the correct one to use when collecting data during the experiment. Check that the bottom-stopping pin (lower pin) is properly in place. In addition, check that the cylinder set screw (figure 1) is loose. Open one of the valves at the bottom and move the piston slowly up and down a couple of times using the attached lever. The piston should move freely and smoothly in the cylinder.

### Part I:

1. Open one of the valves at the bottom, raise the lever and piston as high as possible, and then close the valve. Keep the lever held up so that the piston does not move down the cylinder yet. Also, check that *both* of the bottom valves are closed. Wait for a lab assistant to demonstrate the proper experimental technique.
2. While on the PVT-time graph, press the Record button.
3. Lower the lever and piston quickly and smoothly until stopped by the lower pin. Do not be so forceful that the lever and pin bang together with a hard impact however the compression stroke should take ~ 0.5 seconds.
4. Press the Stop button.
5. Observe the graphs, checking the curves for smoothness without any extreme discontinuities. If there are spikes or data dropouts, delete the trial and collect it again.
6. Now go to the Pressure graph tab. At the top of the graph are icons that activate different features on the graph. Click on the down arrow next to the triangle icon that represents data controls △▾ ; next click on Run #1. Do the same for each of the other tabs (Volume, Temperature, Work from P V graph, and ratio of Heat Capacities).
7. Click on the Pressure graph tab. Click on the statistics icon and the down arrow next to the icon Σ▾ ; if they are not already selected, select Maximum and Minimum from the drop-down menu. Document the Maximum and Minimum pressure in Table 1.
8. Next, go to the Volume graph tab. Click on the statistics icon and the down arrow next to the icon Σ▾ ; if they are not already selected, select Maximum and Minimum from the drop-down menu. Document the Maximum and Minimum volume in Table 1.
9. Next, go to the Temperature graph tab. Click on the statistics icon and the down arrow next to the icon Σ▾ ; if they are not already selected, select Maximum and Minimum from the drop-down menu. Document the Maximum and Minimum temperature in Table 1.
10. The fifth tab is labeled “Work from P V graph”; go to it to display the graph of Pressure as a function of Volume. Click on the area icon ▲ , which will highlight and display the area under the curve. Document this area in Table 2 as the Work from the Pressure Volume Graph.

11. Finally, go to the tab labeled ratio of Heat Capacities to display the graph, log of Pressure as a function of log of Volume. Click on the curve-fit icon and the down arrow next to the icon ; select Linear as the fit from the drop down menu. Next click on the icon for highlight range of data ; move and resize the highlight box to enclose a region of data representing the first third of the compression stroke, which is the last third of the graph. This would start when the pressure was the smallest and the volume was the greatest. Document the value of the slope in Table 3.
12. Repeat steps 1 thru 11 two more times. Keep data from only the three trials that show smooth curves on the graphs and delete any trials that show data collection errors.

**Part II:**

1. Open one of the valves at the bottom, raise the lever and piston as high as possible, and then close the valve. Keep the lever held up so that the piston does not move down the cylinder yet. Again, check that *both* of the valves are closed.
2. While on the PVT-time graph, press the Record button.
3. Wait 5 seconds and then lower the lever and piston quickly and smoothly until stopped by the pin, the lowering should take just under 1 second. Do not be so forceful that the lever and pin bang together with a hard impact. Continue to hold the lever down for 8 seconds then raise the lever to the top pin and hold. The raising stroke should also be quick and smooth also taking just under one second. Continue to hold the lever up at the top for eight seconds.
4. Press the Stop button.
5. Observe the graphs, checking the curves for smoothness without any extreme discontinuities. If there are spikes or data dropouts, delete the trial and collect it again.
6. Go to the Volume graph tab. Click on the down arrow next to the triangle icon that represents data controls , and then select the Run. Do the same for each of the other tabs (Volume, Temperature, Work from P V graph, and ratio of Heat Capacities).
7. Go to the Volume graph tab. Click on the statistics icon and the down arrow next to the icon ; if they are not already selected, select Maximum and Minimum from the drop-down menu. Document the Maximum and Minimum volume in Table 5.
8. Next, go to the tab labeled Work from P V graph. Click on the area icon , which will highlight and display the area inside the curve. Notice that this is the classic P-V diagram of the Otto cycle shown in the background section. This area represents the difference between the work done on the system and the work done by the system. Document the value of the area inside the curve in Table 4.
9. To determine only the work on the system, the data collected during the initial down stroke needs to be isolated. First click on the x-axis label “Volume”, and a small menu will appear. Find in the list “Time (s)”, and click on it to change the x-axis to displaying the time. Now the graph is Pressure as a function of time. The data collected from the beginning until the peak pressure is the data needed, and the data after the peak pressure needs to be excluded. Click on the highlight icon , move and size the box to enclose all of the data on the graph from after the peak pressure thru the end of the graph. Next click on the icon and

select exclude highlighted data. The excluded data will change color to black. After the excluded data has been set, delete the highlighter box by right clicking on the box and selecting delete highlighter. Again, click on the x-axis label “Time”, locate “Volume” in the list and click on it to return the graph to Pressure as a function of Volume. If the area is not still displayed, then click on the area icon. Document in Table 4 the value of this area for the work on the system. Finally click on the icon again and select restore all excluded data for active data sets.

10. Repeat steps 1 thru 9 two more times. Keep data from only the three trials that display data without collection errors.

## Analysis:

### Part I:

1. Calculate the Work from the Pressure Volume graph in units of Joules. Note this is only a unit conversion from (kPa $m^3$) to (J). Document this in Table 2.
2. Calculate the density of air using equation (2). The NIST data table provides all of the information needed to determine the molar mass of air and ideal the gas constant. The initial temperature and the initial pressure are from the measurements in Table 1. Document the density in Table 2.
3. Calculate the number of moles initially in the cylinder using equation (3). Document the number of moles in Table 2.
4. Calculate the change in temperature using the measurements in Table 1. Document this in Table 2.
5. Calculate the change in the Internal Energy of the air using equation (9). Document this in Table 2.
6. Compare the change in the Internal Energy to the Work from the Pressure Volume graph.
7. Calculate the molar heat capacity of air at constant volume and document in Table 3.
8. Calculate the molar heat capacity of air at constant pressure and document in Table 3.
9. Calculate the expected ratio of heat capacities for air using equation (13) and document in Table 3.
10. Compare the ratio determined from the graph to the ratio calculated from the molar heat capacities.

### Part II:

1. Calculate the efficiency of the Otto cycle using equation (15) and the data collected from the Pressure Volume graphs in Table 4. Document the efficiency in Table 4.
2. Calculate the compression ratio for the cylinder, ($V_{max}/V_{min}$) using the Volume data in Table 5. Document the compression ratio in Table 5.
3. Calculate the ideal efficiency of the Otto cycle using equation (17). Use the average expected ratio of heat capacities calculated in Table 3. Document the efficiency in Table 5.
4. Compare the efficiencies determined from the Pressure Volume graphs to the efficiencies determined with the compression ratio and ratio of heat capacities.

# Experiment T17a: Introduction to Thermodynamics

Student Name________________________________________

*Lab Partner Name*________________________________________

*Lab Partner Name*________________________________________

Physics Course________________________________________

Physics Professor______________________________________

Experiment Start Date__________________________________

| *Lab Assistant Name* | *Date* | *Time In* | *Time Out* |
|---|---|---|---|
| | | | |
| | | | |
| | | | |
| | | | |

Experiment Stamped Completed

## Data Sheet 1: T17a: Introduction to Thermodynamics

**NAME:** ____________________________ **DATE:** _________________

### Table 1: Data

| Pressure (kPa) | | Volume ($m^3$) | | Temperature (K) | |
|---|---|---|---|---|---|
| Initial minimum | Final maximum | Initial maximum | Final minimum | Initial minimum | Final maximum |
| | | | | | |
| | | | | | |
| | | | | | |

### Table 2: Internal Energy and Work

| Work from Pressure Volume graph | | Air Density | Number of moles | Temperature change | Internal Energy change |
|---|---|---|---|---|---|
| (kPa $m^3$) | (J) | (kg/$m^3$) | (mol) | (K) | (J) |
| | | | | | |
| | | | | | |
| | | | | | |

## Data Sheet 2: T17a: Introduction to Thermodynamics

**NAME:** ____________________________ **DATE:** _________________

### Table 3: Ratio of Heat Capacities

| Ratio of Heat Capacities from Slope of Graph | Air Heat Capacity at Constant Volume (J/mol K) | Air Heat Capacity at Constant Pressure (J/mol K) | Expected Ratio of Heat Capacities for Air |
|---|---|---|---|
| | | | |
| | | | |
| | | | |

### Table 4: Otto Cycle Efficiency

| Using Data from Pressure Volume Graphs | | | | |
|---|---|---|---|---|
| Work on System minus Work by System (kPa m$^3$) | Work on System minus Work by System (J) | Work on System (kPa m$^3$) | Work on System (J) | Efficiency |
| | | | | |
| | | | | |
| | | | | |

# Data Sheet 3: T17a: Introduction to Thermodynamics

**NAME:** ____________________________ **DATE:** _________________

## Table 5: Otto Cycle Efficiency

| Using Compression Ratio and Ratio of Heat Capacities | | | |
|---|---|---|---|
| Initial Volume Maximum ($m^3$) | Final Volume Minimum ($m^3$) | Compression Ratio ($V_{max}/V_{min}$) | Efficiency |
| | | | |
| | | | |
| | | | |

## Appendix

Consider a standard cup of coffee from the coffee shop; usually a small is about 8 oz., which is around 230 ml. If you were going to write an equation to explain the state of the coffee as it cooled, then you might take the approach of explaining how each molecule of coffee in the cup interacted with every other molecule in the cup. Of course, you must also include how the cup influences the process and the contribution of the surrounding air. Assuming the coffee is predominately water then you might use the volume of the cup, the density of water, the mass of one mole of water and the number of molecules per mole to determine how many molecules of water are in the cup. Roughly it would be:

$$230\ ml \times \frac{1\ gram}{1\ ml} \times \frac{1\ mole}{18\ grams} \times \frac{6.022\times10^{23}\ molecules}{1\ mole} = 7.8\times10^{24}\ molecules\ of\ water$$

That is a significant number of molecules for which to determine the interactions. If you were to considered just the air in the cup after you finished the coffee instead, then the number of molecules would still be about $5.8\times10^{21}\ molecules\ of\ air$. This isn't really any better for determining all of the interactions. This is an example of why the microscopic approach is not typically used for determining the state of a large system of particles.

The macroscopic approach doesn't attempt to examine each particle, but instead uses a few quantities that are measureable and sufficient to determine an equation of state for the system. These quantities are called thermodynamic coordinates, state variables, or sometimes thermodynamic variables. You are already familiar with most of them, such as pressure, volume, temperature, mass and density to name a few of the ones being examined in this experiment. The thermodynamic system is a region of space in which the matter under investigation is defined as a system contained by a boundary that separates it from the surrounding environment. In the coffee example, the coffee in the cup was the system, the cup was the boundary and the air around the cup was the surrounding environment. The thermodynamic variables provide the specific parameters for the equation of state for the system. Any kind of change to these variables is due to a process involving energy.

### Equation of State

One of the simpler examples of an equation of state is the one for an ideal gas. It provides a relationship between the pressure, $P$, in the system, the volume, $V$, of the system, the temperature, $T$, of the system and the number of moles, $n$, in the system. The constant of proportionality, $R$, is called the gas constant.

$$PV = nRT \qquad (1)$$

The first part of the experiment will allow direct observation of this relationship. The apparatus will keep the mass constant, so the number of moles will not change. The output from the pressure, volume and temperature sensors will be recorded graphically. You will be able to observe how the temperature and pressure change as you reduce the volume of the system.

### First Law of Thermodynamics

The first law of thermodynamics is a relationship between the work done by or on the system, the heat added or taken from the system, and the internal energy of the system.

$$dU = dQ - dW \qquad (5)$$

In this equation, $dU$ is the change in the internal energy of the system and it is only dependent upon $dQ$, the heat added or taken from the system and $dW$, the work done on the system (positive) or by the system (negative). The point of view for this equation is the system; meaning that if heat is removed from the system and work is done on the system, then the equation would be $dU = -dQ + dW$.

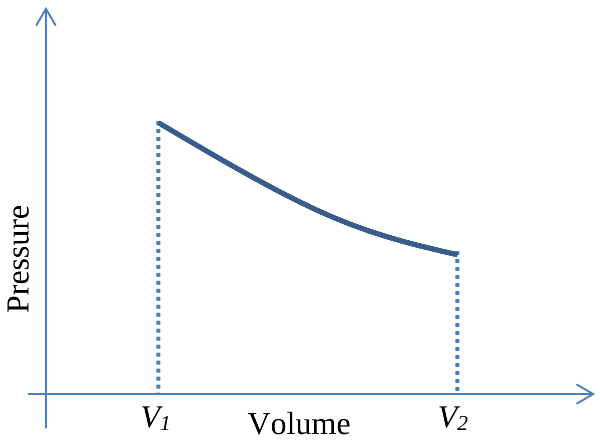

Figure 3 Work from Pressure Volume

## Work

The representation of the work done in the first law uses the thermodynamic variables.

$$dW = PdV \Rightarrow W = \int_{V_1}^{V_2} PdV \qquad (4)$$

Here $P$ is the pressure in the system and $dV$ is the change in volume of the system. Frequently this may be represented by a graph where the area under the curve gives the work. Throughout the experiment, these pressure volume graphs will be used to determine the work done by or on the system.

## Heat

Heat is another form of energy. As with several other forms of energy, there are conditions under which heat is relevant. As an example, consider the cup of coffee you brought with you in the car on your way to class. While the car was moving faster than people were walking along the sidewalk, the coffee had kinetic energy due to its motion relative to the pedestrians. But relative to you, the coffee was not moving and therefore had no kinetic energy. The kinetic energy of motion was relevant only where there was a difference in relative velocities. With heat, the condition is related to the temperature of the system verses the temperature of the surrounding environment. Heat is the amount of energy that is transferred because there is a temperature difference. When there is no temperature difference, then there is no heat. Also, if there is no energy transfer due to a temperature difference, then there is no heat. Heat is energy, but it is specifically related to the energy transferred due to a temperature differential.

The amount of energy necessary, in the form of heat, to change the temperature of a substance is not the same for all matter. Heat capacity or molar heat capacity refers to the specific amount of heat required to change the temperature of a specific material. This is not a constant for all materials; it varies for each type of material. The relationship is given by,

$$Q = nC\Delta T . \qquad (18)$$

Here $Q$ is the heat required to change the temperature by $\Delta T$, $n$ is the number of moles of the material, and $C$ is the heat capacity of the material. Even within a single material, the heat necessary to change the temperature by $\Delta T$ is different depending upon whether the pressure is held constant or the volume is held constant. At constant pressure, the heat capacity is denoted $C_P$ and at constant volume, $C_V$ denotes the heat capacity. For an ideal gas, the two heat capacities are related by the gas constant $R$.

$$R = C_P - C_V \qquad (19)$$

## Adiabatic

Any thermodynamic process that occurs with no heat transfer is called an adiabatic process. The experimental trials completed as Part I will all be adiabatic with no heat transfer. This will be achieved by completing the process quickly so that no heat transfer can occur. For the adiabatic process, the change in internal energy of the system is only dependent upon the work.

$$dU = -dW \qquad (20)$$

## Internal Energy

The internal energy of the system is dependent upon the sum of the energies of the individual particles of the system. This would include both the kinetic energy of the particles and the potential energy of interaction between the particles. The kinetic theory of gas describes the energy using pressure, volume and temperature by initially determining the average pressure due to the collisions between molecules and the walls of the container. The average velocity of the molecules, related to the root mean square velocity, is used to determine the average translational kinetic energy of a molecule. By summing these energies over all of the molecules (using the number of moles), the kinetic energy is obtained.

$$KE_{translatio} = \tfrac{3}{2} nRT \qquad (21)$$

This expression is appropriate for an ideal monoatomic gas where the motion is only translational. For a diatomic gas molecule, as will be used in the experiment, the rotational and vibrational motion must also be accounted for. The equipartition theorem from statistical mechanics provides a description of the energy contribution from each type of freedom of movement. Usually the term used is degrees of freedom and it refers to the number of different types of dimensional motion. For the diatomic molecule, there are three translational motions (x, y, z), three rotational motions, one about each of the three axes, and one vibrational motion possible.

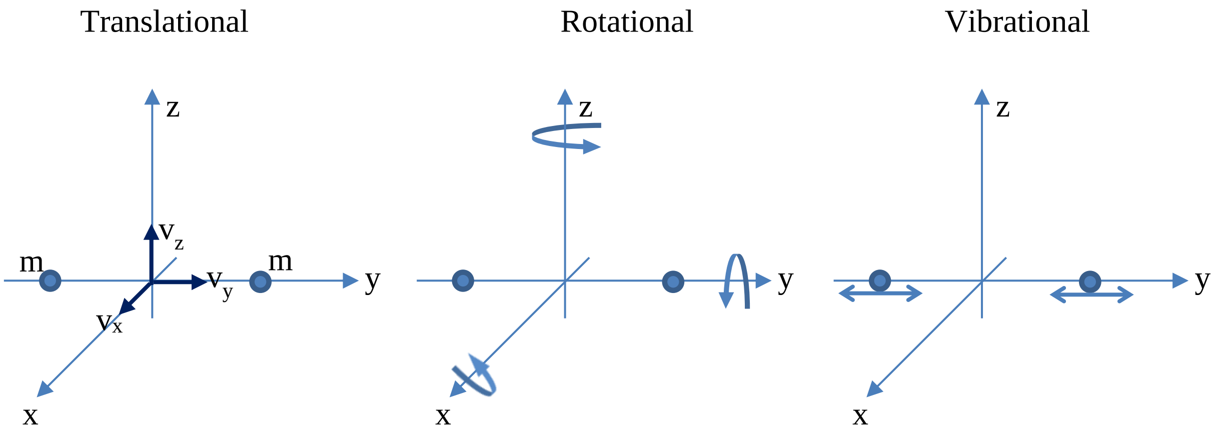

Figure 4 Degrees of Freedom

The equipartition of energy indicates that there is an equivalent amount of energy contribution for each degree of freedom for each molecule. Retaining the number of moles notation, the kinetic energy would be given by,

$$KE = f\,\tfrac{1}{2} nRT\,. \qquad (22)$$

Here *f* is the number of degrees of freedom. For the diatomic molecule, there would be seven degrees of freedom. Due to the quantum mechanical nature of individual molecules, two of these degrees of freedom have a negligible contribution affecting the kinetic energy, only 5 of the degrees of freedom contribute to the kinetic energy except at extremely high temperatures. The kinetic energy for the diatomic molecule is given by,

$$KE = \tfrac{5}{2} nRT\,. \qquad (23)$$

Therefore, the change in the internal energy would be equivalent to this change in the kinetic energy, and for the diatomic gas molecule it is given by the following expression.

$$\Delta U = \tfrac{5}{2} n\, R\, \Delta T \qquad (9)$$

This is the equation you will use to determine the change of internal energy during Part I of the experiment. The gas being used for the experiment is air, which contains a mixture of 78% nitrogen, 21% oxygen and 1% argon along with a few other trace gasses. The nitrogen and oxygen are diatomic while the argon is monoatomic. Since argon only accounts for 1% of the air, the internal energy equation for a diatomic molecule can be used. The change of temperature for the calculation will be determined from the temperature sensors connected to the apparatus. The number of moles of air in the apparatus prior to compression will need to be determined. The following relationship can be used to determine the number of moles of air.

$$n = \frac{\rho \times V_{initial}}{M_{molarmass}} \qquad (3)$$

The initial volume of air will also be determined from the volume sensor connected to the apparatus. The density of air $\rho$ will need to be determined first using the following expression.

$$\rho = \frac{M_{molarmass} P_{initial}}{R T_{initial}} \qquad (2)$$

For air, the molar mass should be replaced with the weighted average of the molar masses of the constituent gasses. The initial pressure, like the initial temperature, will be obtained from the sensors connected to the apparatus.

## Ratio of Heat Capacities

When applying the first law to a process where the volume is constant, the internal energy of the system will change due to the heat. In equation (18), heat has been related to heat capacity and the change in temperature of a material. For the case of a gas at constant volume, the quantity of heat that changes the temperature can be directly related to the change in the internal energy of the gas.

$$dQ = dU \qquad (24)$$

Using equation (16) for the heat and equation (9) for the internal energy and then simplifying.

$$nC_V \Delta T = dU$$

$$nC_V \Delta T = \tfrac{5}{2} nR\Delta T$$

$$C_V = \tfrac{5}{2} R \qquad (25)$$

The gas constant, equation (19), relates the two heat capacities for an ideal gas.

$$C_P = C_V + R$$

$$C_P = \tfrac{5}{2} R + R$$

$$C_P = \tfrac{7}{2} R \qquad (26)$$

The combination of heat capacities, besides being related by the gas constant for an ideal gas, are also related by their ratio. During Part I of the experiment, this important constant called the ratio of heat capacities, $\gamma$, will be determined.

$$\gamma = \frac{C_P}{C_V} \qquad (13)$$

Combining the two heat capacities for the diatomic molecule using equation (25) and equation (26), the ratio of heat capacities for a diatomic molecule is obtained.

$$\gamma = \frac{C_P}{C_V} = \frac{\tfrac{7}{2} R}{\tfrac{5}{2} R}$$

$$\gamma = \tfrac{7}{5} = 1.40$$

This is the theoretical value expected for the ratio assuming an ideal gas diatomic molecule. Note that since the heat capacity at constant pressure will always be greater than the heat capacity at constant volume, the ratio will always be greater than one.

The ratio will be determined experimentally from the slope of a graph created during data collection, which can then be compared to a theoretical value calculated using data from the NIST database. Since air is not exclusively composed of diatomic molecules, the value will be slightly less than this theoretical value.

To develop the expression for experimentally determining the ratio, begin with the ideal gas law, equation (1) and apply the product rule.

$$PV = nRT$$

$$PdV + VdP = nRdT \qquad (27)$$

Substitute equation (19) for $R$ into equation (27) and simplify to isolate $n\,dT$ on the right side.

$$PdV + VdP = n(C_P - C_V)dT$$

$$\frac{PdV + VdP}{C_P - C_V} = n\,dT \qquad (28)$$

Next using the First Law of Thermodynamics, equation (5), for an adiabatic process where no heat is transferred, the change in internal energy of the system is only dependent upon the work.

$$dU = dQ - dW$$

$$dQ = 0$$

$$\therefore dU = -dW$$

This is the same as equation (20). Since the internal energy can be related to the heat capacity using equation (16), and the work can be related to the change in volume using equation (4), these can be combined to form equation (29).

$$n\,C_V dT = -PdV \qquad (29)$$

Simplify this to isolate $n\,dT$ on the left side.

$$n\,dT = -\frac{PdV}{C_V} \qquad (30)$$

Now combine equation (28) with equation (30).

$$\frac{PdV + VdP}{C_P - C_V} = -\frac{PdV}{C_V}$$

Simplify and apply the product rule.

$$PdV + VdP = -\frac{(C_P - C_V)}{C_V} PdV$$

$$PdV + VdP = -\frac{C_P}{C_V} PdV + PdV$$

Again, simplify and substitute in equation (13).

$$VdP = -\gamma\,PdV$$

$$\frac{dP}{P} = -\gamma\,\frac{dV}{V}$$

Finally integrate both sides.

$$\int \frac{dP}{P} = -\gamma \int \frac{dV}{V}$$

$$\ln(P) = -\gamma \ln(V) + const. \qquad (31)$$

Solving for the constant, we also find that

$$PV^{\gamma} = \text{constant} .$$

The relationship in equation (31) is used to experimentally determine the ratio of specific heats. The natural log of Pressure is graphed as a function of the natural log of Volume. The slope is the ratio of heat capacities.

## Determining Efficiency of Otto Cycle

Please refer to Figure 2 Reverse Otto Cycle for the diagram that pertains to this derivation. From the ratio of heat capacities discussion, equation (29) related the change of internal energy to the work done on the system. If the ideal gas law, equation (1), is solved for pressure, it can be substituted into equation (29).

$$n\,C_V\,dT = -\frac{nRT}{V}dV$$

Simplifying and substituting equation (19) for *R*.

$$n\,C_V \frac{dT}{T} = -n\,R\frac{dV}{V}$$

$$C_V \frac{dT}{T} = -(C_P - C_V)\frac{dV}{V}$$

$$\frac{dT}{T} = -\frac{(C_P - C_V)}{C_V}\frac{dV}{V}$$

Again, simplifying and substituting using equation (13).

$$\frac{dT}{T} = -(\gamma - 1)\frac{dV}{V}$$

Integrate both sides from *state* (1) to *state* (2).

$$\int_{T_1}^{T_2} \frac{dT}{T} = -(\gamma - 1)\int_{V_1}^{V_2} \frac{dV}{V}$$

$$\ln\left(\frac{T_2}{T_1}\right) = -(\gamma - 1)\ln\left(\frac{V_2}{V_1}\right)$$

Next, simplify this equation to develop a relationship between the two states, using temperature and volume.

$$\ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{V_2}{V_1}\right)^{\gamma-1} = 0$$

$$\ln\left(\frac{T_2 V_2^{\gamma-1}}{T_1 V_1^{\gamma-1}}\right) = 0$$

$$\frac{T_2 V_2^{\gamma-1}}{T_1 V_1^{\gamma-1}} = 1$$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \qquad (32)$$

The volume of the cylinder at *state* (1) is the maximum volume for the cycle, and the volume at *state* (2) is the minimum volume for the cycle. The ratio between these two volumes is defined as the compression ratio, *r*, given by the following.

$$r = \frac{V_{\max}}{V_{\min}} \qquad (33)$$

Using the cycle's *state* for the cylinder at maximum and minimum in this experiment, the compression ratio would be.

$$r = \frac{V_1}{V_2}$$

Substitute this compression ratio into equation (32).

$$T_2 V_2^{\gamma-1} = T_1 \left(rV_2\right)^{\gamma-1}$$

$$T_2 = T_1 r^{\gamma-1} \qquad (34)$$

Applying this same derivation sequence to the cycle going from *state* (3) to *state* (4) will result in an equivalent expression.

$$T_3 = T_4 r^{\gamma-1} \qquad (35)$$

Note that the work done on a system in an adiabatic process changes the internal energy of the system. This means that the temperature of the system will change and is described by equation (34) given a known ratio of heat capacities and a known compression ratio.

Efficiency is the ratio of the work done by a system to the work done on the system. Efficiency is always less than one; there is always some loss of energy and no system is perfect. Thermal efficiency, *e*, is defined by a ratio of the work done by the system to the heat added into the system.

$$e = \frac{W}{Q_H} \qquad (36)$$

In this case, the work done by the system is equivalent to the difference between the heat added to the system and the heat released by the system.

$$e = \frac{Q_H - Q_C}{Q_H} \qquad (15)$$

$$e = 1 - \frac{Q_C}{Q_H}$$

Once again, equation (16) is used to describe how heat changes the internal energy resulting in a change of temperature.

$$e = 1 - \frac{nC_V \Delta T_C}{nC_V \Delta T_H}$$

$$e = 1 - \frac{\Delta T_C}{\Delta T_H} \qquad (37)$$

For the reverse Otto cycle in this experiment, the temperature change $\Delta T_H$ is the temperature difference between *state* (2) and *state* (3); similarly $\Delta T_C$ is the temperature change from *state* (4) to *state* (1).

$$e = 1 - \frac{(T_1 - T_4)}{(T_2 - T_3)}$$

Using equation (34) for the temperature at *state* (2) and equation (35) for the temperature at *state* (3), this expression can be simplified.

$$e = 1 - \frac{(T_1 - T_4)}{T_1 r^{\gamma-1} - T_4 r^{\gamma-1}}$$

$$e = 1 - \frac{(T_1 - T_4)}{r^{\gamma-1}(T_1 - T_4)}$$

$$e = 1 - \frac{1}{r^{\gamma-1}} \qquad (38)$$

This is the expression that will be used to determine the ideal efficiency for the reverse Otto cycle in the experiment. Remember that this is the ideal case, and when the experimental result is compared, it will typically be somewhat less.

The experimental value for the efficiency will be determined from the pressure volume graphs created during data collection. Essentially, equation (15) is being used to determine the experimental efficiency. When work is done on the system taking it from *state* (1) to *state* (2), the change in the internal energy which increases the temperature in the system is then allowed to cool by releasing heat $Q_H$. Assuming that these are close to equivalent, the area under the curve for the pressure volume graph created during the compression stroke provides the work done on the system. During the expansion stroke from *state* (3) to *state* (4), again the work changes the internal energy which changes the temperature, and again the system is allowed to reach equilibrium by absorbing heat $Q_C$. The difference between areas under the two pressure volume curves, the compression stroke verses the expansion stroke, gives the work done by the system, $Q_H - Q_C$.