A Survey of Thermodynamics

Objective

In this lab various topics relating to the study of thermodynamics will be explored. First, the flow of heat will be examined. Here an ice cube will be placed in a cup of water. The final temperature of the water after the ice has melted will be calculated and then measured experimentally. Next, the ideal gas law will be explored. In this part of the lab, the pressure in a syringe will be measured as the syringe is compressed. From the ideal gas law, the product of the volume and the pressure should remain constant. This theoretical result will be tested experimentally. Finally, the properties of a demonstrative heat engine will be explored. A piston will be used to lift a 100 g mass. While the mass is being lifted, the pressure and volume of the gas in the heat engine will be measured and plotted. Theoretically, the area inside the closed pressure/volume curve should equal the work done by the piston throughout the course of lifting and lowering the mass. This theoretical result will be tested experimentally in the laboratory exercise.

Equipment List

Calorimetry

Calorimeter, Thermometer, Ice Cube, Mass Scale, Water

Ideal Gas Law

Vernier Gas Pressure Sensor, Vernier LabPro Computer Interface, Syringe, Computer

Heat Engines

PASCO Heat Engine/Gas Law Apparatus, 2 Beakers, Vernier Gas Pressure Sensor, Vernier LabPro Computer Signal Interface, Computer, 100 g mass, Steam Generator, Crushed Ice, Turkey Baster

Theoretical Background

Calorimetry

In this section, the theory behind heat flow will be discussed. The study of heat flow to and from objects is known as *calorimetry*. The basic principle behind calorimetry is energy conservation: The heat energy that flows out of a collection of objects, ΔQ_{out}, is balanced by the heat energy flowing into another set of objects, ΔQ_{in}, so that the sum of the heat flowing into and out of the objects is zero

$$\begin{pmatrix} \textit{heat flow into} \\ \textit{objects} \end{pmatrix} + \begin{pmatrix} \textit{heat flow out of} \\ \textit{objects} \end{pmatrix} = \Delta Q_{in} + \Delta Q_{out} = 0. \tag{1}$$

Heat flow into objects can change the object's properties in one of two ways. First, the heat flow can cause the object's temperature to change. The relationship between the heat flow and the temperature change of the object is given by

$$\Delta Q = mc(T_f - T_i) = mc\Delta T. \tag{2}$$

In this equation, ΔQ is the amount of heat energy flowing into or out of the object. This is typically measured in either the standard units of energy, Joules, or in *calories*. (Note: The calories listed on food labels are actually kilocalories, i.e. 1000 standard calories.) The m in Equation 2 is the mass of the object the heat is flowing into or out of, and c is an intrinsic constant of the material known as the specific heat. The initial and final temperature of the object is represented by T_i and T_f, respectively, in Equation 2.

In addition to changing the temperature of an object, heat flow can change an object from one state of matter into another. There are four basic states of matter: solid, liquid, gas, and plasma. If enough heat is added to an object, the object will change from one of these states to the other. While changing state, the temperature of the object will remain more or less constant. The amount of heat necessary to change the object can be represented mathematically by

$$\Delta Q = mL. \tag{3}$$

In this equation, ΔQ is the amount of heat flow, as before, m is the mass of the object, and L is an intrinsic constant of the material. If the material is melting (i.e. changing from a solid to a liquid), then L is known as the *Latent Heat of Fusion* and is written as L_f. If the object is being vaporized (i.e. changing from a liquid to a gas), then L is known as the *Latent Heat of Vaporization* and is written an L_v. It should be noted that an object must first reach a critical temperature before it will begin melting or vaporizing (i.e. the melting point or the boiling point).

In this lab exercise, ice will be added to an amount of water. The initial temperature of the water, as well as the mass of the ice, water, and container will be measured. After the ice is placed into the water, heat will flow from the water and container into the ice, thus the ice begins to melt. Once the ice has melted, heat will continue to flow into the ice until an equilibrium temperature between the melted ice and the water/container has been reached. The heat flow into the ice can be represented mathematically as

$$\begin{aligned}\Delta Q_{in} &= \begin{pmatrix} ice \\ melting \end{pmatrix} + \begin{pmatrix} heating \\ melted\ ice \end{pmatrix} \\ &= m_I L_f + m_I c_w (T_f - T_{i,ice}) \\ &= m_I L_f + m_I c_w T_f, \qquad (T_{i,ice} = 0°C).\end{aligned} \tag{4}$$

In this equation, m_I is the mass of the ice, L_f is the Latent heat of fusion for water which is $3.33 \times 10^5\ J/kg$, c_w is the specific heat of water which is 4186 $J/(kg{\cdot}°C)$, T_f is the final temperature of the system, and $T_{i,ice}$ is the initial temperature of the ice after it has melted, which can be assumed to be $0°C$.

The heat that melts the ice and raises the temperature of the melted ice comes from the water and calorimeter. As the ice melts, and as the melted ice warms, the water and the calorimeter cool. The heat lost by the water and calorimeter is expressed mathematically as

$$\begin{aligned}\Delta Q_{out} &= \begin{pmatrix} water \\ cooling \end{pmatrix} + \begin{pmatrix} calorimeter \\ cooling \end{pmatrix} \\ &= m_w c_w (T_f - T_i) + m_c c_c (T_f - T_i).\end{aligned} \tag{5}$$

In this equation, m_w is the mass of the water in the calorimeter, m_c is the mass of the calorimeter, c_c is the Heat Capacity of the calorimeter, and the T_i is the initial temperature of the water and calorimeter.

Putting these two expressions together using Equation 1 yields

$$\begin{aligned}\Delta Q_{in} &+ \Delta Q_{out} &= 0 \\ m_I L_f + m_I c_w T_f &+ m_w c_w (T_f - T_i) + m_c c_c (T_f - T_i) &= 0.\end{aligned} \tag{6}$$

Solving this equation for the final temperature of the system, T_f yields

$$T_f = \frac{m_w c_w T_i + m_c c_c T_i - m_I L_f}{m_I c_w + m_w c_w + m_c c_c}. \tag{7}$$

This equation will be tested experimentally by using it to calculate the final temperature of the melted ice and water and then measuring it.

Ideal Gas Law

To completely describe a gas, the pressure P, volume V, and temperature T must be specified. The relationship between these parameters, known as the ideal gas law since it only holds exactly for an idealized gas, is

$$PV = NkT = nRT. \tag{8}$$

In this equation, P, V, and T are defined above, N is the number of molecules of the gas sample, and k is a constant known as Boltzmann's constant. The constant R in the above equation is known as the Gas Law constant and n is the number of moles of the gas.

If the temperature of the gas is held constant, and the number of molecules (or moles) does not change, then the product of the pressure and the volume of the gas must be constant from the ideal gas law,

$$PV = constant. \tag{9}$$

This relationship will be tested experimentally by measuring the pressure of a gas as the volume is varied.

Heat Engines

Most engines that are encountered in everyday life are heat engines. The engine in a car, for example, is a heat engine. At its most basic level, heat engines consist of a cylinder filled with a gas and a movable piston at the top of the cylinder. Figure 1 illustrates this situation.

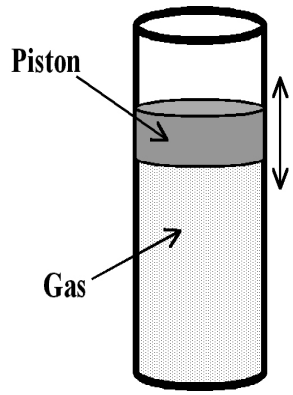

Figure 1: Simple Heat Engine

If the bottom of the cylinder is heated, the gas can respond in one of two ways: (1) it can expand and move the piston upward, or (2) the temperature of the gas can increase. The observation can be expressed mathematically as,

$$\Delta Q = W + \Delta U. \tag{10}$$

In this equation, ΔQ is the heat flow into (or out of) the cylinder, W is the work done by the gas in lifting the piston, and ΔU is known as the change in the internal energy of the gas and is related to the temperature change of the gas. This equation is known as the *First Law of Thermodynamics*, although it is really nothing more than energy conservation.

As pointed out above, when a gas is heated or cooled, it will expand or compress. These expansions or compressions can be done in a variety of ways. One type of expansion occurs when the gas is held at constant pressure. This type of expansion is known as a *isobaric* expansion. For this type of expansion, the work done by the gas is

$$W = P\Delta V = P(V_f - V_i), \tag{11}$$

where P is the constant pressure, V_f is the final volume, and V_i is the initial volume of the gas.

If the volume of the gas is held constant while the pressure and temperature are changed, then the gas is said to undergo an *isovolumetric* or *isochoric* process. Since the volume of the gas does not change, from Equation 11, the gas does no work so that $W = 0$. From the first law of thermodynamics (Equation 10), this means that

$$\Delta Q = W + \Delta U, isovolumetric \rightarrow W = 0 \Longrightarrow \Delta Q = \Delta U, \tag{12}$$

so that all of the heat flowing into or out of the cylinder only changes the temperature of the gas.

If the temperature of the gas is held constant while the pressure and volume change, then the gas undergoes an *isothermal* expansion or compression. Since the temperature of the gas does not change, the internal energy of the gas remains constant. This means that the change in the internal energy, ΔU, is zero. From the first law of thermodynamics, this means that

$$\Delta Q = W + \Delta U, isothermal \rightarrow \Delta U = 0 \Longrightarrow \Delta Q = W, \tag{13}$$

or that all of the heat flowing into or out of the gas goes directly into raising or lowering the piston.

Finally, if the cylinder is insulated so that no heat flows into or out of the gas, then the gas is said to undergo an *adiabatic* expansion or compression. Since no heat flows into or out of the gas, the heat term in the first law of thermodynamics is zero so that,

$$\Delta Q = W + \Delta U, adiabatic \rightarrow \Delta Q = 0 \Longrightarrow 0 = W + \Delta U \Rightarrow W = -\Delta U. \tag{14}$$

This means that any work done by the gas causes a change in the internal energy of the gas. If the gas expands, lifting the piston, then the gas will cool as a result. If the gas compresses, lowering the piston, then the gas will heat up. This process is used to cool the gas used in refrigerators, which in turn keeps food cool and unspoiled.

A heat engine is typically designed to undergo some combination of the processes discussed above to do work by lifting the piston in a cyclic process. If the pressure of the gas is plotted as a function of the volume of the gas in a heat engine, a closed curve is formed from this cyclic process. The enclosed area of the curve is equal to the work done in lifting the piston. Figure 2 illustrates this kind of plot.

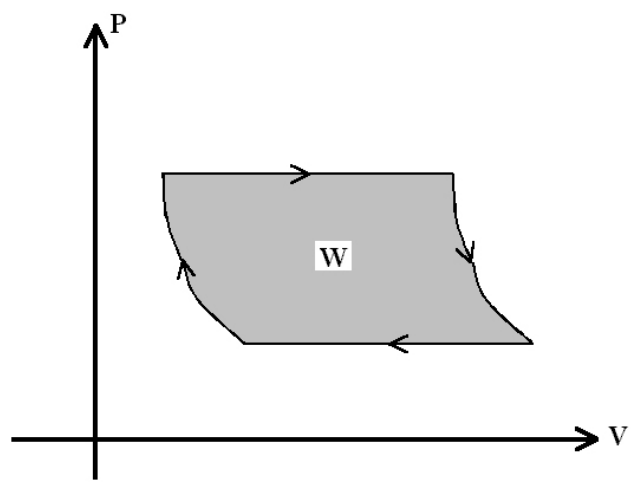

Figure 2: PV plot of a Heat Engine

In this part of the lab exercise, the pressure and volume of a heat engine at various stages (i.e. the "corners" of the closed curve) will be measured. These values will be plotted and the area inside the closed curve formed from this plot will be calculated. This area will be compared with the work done in lifting a mass with the piston,

$$W = mg(h_f - h_i). \tag{15}$$

Procedure

Using one of the beakers on the lab bench, fill the steam generator with water. Turn the steam generator on and set it to its maximum level so that the water will be heating up while the other experiments in this lab are being performed. Be sure to keep the plastic tubing away from the steam generator.

Calorimetry

In this section, the final temperature of an ice/water combination will be predicted and then measured experimentally.

1. Open the calorimeter (i.e. the large silver cup on the lab bench) and remove the inner cup from the calorimeter. Use the scale to measure the mass of the inner cup and record this mass as m_c on your data table.

2. Fill the inner cup of the calorimeter about half-full of water from the water faucet at the front of the lab room. Measure the mass of the calorimeter cup with water and record this mass as m_{c+w} on your data table.

3. Subtract the mass of the calorimeter m_c from the cup with water combination m_{c+w} to obtain the mass of the water in the cup. Record the mass of the water in the cup as m_w on your data table.

4. Place the inner cup back into the calorimeter. Remove the orange sheath from the digital thermometer and place the thermometer into the water. Turn the thermometer on. Wait for a few minutes (1 to 3 minutes) until the temperature displayed on the thermometer stabilizes. Record the temperature the thermometer stabilizes at on your data sheet as T_i.

5. Quickly remove an ice-cube from the silver tray at the front of the lab room. Place the ice-cube on the mass balance to measure its mass. Record this mass on your data table as m_I. Remove the thermometer from the water and quickly place the ice-cube into the water of the calorimeter.

6. After placing the ice-cube into the water, place the calorimeter lid along with the stirring rod back into the calorimeter, and feed the thermometer through the cork of the calorimeter. Carefully watch the temperature of the ice/water. While waiting for the temperature to stabilize, calculate the final temperature $T_{f,\,theo}$ of the water using,

$$T_{f,\,theo} = \frac{m_w c_w T_i + m_c c_c T_i - m_I L_f}{m_I c_w + m_w c_w + m_c c_c},$$

$$c_w = 4186\ J/(kg{\cdot}^\circ\mathrm{C}),\ c_c = 900\ J/(kg{\cdot}^\circ\mathrm{C}), L_f = 3.33 \times 10^5 J/kg. \tag{16}$$

7. After about one minute has elapsed, gently stir the water by moving the stirring rod up and down gently a few times. Continue watching the temperature of the ice/water until the temperature stabilizes. When the temperature has stabilized, record this temperature as $T_{f,\,exp}$ on your data sheet.

8. Calculate the percent difference between the theoretical and experimental values of the final temperature of the water.

$$\%\ difference = 100 \times \frac{Theoretical\ Value\ -\ Experimental\ \ Value}{Theoretical\ Value} \tag{17}$$

9. Estimate and record the uncertainty in the mass and the temperature measurements. Using these estimated uncertainties, and the smallest measured value for the mass and the temperature, calculate the percent uncertainty in each experimental quantity. Record the largest percent uncertainty in the space provided.

Ideal Gas Law

In this section, the ideal gas law will be tested experimentally by determining if the product of the pressure and the volume of a gas is constant for constant temperature.

1. If it is not already plugged in, plug the Vernier Gas Pressure Sensor into CH 1 of the Vernier LabPro Interface. Consult your lab instructor if necessary.

2. One end of the pressure sensor is connected to the LabPro interface. The other end may be attached to the Heat Engine/Piston. If so, unscrew the tubing connected to the valve on the end of the pressure sensor.

3. Double-left-click on the **pressure_sensor** icon on the desktop of the computer at your lab station. If you do not see a **pressure_sensor** icon, your lab instructor will need to load the program onto your computer.

4. Pull the plunger to the 20 mL mark of the syringe. Be sure black ring/line next to the the conical tip of the plunger marks the 20 mL line of the syringe. With the plunger pulled out, screw the syringe onto the valve end of the pressure sensor.

5. The LabPro unit provides live data readouts from the sensor displayed on the digital meter. Pressing buttons on the unit interrupts the data acquisition process. **Never depress any of the buttons on the Vernier LabPro Interface!!!**

6. The pressure in kPa in large **red** letters should appear in the window. If a window titled *LabPro has Data* comes up, left the the `Ignore/Erase Data in LabPro` button. Record the initial pressure and the initial volume of the gas 20 mL on your data table.

7. Compress the plunger to the 18 mL of the syringe and record this volume. Remember to measure the volume from the black ring/line next to conical tip of the plunger. For each new volume, wait a few moments until the pressure stabilizes, then record the new pressure on your data table.

8. Continue compressing the syringe in increments of 2 mL until you have pressure measurements for volumes of 20 mL, 18 mL, 16 mL, 14 mL, and 12 mL. **Do not compress the syringe past** 10 mL**!! Permanent damage to the sensor will result!! Maximum pressure the sensor can withstand without damage is** 210 kPa

9. Estimate and record the uncertainty of the pressure measured in kPa and volume measured in mL. Determine the smallest measured value for each quantity; pressure measurements and volume measurements. Calculate the percent uncertainty for each experimental quantity. Record the largest percent uncertainty in the space provided.

Heat Engines

In this section, the pressure and temperature of a gas in a metal cylinder attached to a heat engine will be varied. These variations will cause the volume of the gas in the heat engine to change. The pressure of the gas in the heat engine and the height of the piston in the heat engine will be measured. The volume of the gas in the heat engine will be calculated using the height of the piston. A graph will be constructed of the pressure as a function of volume. Determination of the work done by the gas on a 100 g mass will be calculated by analyzing the plot. This work will be compared with the change in the potential energy of the mass, $mg(h_f - h_i)$.

1. Unscrew the syringe from the pressure sensor. Consult your lab instructor if necessary.

2. Raise the piston on the heat engine to 50 mm. Measurements are performed from the bottom plate of the piston. You may wish to use the locking screw to lock the piston in place. Later you will be instructed to unlock the piston. **Do not use the locking screw to hold the piston in place while taking data!!!**

3. Open the **pressure_sensor** program from your desktop if it is not currently open. The pressure in kPa in large **red** letters should appear in the window. If a window titled *LabPro has Data* comes up, left the the `Ignore/Erase Data in LabPro` button.As a reminder, pressing buttons on the unit interrupts the data acquisition process. **Never depress any of the buttons on the Vernier LabPro Interface!!!**

4. Inspect the equipment at your station. Attached to the PASCO Heat Engine are two plastic tubes. One tube leads to a sealed aluminum tube. Screw in the other tube from the heat engine into the Vernier gas pressure sensor.

5. Fill a 600 mL beaker with ice. Crushed ice may be obtained from your lab instructor.

6. Use the Turkey Baster to siphon hot water from the steam generator to the other empty 600 mL beaker. Refill the steam generator after siphoning off the hot water **Caution: If not handled with care boiling water may spill out of the turkey baster. If the water spills on you it will cause first degree burns resulting in redness, mild pain and/or swelling of the outer skin layer. For the sake of yourself and others use the turkey baster with care!** Fill the beaker half full of water. Place this beaker next to the ice-filled beaker.

7. Unlock the piston if it was locked in place. Place the aluminum cylinder into the ice bath. As the gas in the aluminum cylinder cools and the gas compresses, the piston will fall.

8. Allow the pressure to stabilize. Record the pressure P $[kPa]$ and the height of the piston h $[mm]$ in the row marked **A** of your data table.

9. Place 100 g on top of the platform attached to the piston. The additional mass will compress the gas. Allow the pressure to stabilize. Record the pressure and height along row **B** of your data table.

10. Place the aluminum cylinder in the hot water beaker. The heat given off by the hot water heats the gas. As the gas expands the piston rises. Allow the pressure to stabilize. Record the pressure and height along row **C** of your data table. **Do not delay. Record pressure and volume values as soon as the pressure has stabilized. The metal cylinder will begin to leak gas. As this happens the piston begins to fall instead of maintaining it's maximum height.**

11. Remove the 100 g mass from the platform. This will reduce the pressure on the gas cause the gas to expand. Allow the pressure to stabilize. Record the pressure and height along row **D** of your data table.

12. Place the aluminum cylinder in the ice bath. Allow the pressure to stabilize. Record the pressure and height along row **E** of your data table.

13. Estimate and record the uncertainty of the pressure measured in kPa and height measured in mm. Determine the smallest measured value for each quantity; pressure measurements and volume measurements. Calculate the percent uncertainty for each experimental quantity. Record the largest percent uncertainty in the space provided.

Data Analysis

Ideal Gas Law

1. Convert each of the volume measurements from milliliters (mL) to cubic meters. The conversion factor is $1\ mL = 10^{-6}\ m^3$.

2. Calculate the inverse of the volume $(1/V)$ in order to graph the pressure as a function of the inverse volume.

3. Calculate the product of the pressure and the volume for each trial. Calculate the percent variation for this set of products.

4. **Plot** the pressure of the gas in the syringe as a function of the inverse volume $(1/V)$. Draw the straight line that comes closest the these data points.

Heat Engines

1. Calculate the volume of the gas in the heat engine using the height of the piston h, the diameter of the piston $D = 32.5\ mm$ and

$$V = \frac{1}{4}\pi D^2 h. \tag{18}$$

   Be sure to convert the height and diameter to meters before calculating the volume.

2. **Plot** the pressure, in Pascals, as a function of the volume of the gas in the heat engine. Do not start the volume or the pressure axis at zero; instead, choose a convenient zero so that the points are widely distributed over the page. Connect each of these points in the following fashion: (V_A, P_A) to (V_B, P_B) to (V_C, P_C) to (V_D, P_D). In theory, the starting point (V_A, P_A) and the ending point (V_E, P_E) should be the same. Experimentally they are not because of gas leaking from the metal cylinder.

3. From the PV plot, calculate the enclosed area of the figure. This is done by counting the number of small squares inside the figure, then multiplying this number by the dimensions of each square. To simplify the process, you might want to count the number of large blocks inside the figure first, then multiply this by 25 since each large block is composed of 25 smaller blocks. This area, multiplied by the dimension of each of the small blocks should equal the work done in lifting the 100 g mass.

4. Calculate the work done lifting the mass using the change in the potential energy

$$-W = \Delta P = mg\Delta h = mg(h_C - h_B), \tag{19}$$

   where m is the mass lifted by the piston (100 g), g is the acceleration of gravity (9.8 m/s^2), h_C is the final height of the mass along row C in the data table, and h_B is the initial height of the mass along row B in the data table.

5. Calculate the percent difference between the two values for the work done lifting the mass.

Selected Questions

Calorimetry

1. In the heat balance equation, heat flow from the thermometer and from the stirring rod was ignored. How would this affect your prediction of the water's final temperature (i.e. would it be higher, lower, or not change)? Is this effect consistent with your data?

2. Suppose that the inner cup of the calorimeter got cold enough so that moisture from the air began to condense on the outer surface. How would this affect the final temperature?

Ideal Gas Law

How close were the data points to the line drawn on the P as a function of $1/V$ graph? What should the slope and the y-intercept of the graph be based on the theoretical prediction? (Hint: Solve for the slope of the line algebraically; do not attempt to calculate a numerical value.)

Heat Engines

Identify what kind of expansion/compression (isobaric, isothermal, isovolumetric, adiabatic) each side of the figure on the PV graph was:

$(V_A, P_A) \rightarrow (V_B, P_B)$:

$(V_B, P_B) \rightarrow (V_C, P_C)$:

$(V_C, P_C) \rightarrow (V_D, P_D)$:

$(V_D, P_D) \rightarrow (V_A, P_A)$:

Explain your choices.

(Hint: Consider what was changing, and what was not changing, as the piston moved. Also determine if the gas expanded or compressed during the thermodynamics processes.)