Name ______________________________ Section ____________ Date ____________

# UNIT 17: THE FIRST LAW OF THERMODYNAMICS

*Objects can only start rising in the atmosphere if there is an upward force on them that is greater that the gravitational force pulling them downward. They must be lighter than air. Each of these balloons has a burner under it to heat air that fills it. Why is hot air at atmospheric pressure lighter than cold air? How will the mass of the air in a full balloon vary with temperature? How much thermal energy must be transferred to a given balloon before it will lift off? In this unit you will learn how to describe the behavior of a gas mathematically when energy is transferred to it and why it becomes lighter.*

## 17.1. OVERVIEW

In the last unit you explored situations in which two substances in thermal contact changed their temperatures without exchanging matter. We attributed these temperature changes to an exchange of thermal energy. But what is this thermal energy exchange that causes a substance of warm up or cool down? In this unit we will develop the concept that all substances store hidden internal energy in their atoms or molecules. We will use this concept of internal energy to explain how thermal energy transfer works and other phenomena that you have not yet explored.

In Section 17.3 you will observe that when $H_2O$ is changing phase (from ice to water or from water to steam) you can transfer thermal energy to a substance without changing its temperature. We will then use the concept of internal energy to explain both why temperatures don't change in phase transitions and why they do change in other circumstances.

In Section 17.4 you will investigate how thermal energy transfer can cause air, which is a gas, to expand and do mechanical work on its surroundings by raising a piston. This is a situation in which the energy transferred to the system is not all stored internally. Some of it is transformed into work.

Then in Section 17.6 you will use the principle of conservation of energy to formulate the first law of thermodynamics. A belief in this law allows us to calculate how much the internal energy stored in a system is increased when work is done on it *or* thermal energy is transferred to it. An understanding of the first law of thermodynamics is important in practical endeavors such as the design of heat engines. It is also used in fundamental scientific research.

In Sections 17.7 through 17.9 you will investigate what happens to air at about room temperature when thermal energy is transferred to it and when it is compressed or expanded. Although we could never hope to follow the motion of each and every particle in a gas, you will learn about certain macroscopic properties of a gas that can be easily measured in our laboratory. These *macroscopic* properties are temperature, pressure, and volume and the mathematical relationship between these properties that you will discover is known as the ideal gas law.

Finally, in Sections 17.10 through 17.12, you will use Newton's laws to explain how macroscopic quantities might be connected to the forces, velocities, and momenta of the billions upon billions of particles we believe are contained in gases whose internal energy is only accounted for by the kinetic energy of its atoms and molecules. Thus, you will construct an idealized *microscopic* picture of a gas and explain the ideal gas laws in terms of the motion of the gas molecules.

# INTERNAL ENERGY, WORK, AND THERMAL ENERGY

## 17.2. THERMAL ENERGY TRANSFER WITHOUT TEMPERATURE CHANGE

As part of our quest to understand more about thermal energy transfer and the internal energy of a substance, let's look at the question of whether energy transfer can take place without a temperature change occurring. Just in case you haven't memorized this yet, let's return to the principle of thermal energy transfer we developed in the last unit:

> Thermal energy exchange takes place between two systems in thermal contact when there is a temperature difference between them.

Heat, or caloric as it was called in the old days, used to be thought of as a substance. Even today the term heat is often used casually in a way that implies that it is a substance. Even though scientists now use the term heat as a shorthand term for a thermal energy transfer process rather than a substance, we will continue to use the term thermal energy transfer to remind you that the transfer of energy from one system to another does not necessarily involve the exchange of matter.

Let's return to the question at hand. Is it possible for a system to absorb thermal energy without changing temperature?

### 17.2.1. Activity: Thermal Energy Absorption Without Temperature Change?

**a.** From your experiences with the warming and cooling of different substances, can you think of any situations in which a system has been in thermal contact with something at a higher temperature and not changed its temperature?

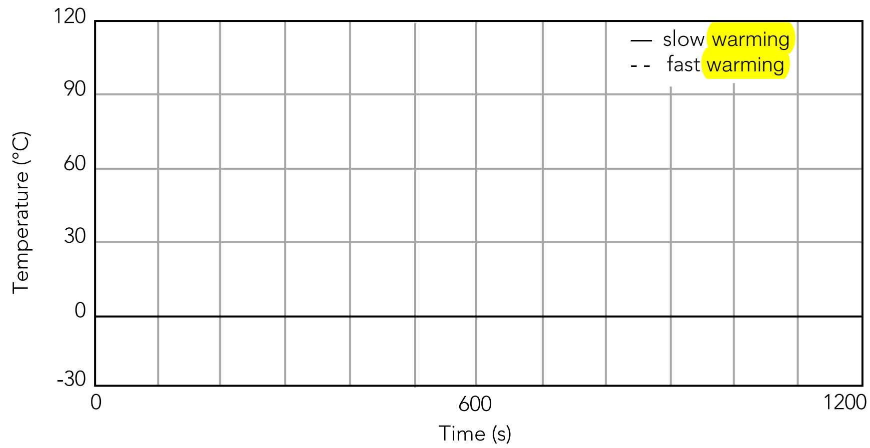
**b.** For the examples you have picked, can you think of any internal changes going on in the system that could help explain the lack of temperature rise?

## 17.3. CHANGING ICE TO WATER AND THEN TO STEAM

Melting ice and boiling water were probably examples that came up in your discussions about substances that can absorb thermal energy without changing temperature. Let's make some predictions about melting and boiling.

**17.3.1. Activity: Predicting *T* vs. *t* for Water**

**a.** Suppose you added energy thermally at a constant rate to a container of water at 0°C (with no ice in it) for 20 minutes at a low enough rate that the water almost reaches its boiling point. Sketch the predicted shape of the warming "curve" on the following graph.




**b.** Suppose that the container had a mixture of ice and water at 0°C when you started warming it at a faster rate and that the water starts boiling after five minutes (300 seconds). You keep adding energy at the same rate for five more minutes. Draw a dotted line on the preceding graph showing your prediction.

### Determining Heats of Fusion and Vaporization

Let's observe what actually happens to temperatures when thermal energy is transferred to a mixture of ice and water at a continuous rate. By transferring a known amount of energy to a mixture that is originally half water and half ice, we can also determine the amount of thermal energy needed to melt a gram of ice. This energy is known as the *latent heat of fusion*. You can also determine the amount of energy needed to turn a gram of boiling water into steam. This energy is known as the *latent heat of vaporization*. It is often measured in joules per gram. For this activity you will need:

- 1 computer data acquisition system
- 1 temperature sensor (calibrated)
- 1 heat pulser
- 1 immersion heater, approximately 200 W
- 1 Styrofoam cup, 300 ml
- 1 electronic balance (or 200 ml graduated cylinder)
- 2 containers, approximately 250 ml (for crushed ice and water at 0°C)
- crushed ice
- paper towels (to dry the ice)

| Recommended Group Size: | 2 | Interactive Demo OK?: | N |
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**Note:** If needed, you should calibrate the temperature sensor using hot and cold water before you begin this experiment.

Set up the temperature sensing software to take temperature vs. time data for 20 minutes while the heat pulser is enabled (or use the experiment file L170302). You do not necessarily have to run the experiment for the full 20 minutes. You should continue transferring thermal energy to the system until all the ice is melted and then keep going until the water reaches the boiling point and boils for 5 minutes or so.

The experiment will go faster if you keep the heat pulser on constantly.

**WARNING!** Do not turn on the heat pulser unless the immersion heater is completely covered by the water! Leave the pulser and coil unplugged until you are ready to start.

You should stir continuously during the experiment and keep the heating coil immersed at all times.

Before beginning your experiment, you need to consider the following:

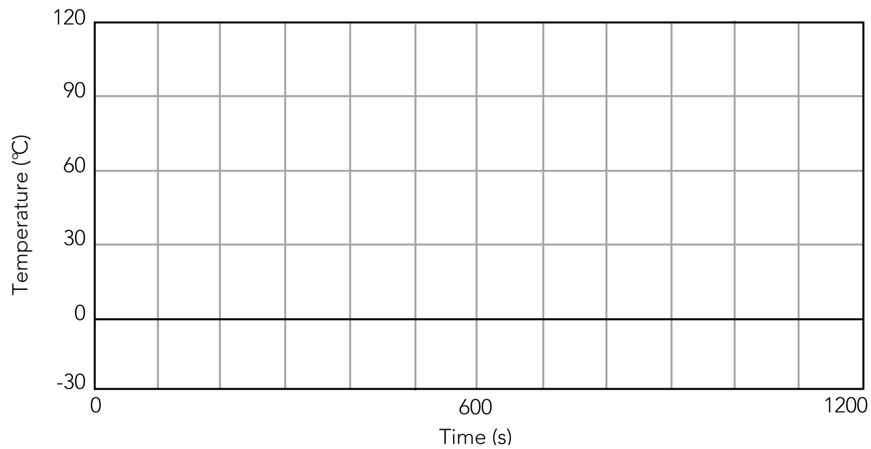
1. Too little water mixed with ice will leave the coil uncovered. Too much water/ice mixture will take a long time to warm up.
2. How can you remove as much water as possible from the crushed ice before mixing it with the ice water? (Paper towels help.)
3. How can you chill the water so it is 0°C before the dry crushed ice is mixed with it?
4. How can you create a mixture of ice water and crushed ice with roughly equal masses of each?
5. In order to calculate the latent heats of fusion and vaporization you must determine the rate at which your immersion heater transfers thermal energy to water. How can you use the specific heat of water, which is 4190 J/kg·C, and the time it takes the melted ice and water to boil to calculate the J/s delivered by the heater?
6. Once you determine the immersion heater output in J/s,
   (a) how can you calculate how many joules of energy you added to the ice and water mixture during the time the ice was melting?
   (b) How can you measure how many grams of water changed to steam during the time the water was boiling?

**Note:** After your group has devised a plan for doing the experiment and figured out what measurements you will need to take, *you should review your plans with your instructor before starting to take data*.

### 17.3.2. Activity: The Actual *T* vs. *t* for Water

**a.** What was the initial mass of the ice in grams? What will the final mass of the water be after all the ice has melted?

**b.** In the following diagram, sketch or affix the graph that resulted from transferring thermal energy (in other words, "heating") at a constant rate to the approximately 50/50 ice and water mixture for about 15 or 20 minutes (until the original water–ice mixture heated to boiling and then boiled for about five minutes).




**c.** Analyze your graph from the time the ice has melted until the water just starts to boil. Use your knowledge of the mass of the melted ice and water mixture along with the known value for the specific heat of water to calculate how many joules per second are delivered by the immersion heater.

**d.** How long did it take the ice to melt? Use your result from part c. to calculate how much energy in joules was added by the heat pulser while the ice was melting.

**e.** Remembering how many grams of ice you started with, calculate $L_f$, the latent heat of fusion of water. In other words, how many joules per gram are needed to melt ice? Show your steps.

$$L_f = \_\_\_\_\_\_ \text{ J / g}$$

**f.** How many minutes did you allow the water to boil before you stopped the experiment? How many grams of water turned to steam in that time? How much thermal energy was transferred to the water in that time?

**g.** What is the value of the Latent Heat of Vaporization? Show your calculations!

$L_v$ = ______ J / g

**h.** Compare the values of the latent heats of fusion and vaporization to the accepted values stated in your textbook or a handbook. What percent discrepancy is there in each case?

| | Experimental | Accepted | Percent discrepancy |
|---|---|---|---|
| Latent heat of fusion ($L_f$) [J/g] | | | |
| Latent heat of vaporization($L_v$) [J/g] | | | |

**j.** Are your values higher or lower than the accepted values in each case? Can you think of any sources of systematic error to explain this?

### Internal Energy

Fig. 17.1.

If you lift an object or compress a spring, it is obvious that a conservative system gains an amount of potential energy, usually denoted $\Delta U$. Is the concept of "potential energy" useful in discussing what happens if work is done on a system such as gas confined in a syringe where there is no apparent change in potential energy? The answer is yes, but we have to give a new meaning to our potential energy. In thermodynamics, it is called a change in the *internal energy* of a system, $\Delta E^{\text{int}}$. Internal energy is defined as the invisible microscopic energy stored in a system. In complex systems, this microscopic energy can consist of both kinetic energy (due to the translational, vibrational, and rotational motions of atoms and molecules) and potential energy (such as that stored in chemical bonds).

### States of Matter

Most substances can exist in three states—solid, liquid, and gas. Some gases, such as helium, become liquid only at extremely low temperatures and some solids, such as a diamond, are very hard to melt. Usually, these *changes of state* or *phase changes* require a transfer of thermal energy. During a phase change, the substance can absorb thermal energy (or transfer thermal energy to its surroundings) without changing the temperature of the substance until the phase change is complete. The standard explanation for this is that the thermal energy transferred to a system is used to raise its potential energy and breaks the interatomic or intermolecular bonds that characterize a phase. But once a phase change has taken place, additional thermal energy is used to increase the kinetic energy of atoms and molecules in the system if we associate an increase in the system's hidden kinetic energy with its temperature.

## 17.4. WORK DONE BY AN EXPANDING GAS

One system we will meet often in our study of thermodynamics is a mass of gas confined in a cylinder with a movable plunger or piston. The use of a gas-filled cylinder to study thermodynamics is not surprising since the development of thermodynamics in the eighteenth and nineteenth centuries was closely tied to the development of the steam engine, which employed hot steam confined in just such a cylinder.

You are to observe the relationship between expansion and compression of a gas and work done on or by the gas. To do this you will need the following:

- 1 glass syringe, 10 cc
- 1 length Tygon® tubing, 5 cm (1/8" ID)
- 1 tubing clamp

| | | | |
|---|---|---|---|
| Recommended Group Size: | 2 | Interactive Demo OK?: | N |

Raise the syringe plunger about halfway up and insert the short tube and clamp at the end of the syringe to seal it.

Try compressing the air in the syringe gently. Do you have to do work on the gas to compress it? What happens when the plunger springs back?

In thermodynamics, pressure (defined as the component of force that is perpendicular to a given surface per unit area of that surface) is often a more useful quantity than force alone. It can be represented by the equation:

$$P = \frac{F_\perp}{A}$$

Let's extend our definition of work developed earlier in the course and this new definition of pressure to see if we can calculate the work done by a gas on its surroundings as it expands out against the piston with a (possibly changing) pressure $P$.*

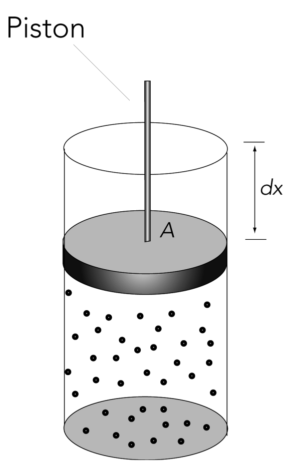



**Fig. 17.2.** Gas at pressure $P$ exerts a force on the piston $F = PA$ as it moves a distance $dx$.

### 17.4.1. Activity: Relating Work and Pressure Mathematically

**a.** Are you doing work when you compress the gas in a syringe?

**b.** You know that work can be written as $W = \int F dx$, where $F$ represents the force you exert on the syringe plunger. Show the mathematical steps to verify that work can be written as $W = \int P dV$ for the situation shown in Figure 17.2.

## 17.5. WORK AND THERMAL ENERGY TRANSFER

As you observed in the last activity, you can do work and compress a gas. But then where did the gas get the energy to do work on the piston? It must have come from an increase in the internal energy you gave it when you did work on it. So, when the compressed gas is allowed to expand, it can do physical work on

* We use capital $P$ to represent pressure to distinguish it from momentum, which is represented by small $p$.

its surroundings by raising a piston. One way to increase the internal energy of a system is to do work on it. Suppose that instead of doing work on a system, you transfer thermal energy to it?

### Thermal Energy Transfer and Work on Surroundings

Let's consider a system consisting of just the air inside a syringe, tube, and flask that are connected to each other. Transferring thermal energy to the system could serve to increase its internal energy. Alternatively, it could cause a system to do work on its surroundings and leave its internal energy unchanged. In thermodynamics we are interested in the relationship between thermal energy transfer to a system's internal energy and work done by the system on its surroundings. What do you think would happen if you attach a cylinder with a low-friction movable piston (or plunger) to a small flask and place the flask in hot water? Would its piston experience a force? Can the air in the system do work on the plunger? For this activity you will need:

- 1 glass syringe, 10 cc*
- 1 test tube clamp
- 1 rod
- 1 rod stand (or table clamp)
- 1 Erlenmeyer flask, 125 ml
- 1 #5 one-hole rubber stopper
- 1 length Tygon® tubing, 30 cm (1/8″ ID)
- 1 coffee mug (for hot tap water)
- 1 tray (to prevent spilling)

| Recommended Group Size: | 2 | Interactive Demo OK?: | N |
|---|---|---|---|

### 17.5.1. Activity: The Heated Syringe

**a.** Predict what happens to a plunger (piston) if a flask attached to it is put into hot tap water that is about 40-50° C as shown in Fig. 17.3.

**b.** Now try it! Clamp a syringe and attach it to the flask with its plunger partway down. *While holding the plunger fixed,* submerge the flask in hot tap water. Explain what might be happening to the gas while you hold the plunger to keep the gas volume constant? Could its internal energy be changing? Explain.

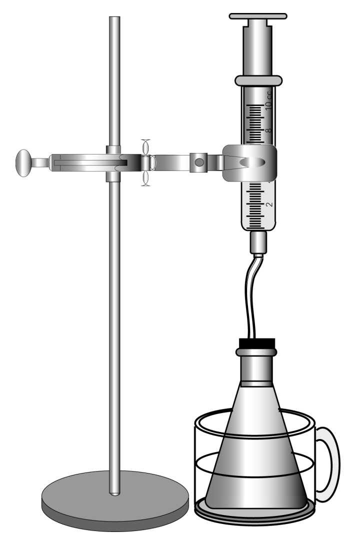


**Fig. 17.3.** Setup to transfer thermal energy to air in a syringe with a *low friction* plunger (or piston) in it.

**c.** After a minute or so, release the plunger and let it move freely. What happens? Is this what you predicted would happen in part a. above?

**d.** Is the system doing work on its surroundings? Why or why not?

* This can be done as a demonstration using the PASCO scientific Heat Engine/Gas Law Apparatus (TD-8572).

## 17.6. THE FIRST LAW OF THERMODYNAMICS

What is the relationship between thermal energy transfer, changes in the system's internal energy, and the work done by (or on) the system? We denote $E^{\text{int}}$ as the total hidden internal energy in the system. To help us understand how $E^{\text{int}}$ is related to work and thermal energy, we will consider the gas confined in a syringe and flask in Activity 17.5.1 to be our system and the flask of water as its surroundings. For simplicity, we will neglect the flask and syringe and assume that thermal energy transfer is just between the system's air and the water surrounding the flask.

Suppose the plunger on the syringe is clamped while the flask attached to it is immersed in hot water. The clamped plunger can't move, so no work is done. Since the water is at a higher temperature than the system air, thermal energy is transferred from the water to the air. This causes the temperature of the water to decrease and the temperature of the air trapped in the syringe and flask to increase. If energy is conserved, the thermal energy transferred to the air can be calculated using the equation $Q = c_w m_w \Delta T$ where $m_w$ is the mass of the water, $c_w$ is its specific heat, and $\Delta T$ is the temperature change of the water.

Assume that no thermal energy can be transferred to the surroundings. Then if no work is done on or by the system, the transferred thermal energy, $Q$, must equal the *increase* in the internal energy of the system air. This assumption is based on a *belief* that energy is conserved in the interaction between the hot water and the trapped air.

Suppose we release the plunger and allow the air to expand and do work on the plunger when the flask is placed in the hot water. How can we calculate the work done by the air and its change in internal energy?

As the trapped air expands we can calculate the amount of work it did on its surroundings by evaluating the integral you derived in Activity 17.4.1b, $W = \int P\,dV$. Where did the energy to do this work come from? The only possible source is the internal energy of the air, which must have decreased by an amount $W$. The total change in the internal energy of our trapped air must be

$$\Delta E^{\text{int}} = Q - W \qquad (W = \text{work } by \text{ system}) \tag{17.1}$$

This relationship between absorbed thermal energy, work done on surroundings, and internal energy change is believed to hold for any system, not just for air trapped in a syringe and a flask. It is known as the *first law of thermodynamics*.

The first law of thermodynamics has been developed by physicists based on a set of very powerful inferences about energy forms and their transformations. We ask you to accept it on faith. The concepts of work, thermal energy transfer, and internal energy are subtle and complex. For example, work is not simply the motion of the center of mass of a rigid object or the movement of a person in the context of the first law. Instead, we have to learn to draw system boundaries and total the mechanical work done by the system inside a boundary on its external surroundings.

The first law of thermodynamics is a very general statement of conservation of energy for thermal systems. It is not easy to verify it in an introductory physics laboratory, and it is not derivable from Newton's laws. Instead, it is an independent assertion about the nature of the physical world based on a belief that energy in the universe is conserved.