

Chapter 6: Entropy and the Laws of Thermodynamics

Goals of Period 6

Section 6.1: To define order, disorder, and entropy

Section 6.2: To discuss equilibrium, entropy and the second law of thermodynamics

Section 6.3: To examine irreversible processes and perpetual motion

In Chapter 6 we will discuss one of the most intriguing concepts in physics – entropy. Entropy is related to the order and disorder of a system. It is sometimes called the arrow of time because time only goes in one direction. We become older, not younger. This is true for the Universe, as well. This is what entropy is.

We will then discuss the second law of thermodynamics. We will find that there are several statements of the second law. All are correct, but they state the same ideas in different ways. We will find that the concept of entropy is critical to our understanding of the second law of thermodynamics.

6.1 Order, Disorder, and Entropy

We now have a better understanding of the energy due to microscopic motion of molecules. This motion is called internal energy. However, there are still features of such motion that our discussions thus far have not considered. For example, it is our common experience that hot objects and cold objects sitting in a room will eventually come to a common temperature, that water runs downhill, not uphill, that electric batteries wear out and do not recharge themselves, and that dye dropped into water spreads throughout the water but does not separate from the water once it has mixed with it. None of these everyday occurrences violates the first law of thermodynamics, but neither does the first law explain them. It is obvious that in our consideration of energy on a microscopic level, we have missed something. To see what we have missed, it is necessary to introduce the concept of order and disorder and a method physicists have devised for measuring order and disorder – a concept called entropy.

Order and Disorder

We have an intuitive feeling of what we mean when we say a situation is ordered. By this we mean that it conforms to a predetermined set of rules. For example, suppose we have a large number of small squares arranged in a periodic array, like a checkerboard. If we have red and black checkers, we can ask in how many ways we could distribute them, one on each square, so that all the red checkers are on one side of the array and all the black checkers on the other. We can also ask in how many ways could we distribute them with no restriction on which color goes where. There are many more ways to arrange them in the latter case. The usual red and black checkerboard in which no similar colors are next to each other is the most ordered system. We can see this from the fact that the interchange of any two neighboring pieces destroys the order. Let us consider a system composed of red (R) and black (B)

molecules. The system is said to be ordered if the R and B molecules stand in a regular periodic arrangement with respect to one another and to be disordered if the R and B molecules are randomly arranged as shown in Figure 6.1.

Figure 6.1 Ordered and Disordered Arrangements

R	B	R	B	R	R	B	B
B	R	B	R	B	R	B	R
R	B	R	B	B	R	B	R
B	R	B	R	R	B	R	B
Ordered				Disordered			

The ordered arrangement shown in Figure 6.1 is characteristic of certain crystals. If one examines a small portion of this ordered system, one can predict the arrangement of molecules for the rest of the system even if the system is very large. Whether we consider a situation ordered or not depends on the set of rules by which we judge the situation, and on the attribute being considered. For example, we would consider a set of floor tiles arranged in a geometrical pattern as a situation exhibiting geometrical order. If the tiles were each of a different color, however, we would probably not ascribe order to the array of tiles on the basis of color.

But whatever we specify to be the ordered situation, the number of disordered situations is much larger than the number of ordered situations. Therefore, if selection is done by chance, we are most likely to obtain a disordered arrangement. For example, suppose we wish to fill a square board with red and black checkers and we choose the color at each location by tossing a coin (i.e., we place a red checker if we toss heads, and a black checker for tails.) How many boards would you guess we would fill only to find that we had a disordered configuration before we filled a board and found that the board was perfectly ordered?

Entropy

Once set up, the checkerboard stays set up until we decide to change it, a situation which we can refer to as static disorder. As we have found, most physical systems change with time, a situation we can refer to as dynamic disorder. Because a system changes with time, the large ratio of the number of disordered situations relative to an ordered situation can be used to predict how the system will change with time. Based on the number of disordered situations compared to the number of ordered situations, it is extremely unlikely that a system will go by itself from a disordered to an ordered condition. If the system is ordered, it is likely to become disordered. It is useful to define a quantity S called *entropy*, which is a measure of the degree of disorder in a system. The entropy of a system increases as the disorder of the system increases.

We now focus on the molecular motion of a system, which gives rise to the internal energy of this system. Adding heat to this system increases the disorder because the heat increases the randomness of the molecular motion. So, the entropy of the system increases. The effect of adding heat to a system increases the molecular motion, and this results in more disorder of the system. The effect of adding heat to a

cold system, one that has small molecular motion, produces more disorder than would happen if one added the same amount of heat to the system if it were at a higher temperature. Why? It is because the hot system already has more molecular motion than the cold system, so the percentage change in motion is not as great.

If the change in entropy only comes about because the internal energy of the system changes, the result is called a reversible process. In this case, the change in entropy ΔS is given by equation 6.1.

$$\begin{aligned} \text{change in entropy} &= \frac{\text{change in the heat of the system}}{\text{temperature}} \\ \text{or} \\ \Delta S &= \frac{\Delta Q}{T} \end{aligned} \quad \text{(Equation 6.1)}$$

where

ΔS = change in entropy of a reversible process (joules/Kelvin or calories/Kelvin)

ΔQ = change in the heat of the system (joules or calories)

T = temperature (Kelvin)

A good example is found in an ice cube at 0 °C placed in a well-insulated chest at 20 °C. The ice cube is the system and the chest is the environment. Heat flows from the chest to the ice cube because there is a difference in their temperatures. As heat is added to the system (the ice cube), after some time the ice cube becomes a puddle of water at 0 °C. If we wait long enough, the puddle of water and the chest will reach the same temperature, which will be less than 20 °C.

Equation 6.1 must be applied carefully, because it is valid only if the temperature of the substance remains approximately constant. However, we learned in Chapter 5 the amount of heat needed to change one gram of ice at 0 °C to one gram of water at 0 °C. This is the latent heat, which is 80 calories/gram for ice. If the ice cube has a mass of 100 grams (0.1 kg), we can find the heat added, which equals the increase in thermal energy, using Equation 5.3.

$$Q = L_{heat} \times M = 80 \text{ cal/g} \times 100 \text{ g} = 8,000 \text{ cal}$$

These 8,000 calories are the difference between the initial and final thermal energy. During this phase change, the temperature remains at 0 °C. This means that we can find the change in entropy by using Equation 6.1.

(Example 6.1)

What is the change in entropy when 100 grams of ice at 0 °C melt into 100 grams of water at 0 °C?

Using the 8,000 calories calculated above and converting the temperature of 0 °C into 273 K, we find

$$\Delta S = \frac{\Delta Q}{T} = \frac{8,000 \text{ cal}}{273 \text{ K}} = 29.3 \text{ cal/K}$$

Equation 6.1 works only in situations with a constant temperature, such as Example 6.1. However, if heat is added after all of the ice has changed into liquid water, the temperature of the water will increase. Clearly the temperature is not constant. Generally, as heat is added to a substance, the temperature of the substance will rise. When this happens, you could use Equation 6.1 only by dividing the temperature changes up into small intervals, calculating ΔS for the initial temperature of each of these intervals, and adding the calculated values of ΔS for each of the intervals to find the total change in the entropy of the system. The smaller the temperature intervals you take for this calculation, the closer you will come to the exact value of the change of entropy of the system as heat is added to the system.

If you have studied calculus, you may realize that the procedure described above implies using calculus to find the change in entropy. Although we do not use calculus in this course, just for fun we will write down how we would use calculus to apply Equation 6.1 to calculate the change in entropy when a change in temperature occurs. A good example would be to find the change in the entropy of the liquid water at 0 °C as the liquid increases in temperature until the temperature of the liquid and the temperature of the chest are at the same temperature. Of course that temperature would be less than 20 °C. The liquid water and the chest are now at the same temperature, i.e. in thermal equilibrium with each other. In order to see what the change in heat would be in this situation, consider Equation 5.2, which tells you the heat required to change the temperature of an object.

$$\text{Heat} = (\text{Specific heat}) \times (\text{Mass}) \times (\text{Change in Temperature})$$

or

$$Q = s_{\text{heat}} \times M \times \Delta T$$

The change in entropy of the system is

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = \int_{T_{\text{initial}}}^{T_{\text{final}}} \left(\frac{s_{\text{heat}} M \Delta T}{T} \right) = s_{\text{heat}} M \ln \left(\frac{T_{\text{final}}}{T_{\text{initial}}} \right)$$

Again, don't worry, we will not use calculus in this course.

You probably know that a diamond is very hard, with molecules tightly bound in an ordered crystal. Oxygen gas, on the other hand, has molecules that move independently of one another in a state of dynamic disorder. The molecular arrangement of the diamond molecules is more ordered than the molecular arrangement of the oxygen gas. Therefore, for an equal number of molecules of diamond and oxygen gas, the oxygen has much greater entropy. A calculation using Equation 6.1 shows that the entropy of the oxygen gas is nearly 100 times greater than the entropy of the diamond. We associate an increase in entropy with an increase in randomness in the system. In order to have zero entropy, a system would have to be perfectly ordered. The entropy of a diamond that is so ordered and that is held at absolute zero (0 Kelvin) is zero joules/Kelvin.

Concept Check 6.1

- a) What happens to the entropy of the system (the ice cube) described above while the ice is melting into liquid water at 0 °C?

- b) What happens to the entropy of the system plus its environment (the ice cube and the well-insulated chest) while the ice is melting into liquid water?

- c) After some time, what has happened to the entropy of the melted ice and its surroundings inside the well-insulated chest? Has it gone to equilibrium?

6.2 Equilibrium and the Second Law of Thermodynamics

As mentioned above, an increase in entropy is associated with an increase in randomness in the system. Thermal energy consists of the random motion of the molecules of which matter is composed. Recall that the random motion of molecules in solids is less vigorous than in liquids; the motion of molecules in liquids is in turn less vigorous than in gases. When thermal energy is added to solid ice, it melts from ice at zero degrees Celsius into liquid water that is also at zero degrees Celsius. When the liquid water is further heated it can evaporate, becoming a gas, water vapor. The more thermal energy a molecule has, the faster it moves and the more disordered the motion of a collection of such molecules becomes. In other words, as the thermal energy of the system of molecules increases (solid to liquid to gas), there is a progression from less disordered to more disordered behavior, that is, from a lower entropy state to a higher entropy state. Recall that the random motion of gas molecules is an example of dynamic disorder. Dynamic arrangements depend on time, but static arrangements do not.

We are now in a position to summarize this discussion into a law that applies to situations for which, although the first law of thermodynamics is valid, the first law gives an incomplete observation of what is happening. This law is known as the second law of thermodynamics, and can be stated in many forms (which may or may not appear at first glance to be equivalent). One form, suggested by the very large number of disordered arrangements is:

The entropy of a physical system left to itself will increase or, if the system is already at its maximum entropy, the entropy will remain the same.

We also find that systems, if left undisturbed, tend to progress towards equilibrium with their surroundings. We are all familiar with this process; hot coffee cools and ice cream melts, for example. These and all other natural systems, which are not influenced by

outside agents, progress towards situations of equilibrium with their surroundings, that is, situations of greater disorder. Thus the entropy of such systems (including their surroundings) must also be increasing as these systems are coming to equilibrium. The equilibrium configuration is the situation of greatest disorder, or maximum entropy.

Another version of the second law of thermodynamics is the following statement:

Any system, when left to itself, tends toward equilibrium with its surroundings.

An object in equilibrium with its surroundings implies that its temperature is the same as the surroundings and there is no net transfer of energy possible between the object and its environment. Another statement of the second law of thermodynamics is:

The entropy of a system that is in equilibrium with its surroundings remains constant.

The second law of thermodynamics does not rule out local reductions in the entropy of a system. To locally reduce entropy, a system is taken from an equilibrium situation to a nonequilibrium one, and energy must be transferred to the system. A compressed air tank with its valve open is approaching equilibrium. Equilibrium occurs when the pressure inside the tank is the same as the pressure outside. To recompress the air in the tank, work is required.

Work and Approach to Equilibrium

Even though we can effect local reductions in entropy by doing work, such as making a bed, the trend is for the entropy of the universe to increase. Each localized entropy decrease such as the entropy of the bed is accompanied by a greater increase in the entropy of the surroundings, thereby causing an increase in the total entropy of the universe.

A system moving towards equilibrium is a system that has the ability to do mechanical work. By the same token, no mechanical work can be obtained from a system in equilibrium with its surroundings. Energy and entropy are measures of different characteristics of a system, and both must be considered in order to know how much work can be extracted from a system.

As long as the system is not in equilibrium with its environment, the entropy it has compared to the entropy it will have when it reaches equilibrium is a measure of the amount of work that can be obtained from the system as it goes to equilibrium. It is true that energy is required to change the system from equilibrium to nonequilibrium. However, it is not necessarily true that all of that energy can be recovered as work. Whether or not the energy is recoverable as work depends strongly on the details of the process by which the system is removed from equilibrium and returned to equilibrium. If we raise a weight to some height, we expend a certain amount of energy in this process. If the weight is now attached to a machine and allowed to fall, some fraction

of the gravitational potential energy may be transformed into useful work by the machine.

Of two similar machines, the one that has the smaller amount of friction in it will produce more useful work. This is because it will have the smaller conversion of mechanical energy to thermal energy. It is the change in the entropy of the system that provides us with a measure of the fraction of the energy that is converted to work. This connection of entropy with the subject of energy is one of the reasons why it is a useful concept. As the entropy of the universe increases, the amount of energy in the universe that can be converted to useful work decreases.

We now consider some specific examples of entropy changes and equilibrium. In decay of radioactive nuclei, the nucleus of the atom is in a nonequilibrium state and approaches equilibrium by emitting particles. When an alpha particle is emitted by a nucleus, the entropy of the nucleus-alpha system increases. It is possible to return the system to its original state by bombarding the nucleus left after alpha decay with other alpha particles. Such a process can be carried out in a particle accelerator, and requires a great deal of energy. In bombarding a nucleus with alpha particles, it is possible that the nucleus will capture one of these particles and return to its state before alpha decay.

There are many examples of the approach of a system to equilibrium in a process involving radiant energy. The sun is attempting to reach equilibrium with the rest of the universe by the process of emitting radiation. If the nuclear processes that take place in the sun were to cease, the sun would eventually cool off in its approach to equilibrium. When the radiation emitted by the cooling sun has decreased to the point that it is the same as the amount of radiation coming to it from the rest of the universe, radiative equilibrium will have been reached.

In the case of electrical energy, energy is required to separate positive and negative charges. Remember that we could accomplish this separation by friction or by using a generator, and the separated charges could be stored on the plates of a capacitor. Discharging the capacitor causes the system to return to electrical equilibrium.

It is a general rule that when systems that are not in equilibrium with each other (although each system may have itself separately reached equilibrium) are combined, the entropy of the resulting combination increases until a new equilibrium situation is obtained. At this point, the entropy remains constant. Suppose a hot brick is placed in a cool, insulated room, and the system (the hot brick and the room) is allowed to come to thermal equilibrium. In the process of reaching equilibrium, the brick has cooled down and has undergone a decrease in entropy. On the other hand, the room has warmed up and undergone an increase in entropy. The total amount of thermal energy of the entire system has remained constant, but for a given amount of heat transfer the entropy decrease of the hot object is less than the entropy increase of the cool room. Thus the overall change in entropy is positive. The entropy of the system has increased.

6.3 Reversible Processes and Perpetual Motion

Any process is *irreversible* if, after a system has undergone such a process, we cannot return the system to its original situation without adding energy to it. A reversible process is one that could return the system to its original state without the addition of energy. Another way of stating the second law of thermodynamics is:

All physical processes are irreversible.

This is true for everything from the mixing of paint to the burning of fuel oil in electric power plants. Because all physical processes are irreversible, if one takes a series of pictures of a system as it progresses from a nonequilibrium to an equilibrium situation, then in many cases a person who did not observe the actual sequence of events can properly arrange the series of pictures on the basis of common experience.

Since energy is conserved, why can't we simply run a process backward and return to the original situation? The answer is that in every process, part of the energy of the system is converted by friction into thermal energy. Frictional effects occur not only in mechanical systems, but also in chemical, electrical, magnetic and nuclear systems. The resulting thermal energy cannot be completely reconverted into other forms of energy. Heat will not flow from any body to a hotter body unless energy is provided to cause the transfer. This is an example of an irreversible process.

When energy is transferred to a system, some energy becomes thermal energy because of the molecules in the system. Regardless of how careful we are, we can never construct a device that is completely free from this energy conversion process. The production of thermal energy in this manner is ordinarily attributed to friction, and we speak of frictional losses when referring to the production of this thermal energy. Because all observable physical processes involve the interaction of material objects with each other or with radiation, all such physical processes are irreversible. Therefore, all designs for perpetual motion machines are unfortunately doomed to failure. All devices or processes result in some production of thermal energy, and this energy cannot be completely converted back into work. An example of a system that is close to reversible is a pendulum that has a support with almost no friction, moving in a vacuum.

The efficiency with which energy contained in any fuel is converted to a useful form varies widely, depending on the method of conversion and the end use desired. The efficiency of a device is equal to the amount of energy converted to the desired form divided by the amount of energy supplied to the device. In this period we discuss the efficiencies of various processes that convert energy to useful forms and the limits imposed by the Second Law of Thermodynamics. All devices or processes result in some production of thermal energy, and this energy cannot be completely converted back into work. Therefore, the efficiency of a process is always less than one.

Period 6 Summary

6.1: An ordered system conforms to a predetermined set of rules.

In nature, disordered systems are more common than ordered systems because there are many more disorderly arrangements than orderly arrangements.

Entropy is a measure of the degree of disorder of a system. The greater the disorder, the greater the amount of entropy. If the temperature is constant,
 $\Delta S = \Delta Q/T$

Entropy tends to increase with time. For example, ice melts at room temperature or metal rusts when exposed to moisture.

6.2: The second law of thermodynamics can be stated in several ways:

- 1) The entropy of a physical system left to itself will increase or, if the system is already at its maximum entropy, the entropy will remain the same.
- 2) Any system, when left to itself, tends toward equilibrium with its surroundings.
- 3) The entropy of a system that is in equilibrium with its surroundings remains constant.

6.3: As systems move toward equilibrium, they can give off energy or do work or do both. To change a system from its equilibrium state requires that work be done on the system or that energy be added to the system or both .

Work can be obtained from a system as it moves from a non-equilibrium situation to an equilibrium situation.

Physical changes are irreversible if energy must be added or work be done or both to return the system to its original state.

All physical processes are irreversible.

Period 6 Exercises

- E.1 In a closed container the motion of the molecules of a gas at room temperature is an example of
- a) static order.
 - b) static disorder.
 - c) dynamic order.
 - d) dynamic disorder.

- E.2 Which of the following statements about the entropy of a system is NOT correct?
- a) It is a measure of the disorder of the system.
 - b) It will increase or remain the same if the system is left to itself.
 - c) It is the same as the energy of the system.
 - d) It can be decreased if energy is added to the system.
 - e) It can be increased without changing the temperature of the system.
- E.3 The entropy of one gram of liquid water at 0 °C is _____ one gram of ice at 0 °C.
- a) greater than
 - b) less than
 - c) the same as
- E.4 When the amount of disorder associated with a system increases, the entropy of the system
- a) increases.
 - b) decreases.
 - c) may increase or decrease.
 - d) remains the same.
- E.5 When a closed system is left to itself, the entropy of that system will
- a) always increase.
 - b) always decrease.
 - c) always increase or remain the same.
 - d) always decrease or remain the same.
 - e) increase or decrease at random.
- E.6 Which of the following is NOT a statement of the second law of thermodynamics?
- a) Any system when left to itself tends toward equilibrium with its surroundings.
 - b) A change of a system from its equilibrium situation involves an increase in entropy of the system.
 - c) The entropy of a system that is in equilibrium with its surroundings remains constant.
 - d) It requires energy to change a system from its equilibrium situation.
 - e) ALL of the above are statements of the Second Law of Thermodynamics.

Period 6 Review Questions

- R.1 You draw M & M candies from a bag and place them on a table. How do you decide if you have an ordered pattern of M & M's?
- R.2 Once your definition of an ordered pattern of M & M's has been decided upon, which are you more likely to draw at random – a ordered pattern or a disordered pattern of candy? Why?
- R.3 An ice cube is dropped into a hot cup of coffee. As the ice cube melts, the coffee cools down. What happens to the entropy of the ice cube, the entropy of the coffee, and the entropy of the system as a whole?
- R.4 Give examples of work done by systems at non-equilibrium as they move toward equilibrium. What is necessary to move a system at equilibrium to a non-equilibrium state?
- R.5 What are irreversible processes? Why are perpetual motion machines doomed to failure?

