

Thermodynamics

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CHAPTER

1

Thermodynamics

CHAPTER OUTLINE

- 1.1 The Laws of Thermodynamics: introduction and historical context
 - 1.2 The 4 Laws
 - 1.3 Second Law of Thermodynamics
 - 1.4 Third Law of Thermodynamics and Practice Problems
 - 1.5 References
-

Thermodynamics Explains It All

Everything happens because heat is flowing from a hot place to a cold place. Nothing happens without heat flow. There are no exceptions.

1.1 The Laws of Thermodynamics: introduction and historical context

Thermodynamics is the study of the inter-relation between heat, work and internal energy of a system. The British scientist and author C.P. Snow had an excellent way of remembering the three laws:

1. You cannot win (that is, you cannot get something for nothing, because matter and energy are conserved).
2. You cannot break even (you cannot return to the same energy state, because there is always an increase in disorder; entropy always increases).
3. You cannot get out of the game (because absolute zero is unattainable).



In simplest terms, the Laws of Thermodynamics dictate the specifics for the movement of heat and work on all levels, including during chemical reactions.

Basically, the First Law of Thermodynamics is a statement of the conservation of energy - the Second Law is a statement about the direction of that conservation - and the Third Law is a statement about reaching Absolute Zero (0° K). However, since their conception, these laws have become some of the most important laws of all science - and are often associated with concepts far beyond what is directly stated in the wording.

To give you a better understanding on how these laws came about and their modern scope of coverage, you have to understand when and why these laws were generated.

Our story begins back in the mid-seventeenth century. Society prior to the eighteenth century favored developments in the life sciences (largely for medical research) and astronomy (for navigation and a record of the passage of time - also a source for early mythology and folklore). Science was viewed as purely a philosophic endeavor, where little research was conducted beyond the most useful fields. Indeed, philosophy and science were inseparable in several emerging disciplines (this is always true of new fields where no firm basis of study has yet been conducted). However, European society was about to experience unforeseeable rapid changes.

Prior to the mid-eighteenth century, the general European populace randomly dotted the land in small agricultural communities, industry was run out of country cottages, and scientific developments were nearly at a standstill. Suddenly, without much of a transition, new pockets of industry arose, focusing towards large-scaled machines rather than small hand tools; large industrial corporations often crushed small agriculturally centered commerce; and in many areas, city life rendered country farm cottages obsolete. Coinciding with an era of vast social and political changes, this historic event would later come to be called the Industrial Revolution.

If necessity were the mother of all innovation, then the Industrial Revolution would be the mother of all necessities. Horrible living conditions in the overcrowded industrial cities bred a plethora of diseases and viruses. This along with other results of spontaneous urbanization demanded science again to address the problems of an ever-changing human civilization. Science of the Industrial Age responded to such needs by centering on medical advances in the early stages of the revolution. Such was the era of crucial medical breakthroughs, and age of greatest physiologists - such as Marie Curie (radium), Wilhelm Roentgen (x-rays), Louis Pasteur (pasteurization), Edward Jenner (smallpox vaccination), Joseph Lister (bacteria antiseptic), and Charles Darwin (evolution).

Once the medical crisis was rectified, science could concentrate on the heart of an industrial society - large-scaled machinery. True of nineteenth century mass industry, the company with the greatest machines produced more products, made more money, and was consequently more successful. It is natural, therefore, that fierce competition arose to find the most industrious machinery possible, and how far the limits of these machines could be pushed as to achieve maximum productivity (without consuming much energy). Again, society would fuel scientific advancement.

Nineteenth century scientists were encouraged to study the machine, and its efficiency. To do this, physicists analyzed the flow of heat in these machines, and the chemical changes that transpire when they perform work. Thus was the establishment of modern thermodynamics. First on the agenda of this new discipline was to find a means convert heat (as produced by machines) into work with full efficiency. If such a flawless conversion could be accomplished, a machine could run off its own heat, producing a never-ending cycle of heat to work, rendering heat, converting to work, and so forth ad infinitum. . . The idea of such a machine that could run continuously off its own exhaust, or 'perpetual-motion' machine as it was dubbed, excited the industrial corporations, who contributed much funding for its development. However, as the research was completed, the results were all but pleasing to the sponsors.

As it turned out, the very same research oriented to create a perpetual-motion machine proved that the very concept is not possible. The proof lies in two theories (now three) that are currently considered the most important laws in the whole body of science - the First and Second Laws of Thermodynamics. The First Law of Thermodynamics is really a prelude to the second. It states that the total energy output (as that produced by a machine) is equal to the amount of heat supplied. Generally, energy can neither be created nor destroyed, so the sum of mass and energy is always conserved. A mathematical approach to this law produced the equation $U = Q - W$ (the change in the internal energy of a closed system equals the heat added to the system minus the work done by the system). By its nature, this finding did not restrict the use of perpetual-motion machines. However, the next law would deal a blow to all believers of such a wonder machine.

The first law, a bellwether in the frontier pastures of Thermodynamics, contained one major flaw that rendered it inaccurate as it stood. This law is based on a conceptual reality, one that does not take into consideration limits placed by transactions occurring in the real world. In other words, the first law failed to recognize that not all circumstances that conserve energy actually ensue naturally. As the impracticality of the first law (to describe all natural phenomenon) became apparent, a revision became essential if science hoped fully to understand thermal interactions, and thus keep pace with a machine-driven society. Born as a modification to its older sibling, the Second Law of Thermodynamics made no early promises of importance.

Further research into the natural tendencies of thermal movement in the latter nineteenth century developed a code of restrictions as to how heat conversion is achieved in the natural world. Physicists attempting to transform heat into work with full efficacy quickly learned that always some heat would escape into the surrounding environment, eternally doomed to be wasted energy (recall that energy can not be destroyed). Being obsolete, this energy can never be converted into anything useful again.

One physicist noted for significant experiments in this field is the Frenchman, Sadi Carnot. His ideal engine, so properly titled the 'Carnot Engine,' would theoretically have a work output equal to that of its heat input (thus not losing any energy in the process). However, he fell into a similar trap as in the first law, and failed to conduct his experiments as would naturally occur. Realizing his error, he concluded (after further experimentation) that no device could completely make the desired conversion, without losing at least some energy to the environment. Carnot created an equation he employed to prove this statement, and currently used to show the thermodynamic efficiency of a heat machine: $e = 1 - T_L / T_H$ (the efficiency of a heat machine is equal to one minus the low operating temperature of the machine in degrees Kelvin, divided by the high operating temperature of the machine in degrees Kelvin). For a machine to attain full efficiency, temperatures of absolute zero would have to be incorporated. Reaching absolute zero is later proved impossible by the Third Law of Thermodynamics (which would surface in the late 19th century).

These findings frustrated the believers of a perpetual motion machine, and angered the industrial tycoons who sponsored the whole endeavor. Yet, not all was completely lost. Carnot's equation helped industrial engineers design engines that could operate up to an 80% efficiency level - an enormous improvement over prior designs, increasing productivity exponentially. Moreover, by reversing the heat-to-work process, the invention of the refrigerator was made possible! Yet, the greatest overall fruit of this venture was the development of the Second Thermodynamic Law, which would later achieve a legendary status as a fundamental law of natural science. Let us shortly return to Carnot and the heat engine.

The irrevocable loss of some energy to the environment was associated with an increase of disorder in that system. Scientists wishing to further penetrate the realm of chaos needed a variable that could be used to calculate disorder.

Thanks to mid-nineteenth century physicist, R.J.E. Clausius, this Pandemonium could be measured in terms of a quantity named entropy (the variable S). Entropy acts as a function of the state of a system - where a high amount of entropy translates to higher chaos within the system, and low entropy signals a highly ordered state. Like Carnot, Clausius worked out a general equation, his being devoted to the measurement of entropy change over a period of time: $(\text{change})S = Q / T$ (the change in entropy is equal to the amount of heat added to the system [by an invertible process] divided by the temperature in degrees Kelvin).

The beauty of this equation is that it can be used to compute the entropic change of any exchange in nature, not solely limited to machines. This development brought thermodynamics out of the industrial workplace, and opened the possibility for further studies into the tendencies of natural order (and lack therefore of), eventually extending to the universe as a whole. Applying this knowledge to nature, physicists found that the total entropy change (change in S) always increases for every naturally occurring event (within a closed system) that could be then observed. Thus, they theorized, disorder must be continually augmenting evenly throughout the universe. When you put ice into a hot cup of tea (aristocrats of the Victorian era were constantly thinking of tea), heat will flow from the hot tea to the cold ice and melt the ice in the beloved beverage. Then, once the energy in the cup is evenly distributed, the cooled tea would reach a maximum state of entropy. This situation represents a standard increase in disorder, believed to be perpetually occurring throughout the entire universe.

Thank you to Andrew V. Liaugminas, Independent Researcher - Chicago, Illinois, PhysLink.com

1.2 The 4 Laws

Thermodynamics Explains It All

Everything happens because heat is flowing from a hot place to a cold place. Nothing happens without heat flow. There are no exceptions.

Temperature is not Heat

It is natural to confuse heat with temperature. That's because the more you heat something, the higher its temperature becomes. But heat and temperature aren't the same things. Heat is a form of energy. A difference in temperature causes heat to flow. Just remember, **heat is something that flows and temperature is what makes heat flow.**

Water is a little bit easier to visualize than heat, so let us explain heat flow using a water flow analogy. Suppose you have two cylinders of water connected by a pipe at their base, as shown (viewed from the side) below.

TABLE 1.1:

Water will flow from the cylinder on the left into the cylinder on the right because there is a difference in water levels. It doesn't matter that there already is more water in the cylinder on the right. Water will flow until the levels are equal. It doesn't flow until the amounts of water in each cylinder are equal. Heat, like water, flows in such a way to produce a uniform temperature level.

The Zero Law

There are four laws of thermodynamics which build upon each other. They are numbered 0 through 3 because the most fundamental law was discovered after the First Law had already been given the number 1. Therefore, they had to assign the most fundamental law the number 0. The Zeroth Law simply says there is no heat flow between objects that are the same temperature. In essence, the Zeroth Law is just a definition of what temperature is.

The First Law

The First Law is that heat cannot be created or destroyed. (This is also known as the law of conservation of energy.) Heat can only flow from place to place, or change form. Heat usually manifests itself as the kinetic energy of the molecules of a gas, liquid, or solid. That is a rather limited view of what heat really is. Heat is work waiting to happen. Work will be done (or wasted) when heat flows from a hot place to a cold place. So, heat is really work-in-waiting.

Consider an unlit candle at room temperature. There is some chemical energy in the wax of the candle. But there is no heat flow from an unlit candle, so it can't do any work. A burning candle does not **create** heat because heat cannot be created or destroyed. A burning candle **liberates** heat. Heat that already was in the candle (in the form of chemical energy) flows out. The melted wax is hot because heat has changed to a form that can escape. Heat flows from the flame and hot wax into the cooler atmosphere, and could do some useful work. A (small) pot of water could be suspended over the flame, and the heat flowing into the water could boil it, creating steam which could turn a tiny steam engine, which could do a little bit of work.

But even if the candle doesn't boil any water, heat is not destroyed. Heat has merely moved from a hot place to a cold place, making the hot place cooler and the cold place warmer, wasting the opportunity to do some work. When both places are the same temperature there will still be the same amount of heat as there was before the candle was lit. The only difference is that the heat is less well organized than it was. Previously the heat was concentrated in the candle. After the candle burns out, and everything reaches the same temperature, the heat is more uniformly distributed. It is more disorganized because it isn't localized in one place.

The Second Law

"Entropy" is a quantifiable measure of how evenly distributed heat is. The actual calculation of entropy involves some partial differential equations which can be simplified somewhat by keeping temperature or pressure constant, and can be calculated by someone sufficiently skilled in mathematics. The results of countless calculations have shown that every time heat flows from a hot spot to a cold spot, entropy **increases**. Every time heat flows from a cold spot to a hot spot, entropy **decreases**.

The Second Law says that entropy always increases in a **closed** system. (A closed system is one that does not exchange any energy with the surrounding environment. The universe is a closed system because there is nothing outside of it to exchange heat with.)

The entropy of a closed system always increases if work is done (or if work is wasted). The only way the change in entropy can remain the same is if a "reversible" process occurs. For a process to be reversible, energy has to be transferred without any loss. In real life there are some **nearly** reversible processes; but the **Third Law** (which we will see in a moment) says that there are no truly reversible processes.

The Third Law

The Third Law says that an ideal engine would convert 100% of the heat into useful work only if its exhaust temperature were absolute zero. In other words, 100% efficiency is impossible. Since 100% efficiency is impossible, it means that there are no truly reversible processes. That, in turn, means that all processes are irreversible. That means, all processes have a natural direction which causes entropy to increase.

Applying the Laws

- There is a fixed amount of heat in the universe. Heat is neither created, nor destroyed.
- Heat is "organized" when there are some places that are hotter than others.
- Heat always tries to disorganize itself by moving from a hot place to a cold place, spreading itself out as evenly as possible.
- Entropy is a measure of how evenly spread out the heat is. (In other words, entropy is a measure of heat disorder.)
- As heat flows from one place to another, it either does work or wastes the opportunity to do work.
- Natural processes cannot violate these laws

- See more at: <http://www.ck12.org/user:a2Jhcm5ldHRAYWJocy5rMTIubm0udXM./book/ABHS-Q2-Chemistry-2-Flexbook/r12/section/1.0/#sthash.bYBKx5OR.dpuf>

1.3 Second Law of Thermodynamics

Introduction

Have you ever wondered why it is easy to let your bedroom get messy, but much more difficult to keep it neat? When your bedroom is neat and orderly, everything is in a place where it belongs. When it's messy, everything seems to be out of order. It's as if your bedroom naturally becomes messy, but you have to make an effort to keep it neat. Physical and chemical processes can be thought of in a similar way. There is a natural tendency for a physical or chemical process to progress in a certain direction. In this lesson, you will learn about the quantity used to describe orderliness and how to predict the reaction direction in physical and chemical processes.

What is a Spontaneous Process?

Chemists want to be able to predict the outcome of reactions. They would like it to be possible to predict what will happen when reactants are added together under a given set of conditions. The conditions of a reaction might include things like temperature, pressure, and concentrations of various reaction components. If the given conditions favor the formation of products, the reaction is said to be **spontaneous**.

It should be noted that just because a process is spontaneous does not mean that it occurs quickly. The rusting of iron is a spontaneous process that takes place over a long period of time. The combustion of gasoline in oxygen (also a spontaneous process) is extremely fast when provided with a spark, but gasoline can be stored in air for quite a while without spontaneously combusting. Thermodynamics predicts the direction in which a reaction will eventually proceed, but it does not tell us anything about the rate at which the reaction occurs. The rate of a reaction depends on many factors, including activation energy, temperature, concentration, and the presence or absence of a catalyst. Chemical kinetics focuses on the pathway between reactants and products, while thermodynamics considers only the difference between the initial and final states.

We know of many examples of processes that occur spontaneously. If the temperature is below 0°C , a glass of liquid water will freeze. If the temperature is above 0°C , a cube of ice will melt. A hot object will gradually lose heat to its surroundings. Many chemical reactions also occur spontaneously. Two molecules of hydrogen will react with one molecule of oxygen to form water, releasing a significant amount of energy in the process. The spontaneous reaction between aluminum and bromine to form aluminum bromide also releases energy.

However, a process does not need to be exothermic in order to be spontaneous. For example, the melting of ice is an endothermic process, but it is still spontaneous at high enough temperatures. If we add ammonium nitrate to water, it will spontaneously dissolve, but the resulting solution will be cooler, indicating that energy in the form of heat was consumed in the process. To determine whether a process is spontaneous, we need to look not only at the change in enthalpy, but also the change in a factor called entropy.

What Is Entropy?

At its most basic level, **entropy** (S) is a measure of probability. States that have a high probability of occurring by random chance have a high entropy value, and states that are unlikely to occur by random chance have a low entropy value. There is a natural tendency for things to increase in entropy over time. An equivalent statement is that nature will spontaneously move toward the states that have the highest probability of existing.

Entropy can also be thought of as the number of possible arrangements that lead to a certain state. The more ways that a given state can be achieved, the greater the probability of finding that state, and the higher its entropy value.

**FIGURE 1.1**

Melting ice in the Beaufort Sea off the North Slope of Alaska.

For example, think about the objects in your bedroom. Imagine every item being randomly placed at some location within the room. Now imagine this happening again and again. How many of the resulting arrangements would lead you to classify your room as "messy?" How many would qualify as a "clean" room? In this hypothetical example, every state has an equal possibility of happening, but because there are so many more ways to arrange items to make a messy room than a clean room, the "messy" state would have a higher entropy value than the "clean" state.

There are many examples in the chemical world of changes in entropy. Phase transitions are one obvious example. When a substance makes a transition from the liquid state to the gaseous state, the particles have many more possible arrangements, because they are no longer confined to a specified volume in which they are close to each other; gas particles can move freely throughout their container. Vaporization represents an increase in entropy. In the opposite direction, a liquid loses entropy when it freezes to a solid. Because solids have very ordered structures, there are fewer possible arrangements of particles that would result in the properties associated with a solid.

The Second Law of Thermodynamics

Recall that, according to the first law of thermodynamics, the total amount of energy in the universe is conserved for any given process. Entropy is not conserved; in fact, it is always increasing. Nature is constantly moving from less probable states to more probable ones. The **second law of thermodynamics** states that the entropy of the universe will increase for any spontaneous process.

To determine whether a given process is spontaneous, it is often helpful to break down the total entropy change as follows:

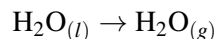
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

where ΔS_{sys} and ΔS_{surr} represent the changes in entropy that occur in the system and in the surroundings, respectively.

To predict whether a given reaction will be spontaneous, we need to know the sign of ΔS_{univ} . If ΔS_{univ} is positive, the entropy of the universe increases, and the reaction is spontaneous in the direction that it is written. If ΔS_{univ} is negative, the reaction is spontaneous in the reverse direction. If ΔS_{univ} is equal to zero, the system is at equilibrium. To predict whether a reaction is spontaneous, we need to determine the entropy changes in the system and in the surroundings.

Entropy of a System (ΔS_{sys})

Let's consider the change of state for one mole of water from liquid to gas:



In this case, the water is the system, and the surrounding are everything else. How does the entropy of the water change in this process? As we saw earlier, the vaporization process leads to an increase in entropy, because there are many more possible ways to arrange the individual water molecules when they are allowed to move freely about their container. The entropy of the system increases, so ΔS_{sys} will be a positive value.

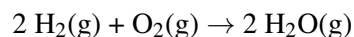


FIGURE 1.2

Phase changes are one type of process for which we can reliably predict the sign of the change in entropy. Not all transformations are quite so obvious, but the direction of the change in entropy can be easily predicted for certain types of chemical reactions.

1. If there is a difference in the number of gaseous components between the reactants and the products, the side with more moles of gas will most likely have a higher entropy value. This is because a greater number of moles indicates a greater number of gas particles and a greater number of arrangements of the gas particles.

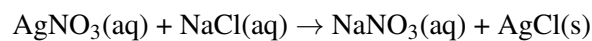
For example, consider the following reaction:



Three moles of gaseous reactants combine to make two moles of gaseous products. Therefore, we would expect this process to result in a decrease in entropy. ΔS_{sys} will have a negative value for this reaction.

2. Dissolved substances have a higher entropy value than their corresponding precipitate.

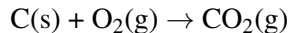
For example, if we mix silver nitrate with sodium chloride, we have the following reaction:



The ions from the aqueous components are free to move around the entire solution, but the silver and chloride ions in the solid AgCl are all clustered together into a precipitate, ordered into a specific pattern of alternating cations and anions. Overall, this transformation represents a decrease in the entropy of the system.

- All else being equal, more separate particles corresponds to a higher degree of entropy.

This makes sense when we think about the arrangements available. Consider the following reaction:



Each side of this equation contains one mole of gas particles, so that will not be a deciding factor. However, there are more total particles on the reactants side than on the products side. Because there are more ways to arrange two moles of particles than one mole of particles, this process represents an overall decrease in entropy.

- If there is an increase in temperature, entropy will increase.

So far, we have been thinking about entropy in terms of the ways in which particles can be distributed over a certain amount of space. However, other factors that are subject to random distributions also make contributions to the entropy of a system. As you know, an increase in temperature means that there is more overall kinetic energy available to the individual particles. This energy is distributed randomly through enormous amounts of collisions between particles. Having more energy available means that there are more ways that it can be distributed, so an increase in temperature also corresponds to an increase in entropy.

Entropy of the Surroundings (ΔS_{surr})

In general, the process of interest is taking place in the system, and there are no changes in the composition of the surroundings. However, the temperature of the surroundings does generally change. Entropy changes in the surroundings are determined primarily by the flow of heat into or out of the system. In an exothermic process, heat flows into the surroundings, increasing the kinetic energy of the nearby particles. For an exothermic reaction, ΔS_{surr} is positive. Conversely, heat flows from the surroundings into the system during an endothermic process, lowering the kinetic energy available to the surroundings and resulting in a negative value for ΔS_{surr} .

As it turns out, the amount of entropy change for a given amount of heat transfer also depends on the absolute temperature. We will not go into the exact derivation, but it turns out that the entropy change of the surroundings can be defined in terms of the enthalpy change of the system:

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

where T is the temperature in Kelvin. For an exothermic reaction, ΔH_{sys} is negative, so ΔS_{surr} would be a positive value. This makes sense, because heat is being released into the surroundings, increasing the amount of kinetic energy available to the surrounding particles. For an endothermic reaction, ΔH_{sys} is positive, so ΔS_{surr} would be a negative value.

Entropy of the Universe (ΔS_{univ})

Substituting this into our earlier equation for ΔS_{univ} , we get the following:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} \\ \Delta S_{univ} &= \Delta S_{sys} - \frac{\Delta H_{sys}}{T}\end{aligned}$$

This is a particularly useful equation, because it allows us to determine whether a process is spontaneous by looking only at the system of interest. It also helps to explain why not all exothermic reactions are spontaneous, and not all reactions that increase the entropy of the system are spontaneous. The enthalpy change, entropy change, and overall temperature all factor into whether a given transformation will proceed spontaneously.

1.4 Third Law of Thermodynamics and Practice Problems

The Third Law of Thermodynamics

When we discussed enthalpy, we always talked about changes in enthalpy, never about the absolute enthalpy of a substance. Even the standard enthalpy of formation value (ΔH°_f) is a measure of the change in enthalpy between a compound and its elements in their standard states. There is no absolute zero for enthalpy, but this is not true for entropy. The **third law of thermodynamics** says that a perfectly regular crystal at a temperature of 0 K (absolute zero) would have an entropy value of 0.

As the temperature of a perfect crystal increases, its particles start to vibrate slightly around their optimal positions, thus increasing the entropy of the system. The dependence of entropy on temperature varies by substance, so the only temperature at which all crystals have the same entropy is absolute zero. The **standard entropy** of a substance is a measure of its entropy at 25°C and 1 atm of pressure. Like standard enthalpy of formation values, standard entropies are tabulated for a wide range of substances. However, unlike enthalpy of formation values, all standard entropy values are positive, because the absolute zero for entropy is the most ordered possible state. Additionally, this means that pure elements in their standard states do *not* have a standard entropy of zero.

Because entropy changes are generally small compared to enthalpy changes, we generally express their units in terms of joules instead of kilojoules. Standard entropy values are most commonly given in units of J/K•mol. A few representative values are given in the following table:

TABLE 1.2: Selected standard entropy values

Substance	Standard Entropy S° J/K•mol
$\text{H}_2\text{O}_{(l)}$	69.95
$\text{H}_2\text{O}_{(g)}$	188.84
carbon (graphite)	5.6
carbon (diamond)	2.377
carbon (vapor)	158.1
methane - $\text{CH}_4(g)$	186.26
ethane - $\text{C}_2\text{H}_6(g)$	229.2
propane - $\text{C}_3\text{H}_8(g)$	270.3

Note: When referring to standard entropy, standard enthalpy of formation, and standard heat of formation, we use the notation with the degree symbol to indicate the standard conditions of 25°C and 1 atm. Without the degree symbol these values are not necessarily from the standard state.

As expected, the entropy values for solids are low, the values for gases are high, and the ones for liquids are intermediate. Another observation can be made by looking at the three hydrocarbon gases at the end of the table. For similar molecules, a higher molecular weight generally leads to a larger standard entropy value. Although this is a drastic oversimplification, we can think of this in terms of the electrons that make up each molecule. A larger molecular weight generally means more protons, which also means more electrons. There are more ways to arrange a large number of electrons within a molecule than there are to arrange a smaller number. Although these arrangements are heavily constrained by the positions of the various nuclei, there is still an overall trend for larger molecules to have higher entropy values.

Calculating ΔS_{rxn}

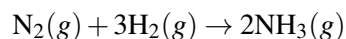
Calculations of the change in entropy for a given reaction are analogous to those used to determine ΔH_{rxn} . The entropy change for a reaction can be calculated by taking the difference between the total of the standard entropy values of the products and those of the reactants:

$$\Delta S_{rxn}^{\circ} = \Sigma nS^{\circ}(\text{products}) - \Sigma nS^{\circ}(\text{reactants})$$

As with our enthalpy calculations, each standard entropy value is multiplied by the coefficient of the corresponding substance in the balanced equation. Extensive tables of standard entropy values can be found on the internet.

Example 20.1

Calculate ΔS_{rxn} for the following reaction:



The standard entropy values for N_2 , H_2 , and NH_3 are 191.6, 130.7, and 192.5 J/K•mol, respectively.

Answer:

Multiply the standard entropy value of each component by its coefficient from the balanced equation, and subtract the values of the reactants from those of the products.

$$\begin{aligned}\Delta S_{rxn}^{\circ} &= \Sigma nS^{\circ}(\text{products}) - \Sigma nS^{\circ}(\text{reactants}) \\ \Delta S_{rxn}^{\circ} &= 2S^{\circ}(\text{NH}_3) - [S^{\circ}(\text{N}_2) + 3S^{\circ}(\text{H}_2)] \\ \Delta S_{rxn}^{\circ} &= 2(192.5 \text{ J/K} \cdot \text{mol}) - [191.6 \text{ J/K} \cdot \text{mol} + 3(130.7 \text{ J/K} \cdot \text{mol})] \\ \Delta S_{rxn}^{\circ} &= -198.7 \text{ J/K} \cdot \text{mol}\end{aligned}$$

There is a substantial decrease in entropy over the course of this reaction. This could have been predicted simply by looking at the balanced equation. There are four moles of gaseous reactants and just two moles of gaseous products. In general, the side of the equation with more moles of gas has a higher total entropy.

Example 20.2

Predict whether the change in entropy would be positive or negative for the following reaction:



Then, use the standard entropy values for each substance to calculate the exact change in entropy.

Answer:

A single solid reactant is splitting into two products, one of which is a gas. We would expect the entropy of the system to increase over the course of this reaction. The exact change can be calculated as follows:

$$\begin{aligned}\Delta S_{rxn}^{\circ} &= \Sigma nS^{\circ}(\text{products}) - \Sigma nS^{\circ}(\text{reactants}) \\ \Delta S_{rxn}^{\circ} &= [S^{\circ}(\text{CaO}) + S^{\circ}(\text{CO}_2)] - S^{\circ}(\text{CaCO}_3) \\ \Delta S_{rxn}^{\circ} &= [39.8 \text{ J/K} \cdot \text{mol} + 213.6 \text{ J/K} \cdot \text{mol}] - 92.9 \text{ J/K} \cdot \text{mol} \\ \Delta S_{rxn}^{\circ} &= 160.5 \text{ J/K} \cdot \text{mol}\end{aligned}$$

As predicted, ΔS_{rxn} is a positive value, indicating that entropy increases upon going from reactants to products.

Lesson Summary

- A process is spontaneous if the formation of products is favored under the given conditions. Spontaneous processes may be fast or slow.
- Entropy (S) measures the probability of attaining a given state. Things naturally progress towards more probable states, so entropy has a tendency to increase.
- The second law of thermodynamics states that the entropy of the universe will increase during any spontaneous process.
- The change in the entropy of the universe can be broken down into the following components:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

- The sign of ΔS_{univ} tells us whether or not a process is spontaneous in the direction that it is written. If ΔS_{univ} is positive, then the forward reaction is spontaneous.
- The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero.
- Standard entropy is the entropy of a substance at 25°C and 1 atm of pressure.
- The entropy change for a reaction can be calculated using standard entropy values.

Lesson Review Questions

1. Define entropy.
2. State the second law of thermodynamics.
3. For each of the following situations, state whether there is an increase or decrease in entropy. Explain your reasoning in each case.
 - a. liquid water freezes.
 - b. a car is in a collision that completely demolishes it.
 - c. wood burns.
 - d. $I_2(s) \rightarrow I_2(g)$.
 - e. $2 Mg(s) + O_2(g) \rightarrow 2 MgO(s)$.

Use the entropy values from <http://chemed.chem.wisc.edu/chempaths/Table-of-Standard-Molar-Entropies-1184.htm> for the following calculations:

4. Calculate ΔS°_{rxn} for the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$.
5. Calculate ΔS°_{rxn} for reactions d and e of question 3, and comment on how well your predictions matched the actual entropy changes.
6. Which form of carbon has a higher degree of organization: diamond or graphite? Explain your answer.
7. Compare the S° of ethane with that of ethanol (159.9 J/K•mol). Explain why ethane has a higher standard entropy value than ethanol. (Hint: the boiling point of ethane is -89°C, and the boiling point of ethanol is 78°C. At what temperature are standard entropy values tabulated?)

Further Reading/Supplementary Links

- Some basic ideas about entropy: <http://entropysimple.oxy.edu/content.htm>
- Entropy values: <http://boomeria.org/chemtextbook/cch20.html>
- Table of standard molar entropies: <http://chemed.chem.wisc.edu/chempaths/Table-of-Standard-Molar-Entropies-1184.html>

Points to Consider

- Can we reliably predict under what conditions a reaction will be spontaneous?

1.5 References

1. Courtesy of NOAA. http://commons.wikimedia.org/wiki/File:NOAA_arctic_spring_1950_corp1104.jpg . Public Domain
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