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2nd Law of Thermodynamics – Academic

Welcome to the wonderful world of thermodynamics! As a science or engineering student, a basic understanding of thermodynamics is essential for your future studies. Believe it or not, it is a pretty interesting subject, not just for scientists, but also for examining your everyday life. Thermodynamic principles affect you and the world around you all day every day. You've got some question eh? Fire away!

So, what are we going to learn about here?

Thermodynamics, in general, is the study of energy. It specifically looks at heat, temperature, energy, and work. The origin of the name thermodynamics is Greek and roughly translates to the study of the movement of heat. It allows us to describe, analyze, and calculate how energy is used and how it changes from one form to another. Many modern applications of thermodynamics involve turning heat into power (using heat to provide work).

Thermodynamics is a broad, involved topic, hence we're going to keep this paper relatively short and look at just one law – probably the most fascinating law – and that is the 2nd Law of Thermodynamics.

What about all those other laws?

Well, there aren't that many laws, just four. There are many ways to explain the laws. Various textbooks define them in different ways. The important thing to note here is that what follows is a brief, general description of the laws – keep in mind that these descriptions are not all encompassing, and they can be explained in different ways that highlight different aspects when applied to different concepts in physics and engineering. Further study is recommended for an in depth discussion of each law. The rest of this paper will focus on an in-depth analysis of the 2nd Law of Thermodynamics.

Zeroth Law of Thermodynamics

Yes, you heard it here folks, there is actually a zeroth law! Often times in the sciences, revision is necessary when new data comes to light. Therefore, because of the underlying importance of the zeroth law it was thought best to put it before the 1st, 2nd, and 3rd laws, hence we have the zeroth law.

The law simply states that: If two bodies, say X and Y, are each in thermal equilibrium with a third body Z, then X and Y are in thermal equilibrium with each other.

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1st Law of Thermodynamics

Heat is a form of energy flow and internal energy changes are subject to the laws of conservation of energy (energy cannot be created or destroyed).

2nd Law of Thermodynamics

There are reversible and irreversible processes. In processes that occur in an isolated system, the entropy (we'll talk about this guy in a bit) of the system will increase for irreversible processes and remain constant for reversible processes. Entropy cannot decrease in an isolated system. Keep in mind that the universe (as far as we know) is a closed (isolated) system.

3rd Law of Thermodynamics

The entropy of a system approaches zero as its temperature approaches absolute zero (0 K or –273.15 degrees Celsius).

Ok, so you said that there are a lot of ways to describe the laws. Since we are looking at the 2nd Law, shouldn't we know some of them?

Most definitely! In fact, many famous physicists have described the 2nd Law in their own way. Let's take a look at some other descriptions of the 2nd Law.

A process whose only result is to exchange heat with fewer than two different heat reservoirs and produce work is impossible. (Carnot's version – from Mere Thermodynamics by Don S. Lemons).

A process whose only result is to extract heat from one heat reservoir and produce work is impossible. (Thompson's version – from Mere Thermodynamics by Don S. Lemons).

A process whose only result is to extract heat from one heat reservoir and reject heat to another hotter reservoir is impossible. (Clausius' version – from Mere Thermodynamics by Don S. Lemons).

No process is possible whose sole result is the absorption of heat from a reservoir and conversion of this heat into work. (Kelvin-Planck version – from Heat and Thermodynamics by Mark Zemansky and Richard Dittman).

In the neighborhood (however close) of any equilibrium state of a system of any number of thermodynamic coordinates, there exist states that cannot be reached (are

inaccessible) by reversible adiabatic processes. (Caratheodory version – Heat and Thermodynamics by Mark Zemansky and Richard Dittman).

The entropy of a closed (isolated) system tends to remain constant or to increase when a constraint internal to the system is removed. (From Thermal Physics by Charles Kittel and Herbert Kroemer).

Any large system in equilibrium will be found in the macrostate with the greatest entropy (aside from fluctuations that are normally too small too measure). (From Thermal Physics by Daniel V. Schroeder).

There is no process that can decrease the total entropy in the universe. (From Thermodynamics: A Grass Roots Approach by Marshall Thompsen).

There is no process that can decrease the entropy of an isolated system. (From Thermodynamics: A Grass Roots Approach by Marshall Thompsen).

What do I need to know to understand this stuff?

What do you need to know? Well, lots of math of course. Everybody loves math, right? It's part of the deal. So, you're going to want to have a good handle on calculus I, II, and III. You'll also need to have calculus-based physics covered – mechanics, sound, electricity, light, and magnetism.

Are there any basic thermodynamics concepts or definitions I need to know (or be reminded of)?

You bet there are. Let's go over some important concepts and definitions.

Energy is often defined as the ability to do work. Energy can transfer from one system to another through work, heat transfer, and mass transfer. The quality of energy is its ability to do work or be useful in some way. In thermodynamics, energy is examined from both the macroscopic and microscopic perspective. Total energy, E_{tot}, is the sum of energy from both groups.

$$E_{tot} = E_{macro} + E_{micro}$$

Kinetic energy (KE) is energy that involves moving a mass so that it has velocity. You will remember this guy as:

$$KE = \frac{1}{2}mv^2$$

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Potential energy (U) is energy that has the potential to be converted into other types of energy. For example: a car on the top of a hill has gravitational potential energy due to its position. Gravitational potential energy will be converted to kinetic energy as the car rolls down the hill. Common types of potential energy are gravitational, elastic, and electric potential energy.

$$U = mgh \qquad \text{(gravitational potential energy)}$$

$$U = \frac{1}{2}kx^2 \qquad \text{(elastic potential energy)}$$

$$U = \frac{KQq}{r} \qquad \text{(electric potential energy)}$$

Work (W) is an energy transfer that you should already be familiar with. Work is performed when one system exerts a force on another system. There is a component of the displacement vector of one of the systems along the line of force. The work by force (F) on an object as it moves from $\vec{r}_x$ to $\vec{r}_y$ is:

$$W_{x \to y} = \int_x^y \vec{F} \bullet d\vec{r}$$

Internal energy (u) is the energy associated with the random, disordered motion of molecules.

A **state** is used to describe the properties of a material at the beginning and at the end of a process.

A **thermodynamic process** is a process in which a system changes from one state to another.

Phases are states such as solid, liquid, or gas. Temperature and pressure conditions determine which phase a material will be in.

It's important to have a thorough understanding of systems and surroundings. A **system** is an object or collection of objects that you want to analyze. A system also has a **boundary** that can be described geometrically. A system is considered **closed** if no mass can cross the boundary of the system (imagine a lidded and taped up box with ping pong balls inside – none can get out). A system is **open** if objects can cross the boundary. Imagine your classroom with the door open. If the classroom is the bound system, air can travel in and out of the system through the doorway, thus it is an open system. The area outside of the system is called the **surroundings**.

For example, let's say there is a recycling bin full of crumpled up papers. Let's make the crumpled up papers the objects of study in this system. Let's make the boundary

of the system the confines of the bin. If there is no lid on the bin, then any papers heaped up over the top are outside of the system (and are in the surroundings) and it is an open system. If the lid is on tight, then it is a closed system. The surroundings are everything outside of the bin.

In thermodynamics, heat and temperature are big players. Here are some fancy definitions. **Temperature** (T) measures the average translational random kinetic energy of a group of particles (the average of all collisions). **Heat** (Q) is that fraction of the total micro energy of a group of particles that can be made to flow (transfer) as a result of some process (such as a temperature difference).

Let's say that you take a nice cold pitcher of water out of your refrigerator and pour it into a glass. If you leave the glass on a table in the kitchen, the temperature of the water will eventually be the same temperature as that of the room. They will then be in **thermal equilibrium**. In this case the water is the system and the kitchen is the environment. This **temperature** change is due to a change in thermal energy. This transferred energy is **heat**.

Thermodynamics processes that produce work use energy from a **thermal reservoir**. A thermal energy reservoir that supplies energy to a process is a **heat source reservoir**. A thermal energy reservoir that receives energy from a process is a **heat sink reservoir**.

Make sure you remember the old ideal gas law.

$PV = nRT$

Ok, lay it on me! What is this mysterious entropy stuff all about? Isn't it like the end of the world or something?

Well, the "easy answer" is that entropy is the measure of disorder in a system. Think of moving to a new apartment. You first move in and bring all your nicely labeled boxes of stuff with you. You unpack, put everything in its place, and all is well – neat, organized, and ordered. When time goes on, you get busy, and life happens. There are dishes in the sink, clothes in the laundry basket, and some dust on the furniture. Things that start out neat and organized tend to become less so over time. To clean everything back up takes work.

Hooray you say! I cleaned it back up and order is restored. Not so fast my friends. Although you did clean up your apartment and you decreased the entropy in the apartment, you have to keep in mind that total entropy in a closed system cannot be decreased according to the 2nd Law. The universe is a closed system. So, the increased entropy that you "cleaned up" (worked on) has just gone somewhere else in the universe, but it still adds to total entropy.

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Using this same analogy, the universe started out small, neat, and tidy. In the beginning the potential energy to do work in the universe was at its greatest and entropy was at its minimum. However, as time went on and the universe aged, it expanded, and became less ordered – and this expanding process continues. Whenever energy is used to do work, the quality of the energy is reduced. When the quality of the energy is reduced, so is its capacity to do work – entropy increases as the quality of energy decreases. At some point in time, entropy will reach a maximum and the quality of energy will reach a minimum. This point may be the death of the universe.

Entropy is also described as a quantity that represents the unavailability of a system's thermal energy for conversion into mechanical work. The more entropy the less energy is available to do work. Pretty soon there won't be energy available for you to use to clean up the old apartment anymore!

Entropy is a very useful property in thermodynamic calculations. The symbol for entropy is **S**. There are reversible and irreversible processes that affect entropy calculations. We'll return to cover these aspects in a bit.

Conventional entropy (S in Joules/Kelvin) is defined as:

$$\delta Q = T \delta S$$

This tells us that whenever heat enters a system there is also an entropy increase in the system (note: δ means small quantity).

Ok, wait, hold on a second here, isn't there something about entropy staying the same and not increasing? I remember something about Reversible or irreversible?

Yes, excellent, you were paying attention! The entropy of a system will increase for irreversible processes and remain constant for reversible processes. The difference between reversible and irreversible processes plays an important role in the 2nd Law of Thermodynamics.

Irreversible processes increase the entropy of the universe.

Reversible processes do not increase entropy in the universe.

It's important to note that reversible processes are like the frictionless pulleys that you've studied in previous physics courses. They are idealizations that are useful for problem solving, but they are just that, idealizations. Even if an experiment was designed to produce an ideal reversible process, it's likely that any external mechanisms required to initiate it would be irreversible, making the entire process

irreversible. What we usually deal with are **locally reversible processes**, which do not involve irreversibilities within the system we are studying. This would be something akin to us imagining that we are confining a gas to a cylinder within a piston.

One way to think about reversible versus irreversible is to imagine what you're looking at on video. Would it make sense for the process to naturally and spontaneously reverse? If yes, it is reversible. If no, it is not reversible. For example, if you were watching a pitcher of water being poured onto the ground in a video, would the reverse ever happen in nature? In other words, would the water ever come up off of the ground, flow up into the air, and go into the pitcher? It would not, thus the process is irreversible.

Frictionless movement and zero resistance electrical flow are examples of reversible processes. They art both idealizations just like the old frictionless pulley.

The mixing of matter of different compositions is a good example of an irreversible process. If you put sugar into iced tea, would the sugar ever completely remove itself and jump back out of the iced tea without intervention. It would not.

When looking at a reversible process:

$$dS = \frac{\delta Q}{T}$$

There seems to be a lot of talk about heat engines, and refrigerators, what's that all about?

Engines let energy do the work. A heat engine is a device that can take a source of heat and make it do work. The source of heat could be gasoline, natural gas, the sun, or any other suitable source. Generally, heat engines use the source of heat to turn a shaft. This rotating shaft can make things move (cars, boats, elevators, winches, etc.). Heat engines have four basic processes: **work input**, **heat input**, **work output**, **heat rejection**.

Imagine a truck engine. Work input is the compression of air in the cylinders. Heat input is the fuel burned in the cylinder. Work output pushes the piston, as work is output from the engine. Heat rejection is the exhaust from the engine.

Refrigerators, air conditioners, freezers, and heat pumps use the same thermodynamics. There are three basic processes: **heat input**, **work input**, and **heat rejection**.

Imagine a refrigerator. Heat input is absorbed from the cold space. Work input is added to the system. It pumps the heat absorbed from the cold space out to the hot space. Heat rejection is heat rejected to the hot space.

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To analyze thermodynamic processes such as heat engines and refrigerators it I necessary to follow a process path. To get an idea of a path, imagine making yourself a bowl of cereal. You could put the cereal in first and then the milk or you could put the milk in and then the cereal. When analyzing paths in thermodynamics it is easier when a path follows a property of the system that remains constant. You will learn more about this when you take an in-depth course in thermodynamics. Here's a brief overview of thermodynamic path types:

Isochoric or **isometric** paths have constant volume.
Isobaric paths have constant pressure.
Isothermal paths have constant temperature.
**Isenthalpic** paths have constant enthalpy.
Isentropic paths have constant entropy.
Adiabatic paths have no heat transfer.
Reversible paths return to their initial state unchanged.

There are also several cycles that you will learn about in your further studies in thermodynamics. Carnot, Rankine, and Stirling cycles are just a few of the most common you will study.

We'll limit this paper to a discussion of the Carnot cycle operating as a heat engine. The Carnot cycle is an ideal cycle in which all processes are reversible. It has four steps that alternate between isothermal and isentropic processes. Shown below is a Carnot cycle diagram.
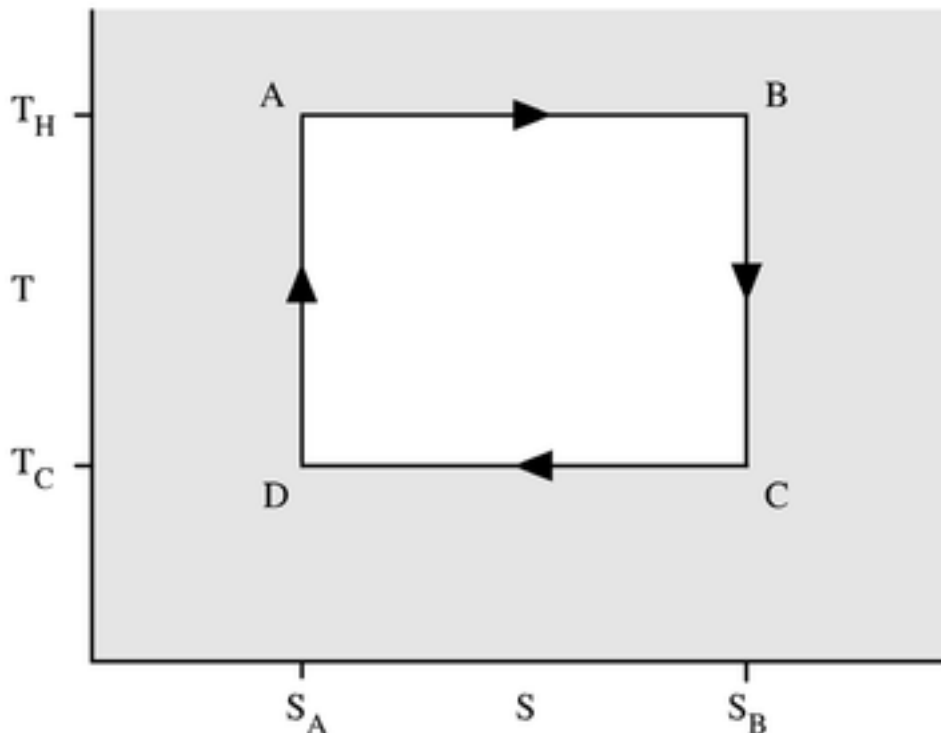
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This type of diagram is how heat engines are analyzed and you can see how entropy, thus the 2nd Law, plays an important role in the analysis.

The arrows indicate the direction of the process. In this case the direction is that of a heat engine. Starting at A and moving around the square: At AB heat flows in (isothermal) and work is being done on the system by the surroundings, at BC there is no heat flow (adiabatic) and this process disposes of excess entropy at a lower cost in heat, at CD heat is exhausted (isothermal) and excess entropy is eliminated at a lower temperature and lower cost in heat, at DA (adiabatic) isentropic work is done until the system is restored to its original temperature.

For the Carnot cycle:

$$Q_{entering system} = T_H \Delta S = T_H (S_B - S_A)$$

$$Q_{exhaust} = T_L |\Delta S| = T_L |S_B - S_A| = T_L (S_B - S_A)$$

Where does this get us you ask? Well, one place it gets us is that it allows us to calculate the **efficiency** (n) of a system. For the Carnot cycle the efficiency is calculated using:

$$n = 1 - \frac{Q_{exhaust}}{Q_{entering system}} = 1 - \frac{T_L (S_B - S_A)}{T_H (S_B - S_A)} = 1 - \frac{T_L}{T_H}$$

Hey, we got lucky, for the Carnot cycle efficiency is just a matter of knowing the upper and lower temperatures. You can see by the formula derivation, however, that entropy plays an important role in determining the efficiency of a heat engine. In most other cycles, entropy will not cancel out.

Furthermore, you can use this idealized cycle to determine what's called the **2nd Law efficiency**. This is found by dividing the coefficient of performance (the efficiency you need to get) by the efficiency (coefficient of performance) of a reversible heat cycle.

$$n_{2ndLaw} = \frac{COP}{COP_{reversible}}$$

So, okay, I get it, but what can we do with the 2nd Law?

Ok, so the 2nd Law of Thermodynamics helps us to understand a lot of things. First off, we've got the basic version of the law, which states that no process can decrease the total entropy of the universe. But, the universe is a pretty big place and we don't want to have to worry about calculating all of the entropy in the universe. So, a more

usable version of the 2nd Law is that no process can decrease the entropy of an isolated system. Calculating entropy in an isolated system is much more practical. Thermodynamic processes change energy from one form to another. The 2nd Law of Thermodynamics allows us to analyze the energy limits for thermodynamic processes. Basically, the 2nd Law can allow us to determine what is and isn't possible when creating something that uses energy to produce work or work to move heat.

Here are just some of the things that the 2nd Law of Thermodynamics allows us to do: determine the efficiency of refrigerators and heat engines, determine the degradation in energy quality in a process, understand the heat rejection process in refrigerators and heat engines, understand the heat input process in refrigerators and heat engines, understand energy quality, identify the natural direction of a process, see that disorder in a system and its surroundings always increases – that increasing the order of the system through work increases disorder on the surroundings of the system.

Okay, I'm ready, I'm excited, show me what I can do with the 2nd Law!

Okay, I'm glad you're excited. Let's put some of this new knowledge to work. These examples just scratch the surface of what you can do with knowledge of the 2nd Law and entropy.

Example 1:

It's a cold day outside and the building that you work in leaks heat to the outside at the rate of 2000 W. If the outdoor temperature is -10⁰ C how much is the outdoor entropy increasing per second?

Since heat flow is going to the outdoors, Q is positive. The heat from the building is very unlikely to cause any significant temperature increase outside of the building. Therefore we can assume $-10^0 C$ is a constant. The temperature must be in Kelvin. We haven't talked about this yet, but you should already be familiar with temperature conversion calculations from other science classes.

$$T_{Kelvin} = T_{Celsius} + 273.15$$
$$T_{Kelvin} = -10 + 273.15$$
$$T_{Kelvin} = 263.15$$

Remember that a 2000 W is equal to 2000 J/s. Therefore the heat (Q) leaked is a steady rate. The temperature is constant. We grab our formula from above $dS = \dfrac{\delta Q}{T}$.

Since Q and T are constant we can directly calculate the change in entropy (ΔS).

$$\Delta S = \frac{Q}{T} = \frac{2000\,J}{263.15\,K} \approx 7.600\,J/K$$

There we have it, the outdoor entropy is increasing at 7.600 J/K. Think of all of the buildings in the world. They all contribute to an entropy increase, thus less energy that can be used to do work in the future. Think about it!

Example 2:

You observe that when turning 20 g of liquid water at 0^0 C to solid water at 0^0 C (freezing it), 5,000 J of heat flows out of the water. How much does the entropy of the water decrease? If your lab partner said that the result is incorrect because the 2nd Law of Thermodynamics states that entropy cannot decrease, what would you say? Does this violate the 2nd Law?

Since heat flow is going out of the water, Q is negative.

Using the same calculations as in example 1 we have:

$$\Delta S = \frac{Q}{T} = \frac{-5,000\,J}{273.15\,K} \approx -18.3\,J/K$$

So, what gives here? It looks like we're losing entropy. Remember the 2nd Law:

There are reversible and irreversible processes. In processes that occur in an **isolated system**, the entropy of the system will increase for irreversible processes and remain constant for reversible processes. Entropy doesn't decrease. Keep in mind that the universe (as far as we know) is a closed system.

Since heat is flowing out of the system, it is **not isolated**. Once again we can see that just because we are shuffling entropy around and decreasing it in the water, overall entropy is not decreasing in the universe.

Example 3:

You are asked to design a steam engine that has a thermal efficiency of 45%.. Administrators at your company give you the choice between two different heat sources for the steam engine. One heat source reservoir is at 800^0C (high temperature) and the other is at $1,400^0$C (high temperature). The heat sink temperature (low temperature) is 30^0C. Determine the best choice for the heat source.

Change the temperatures to Kelvin.

30^0C = 303.15 K

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800^0C = 1073.15 K

$1,400^0$C = 1673.15

Calculate the Carnot efficiency for both designs using:

$$n = 1 - \frac{T_L}{T_H}$$

$$n_{800C} = 1 - \frac{303.15 K}{1073.15 K} \approx .718$$

$$n_{1400C} = 1 - \frac{303.15 K}{1673.15 K} \approx .819$$

Now let's find the 2nd Law efficiency.

$$n_{2ndLaw} = \frac{COP}{COP_{reversible}}$$

We want a thermal efficiency of 45% so COP = .45. We have two values to test using $COP_{reversible}$.

$$n_{2nd800} = \frac{.45}{.718} \approx .627$$

$$n_{2nd1400} = \frac{.45}{.819} \approx .549$$

Note that the higher temperature gives a better Carnot efficiency in the first calculation. However, the 800^0C heat source has a higher 2nd Law efficiency. It is better suited for this particular steam engine.

Ok, those questions aren't too bad. Does it get tougher?

Well, honesty is the best policy. It does get quite a bit tougher. Thermodynamics will put your math and physics skills to the test. Depending on your school and your instructor you may end up doing quite a few calculus-based derivations and even get into some differential equations. On the whole, it will be worth it. You will learn a lot and see the world in a new way.

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On that note, let's end on a final interesting tidbit regarding the 2nd Law. The 2nd Law makes it impossible to create a perpetual motion machine. A perpetual motion machine is one that can do limitless work without an energy source. Conmen have been "selling" the idea of perpetual motion machines for quite some time. A perpetual motion machine violates the 2nd Law of Thermodynamics. How, you say?

I'm going to let you look this one up on your own. It's a fascinating subject with a fascinating history.