Lesson 42d: Second Law of Thermodynamics & Entropy

The Second Law of Thermodynamics

If you take a can of Dr Pepper out of the fridge and walk outside on a hot summer day, you expect the drink to get warmer as time passes. You would never expect it to get colder.

- This is what the second law of thermodynamics is all about. If two objects at different temperatures come in contact with each other, the hotter one will get colder as the colder one gets hotter, until eventually they would be the same temperature.
- **The second law of thermodynamics says that heat will always spontaneously flow from a hotter to a colder object.**

We must consider this law (along with the first law) to be able to explain things like heat engines, refrigerators, and heat pumps.

Heat Engines

A heat engine uses energy to perform work, as shown in *Illustration 1*.

- The heat that is the **input** to run the engine comes from an area at a higher temperature, called a **hot reservoir**.
- Some of the input is used to do some actual **work**. This is the **output that we actually want**.
- The rest of the heat is released (basically as **waste**) to a **cold reservoir**.

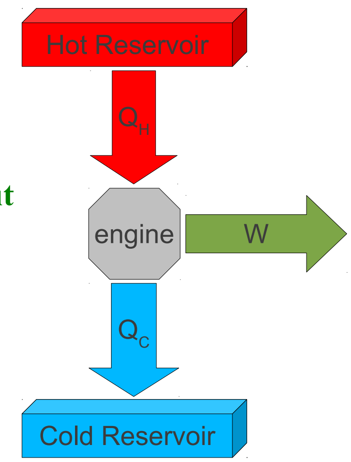


Illustration 1: A heat engine.

Notice how this obeys both the first and second laws.

- The **input heat** is equal to the **work** done plus the **heat released** (first law).

$$Q_h = W + Q_c$$

- The heat is flowing from the **hot** to the **cold** reservoir (second law).

An efficient heat engine should produce as much work as possible from the least input heat possible.

- To calculate the efficiency of a heat engine, we need to compare the work done to the input heat by dividing them.

$$e = \frac{W}{Q_h}$$

e = efficiency (%)
W = Work done (J)
Q_h = input heat from hot reservoir (J)
* N.B. All done as absolute values

Example 1: A automobile engine is able to do 2000 J of work to move a car. If the heat generated in the engine from burning the gas is 9000 J, **determine** the efficiency of the engine.

$$e = \frac{W}{Q_h} = \frac{2000}{9000} = 22.22\%$$

- We can take our formula for efficiency and combine it with the formula we have from above for the first law.

1st Law Formula...

$$\mathbf{Q_h = W + Q_c \rightarrow W = Q_h - Q_c}$$

combined with 2nd Law formula for efficiency...

$$e=\frac{W}{Q_h}$$

$$e=\frac{(Q_h-Q_c)}{Q_h}$$

We can divide each term on the top individually by Q_h.

$$e=\frac{Q_h}{Q_h}-\frac{Q_c}{Q_h}$$

$$e=1-\frac{Q_c}{Q_h}$$

To be able to solve for a formula in the next section, we need to write this formula this way. Trust me.

- This version of the formula for the efficiency of a heat engine lets us do a calculation if we know the input heat from the hot reservoir and the output heat to the cold reservoir.

Example 2: A heat engine is running with an input of heat of 1.45e4 J. If it dumps 1.02e4 J of waste heat into its surroundings, **determine** the efficiency of the engine.

$$e=1-\frac{Q_c}{Q_h}$$

$$e=1-\frac{1.02\text{e}4}{1.45\text{e}4}$$

$$e=29.7\%$$

Carnot's Heat Engine

By the early 1800's physicists were asking themselves if there was a limit to how efficient an engine *could* be.

- It may sound like an easy question, with an answer of 100%.
  - Sadly, this is impossible, and Sadi Carnot is the man who proved it using his own way of looking at the second law.
- According to Carnot, a heat engine reaches maximum efficiency if everything about it is reversible.
  - What he meant by reversible is that it would be possible for the engine itself(the system), and everything around the engine (the surroundings) to return to exactly the same states they were in before the engine was running.
    - In real life this is most often impossible because of the effect of friction. The waste heat that is released from friction can not be returned.
    - Even without friction, many processes would not be reversible since heat would need to flow on its own from cold to hot, and the second law says that can't happen.
  - Still Carnot's ideas about heat engines are helpful, since **a Carnot Engine let us predict the best theoretical efficiency of an engine in a particular situation. We know that any real engine must have an efficiency less than the Carnot engine in that same situation.**

The second law can be said this way.

To figure this all out, Carnot focused on the temperatures of the hot and cold reservoirs of the heat engine.

- He reasoned that the best possible engine would be one that did the most work based on the temperature difference that it had available between the two reservoirs.
  - Kind of think of it like we want the hottest hot reservoir possible to draw from, and the coldest cold reservoir to dump in to. We hope this means a lot of heat will be available to change into work.
- It can be shown that the ratio of the heat of the two reservoirs is equivalent to the ratio of their temperatures.

$$\frac{Q_c}{Q_h}=\frac{T_c}{T_h}$$

*N.B. Temperatures must be measure in Kelvin.

- We can substitute this into the formula for efficiency that we came up with above.

$$e=1-\frac{Q_c}{Q_h}$$

$$e_c=1-\frac{T_c}{T_h}$$

$$e_c=\frac{(T_h-T_c)}{T_h}$$

This is the efficiency of a Carnot heat engine as it appears on the data sheet. Remember to use Kelvin for the temperature.

If you look at the second last line of formula substitution above, you might get an idea of why a 100% efficient engine is simply impossible.

$$e_c=1-\frac{T_c}{T_h}$$

Even in Carnot's perfectly reversible engine, there must be a difference in temperature between the two reservoirs, so that heat can flow on its own (second law). Since $T_c < T_h$, we will always be subtracting some decimal from 1 in the formula. That gives us an efficiency less that 100%.

Example 3: You want to set up a heat engine that attaches to your window in the winter time, so that it uses the inside of your house at 22ºC as the hot reservoir, and the outdoors at -18ºC as the cold reservoir. **Determine** the maximum efficiency of this engine. Also **explain** a drawback of this setup.

$$e_c=\frac{(T_h-T_c)}{T_h}$$

$$e_c=\frac{(295-255)}{295}$$

$$e_c=13.6\%$$

There are a couple of drawbacks that might be worth mentioning. First of all, 13.6% is not exactly a great efficiency; there's probably a better way to get some work done.
The second reason goes against the common idea that this is still free work you're getting just because your home is warmer than outside. You're forgetting that the heating system of your home needs to use energy to heat your home. By using you heat engine on your window, you force your home heating system to work harder to keep the temperature of the house up. Since the heating system can not work at 100% efficiency, you are actually wasting more heat.

Refrigerators and Heat Pumps

Heat will never flow on its own (spontaneously) from cold to hot, but that doesn't mean we can't force it to!

- A device like a **refrigerator** is basically a heat engine that runs in reverse, so that we do **work** to move heat from a **cold reservoir** to a **hot reservoir**.
- For a fridge in your home, doing **work** to pump the heat out of **cold reservoir** (**inside** the fridge) to the **hot reservoir** (the **coils** on the back / bottom on the outside of the fridge) will make the **inside** colder and the **outside** (your **kitchen**) warmer.
- This still agrees with the 1st law, since $\mathbf{Q_h = W + Q_c}$ is still true.
- It also agrees with the 2nd law, since none of this happened spontaneously.

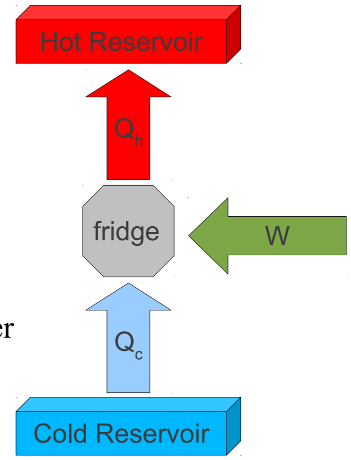


Illustration 2: A refrigerator.

A **heat pump** is a device that works like a refrigerator, except that it is used to heat a building in cold weather.

- For a heat pump, the cold reservoir is the outdoors, and the hot reservoir is the inside of the building.
- Electricity is used to do the work of pumping the heat.

DID YOU KNOW?
An air conditioner is basically the same as a refrigerator. The difference is that your entire house is the cold reservoir, and the outdoors is the hot reservoir.

Example 4: **Explain** why a heat pump is better for heating a home than a regular plug in space heater from WalMart. Assume that you have 500 J of electrical energy to do the work of running either one.

Let's start with the regular space heater you bought for cheap at WalMart. It probably just has a bunch of heating coils that get hot when you plug it in. We'll give it the benefit of the doubt and say it is 100% efficient, so that all 500 J of electricity going in (the work) becomes 500 J of heat for your home.

$$Q_h = W + Q_c$$
$$Q_h = W + 0$$
$$Q_h = W$$
$$Q_h = 500 \text{ J}$$

There is no cold reservoir for a space heater.

Now we look at the heat pump. It follows the same rules a refrigerator, so it is moving heat from a cold reservoir to a hot reservoir. Because of this, Q_c must be more than zero!

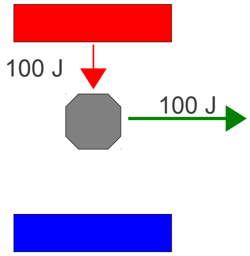
$$Q_h = W + Q_c$$
$$Q_h = 500 + Q_c$$
$$Q_h > 500 \text{ J}$$

If Q_c is some number bigger than zero, Q_h must be more than just 500 J.

So the heat pump results in more heat being transferred to the room than just the 500 J from the work done. Although this is great, the disadvantage is that a heat pump must be installed with some sort of hose to the outside to use outdoors as a cold reservoir.

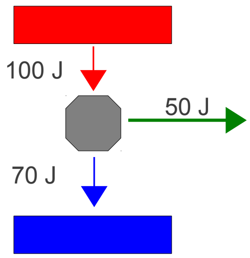
Example 5: For each of these diagrams, **explain** why the process shown is impossible.

a)



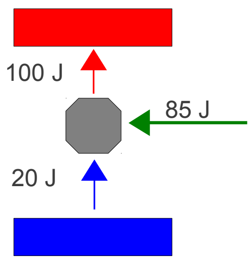
In this situation all of the heat from the hot reservoir is being converted to work; no heat is going to the cold reservoir. This violates the 2nd law, since heat flows from hot to cold, and no system can be 100% efficient.

b)



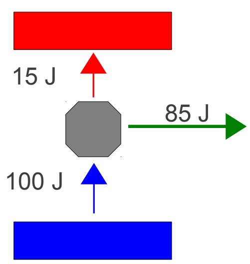
In this case we have 100 J of heat from the hot reservoir doing 50 J of work and 70 J of heat moving to the cold reservoir. A quick check shows that this breaks the first law, since $Q_h = W + Q_c \rightarrow 100 \neq 50 + 70$

c)



This one is acting as a refrigerator, which on its own is fine, but it's the numbers that are all screwed up. It breaks the first law (sort of like the last example), since $Q_h = W + Q_c \rightarrow 100 \neq 85 + 20$

d)



Again, a refrigerator. This one looks like it might be fine because as 100 J goes into the engine, 100 J comes out (15 J to the hot reservoir and 85 J of work). The only problem is that for a fridge to function, the work has to be done on the engine, not by the engine. This violates the 2nd law.

Entropy

In the real world, no matter what we do there is no such think as a perfect engine or fridge. Every process is going to involve some friction and loss of usable energy.

- Even in a perfect situation with a Carnot engine, the temperature between the hot and cold reservoirs will eventually become the same (thermal equilibrium) since the heat will always flow from hot to cold.
    - When we reach this point and $T_c = T_h$, efficiency becomes zero according to the formula...

$$e_c = 1 - \frac{T_c}{T_h}$$

$$e_c = 1 - \frac{T_h}{T_h}$$

$$e_c = 1 - 1 = 0\%$$

- Eventually, some day in the very distant future, when all the possible processes have happened, all the universe will be at the same temperature with absolutely no way for anything to do any work any more.
    - This is sometimes referred to as the "heat death of the universe," or less dramatically ***entropy***.

Entropy is a measure of the disorder of a system.
- On their own, all systems tend towards an increase in entropy unless work is done on them.
- This is actually just a different way of stating the second law.

As an example, you accidentally push a vase off a table and it breaks when it hits the ground.
- This increases the disorder of the system.
    - Although we could put it back together with glue and a bit of effort, this means that we would have to do work on the system to decrease its entropy.
    - If we left it alone, we would never expect the vase to glue itself back together. Although this would not break the first law, it does violate the second law.