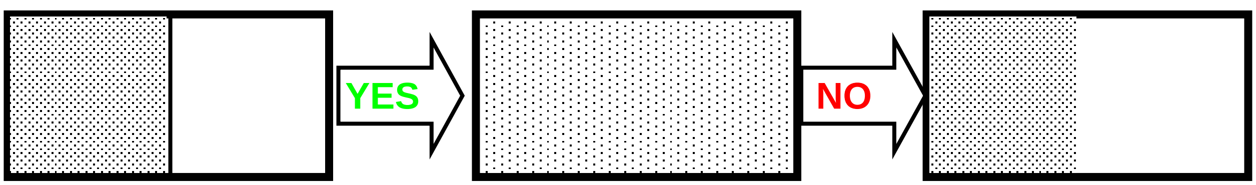
29:011 THE SECOND LAW OF THERMODYNAMICS

I. There are no processes that violate the 1st law ($\Delta U = Q - W$). There are processes, however, that although they *do not violate* the 1st law, never occur. Some examples:

[1] If an aluminum block is given a kick on a rough surface, it moves a bit, then stops. The kinetic energy given to the block is dissipated as heat due to friction. The opposite process is never observed. If a stationary aluminum block is heated with a torch, we never observe that it begins to move. Why not? The heat that enters the block is shared among all the Al atoms- increasing their kinetic energy. This kinetic energy, however, is random kinetic energy – the atoms move around in all directions. Now for the heated block to begin to move in a particular direction, all the atoms in the block would have to move all in the same direction. While it is not impossible, that by chance all the atoms happen to be moving in the same direction at the same time, it is extremely unlikely. What is the chance that 10^{25} atoms which were all given some random energy suddenly all move in the same direction? Notice that according to energy conservation (1st Law) this would not be prohibited. It is prohibited by the 2nd Law.

[2] Suppose we have a gas in a box that has a partition separating the left and right sides. Initially all the gas atoms are put into the left side of the box. When the partition is removed, we observe that the gas atoms spread out and completely fill the box. This is the outcome of the



spontaneous process of gas expansion. Now, think about the possibility that at some later time we observe that the atoms are all on either the right or left side of the box. It is possible that by chance all the atoms happen to be moving in the same direction, say to the left, at some time, so they all end up momentarily on the left side of the box. What are the chances that 10^{23} atoms all move to the left at the same time? This does not occur.

[3] We always observe that when ice is placed in water, the ice melts and the water gets colder. We never observe that the ice gets colder and the water gets warmer. This later possibility is NOT prohibited by the 1st Law – which tells us that if there is a heat transfer between the ice and the water, it is perfectly fine if a certain amount of heat flows from the ice (making it colder) while an equivalent amount of heat flows into the water (making it warmer). The direction of heat flow in a spontaneous process is from hot to cold as required by the 2nd law.

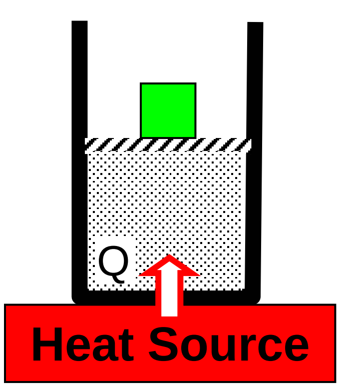
II. The principle that specifies the direction in which spontaneous processes proceed is the Second Law of Thermodynamics.

When we say that a certain process does not occur, we a really saying that the probability for it to occur is extremely low. The behavior of systems having very large numbers of particles (macroscopic systems) is to a certain degree governed by probabilities. We might find that a process may be possible, but it may only occur after a time longer than the age of the universe, so effectively it never occurs. Processes that would otherwise not be prohibited by the 1st law may never be observed because out of the trillion-trillions of ways that the system can evolve, very few of these outcomes leads to that state.

For example: Think about tossing 100 coins. What are the chances that they all land heads up or all tails up? It is about one chance in 10^{15}! If you could toss the coils once per second, you would, on average, need at least 10^{17} s to see this occurrence. (The age of the universe is about 10^{17} s.) The reason why this occurrence is so rare is that there is only one way to achieve it – every coin lands heads up.

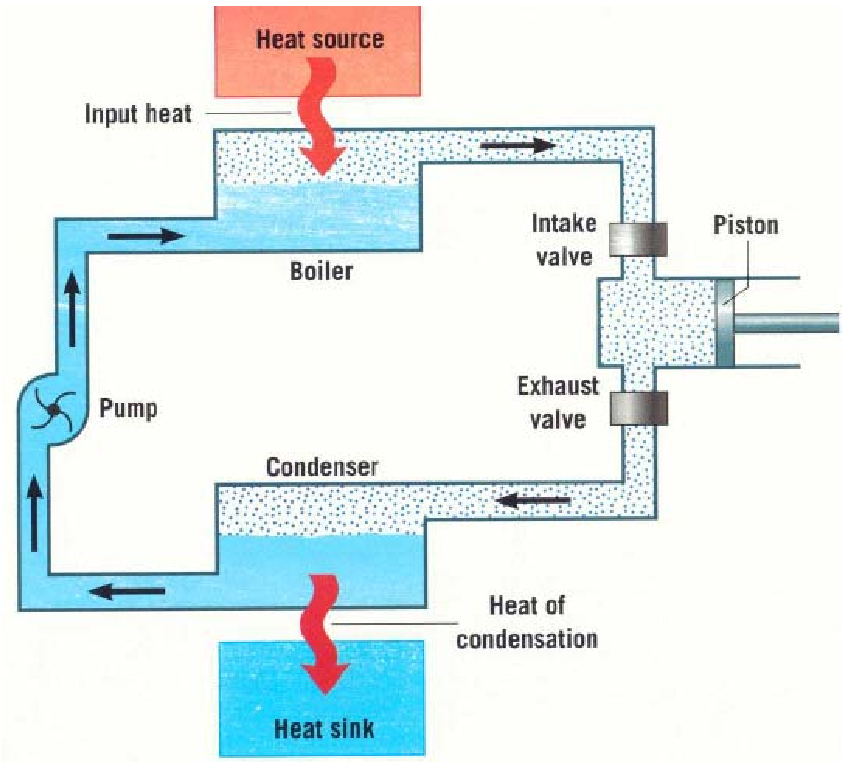
III. Heat Engines

Heat engines are devices which use heat to perform work. They are constrained by the 1st law of thermodynamics. For example, a gas absorbs heat, and does work on the weight as it expands and lifts the weight. In a practical sense however, this is not a useful engine because it cannot be carried on indefinitely.

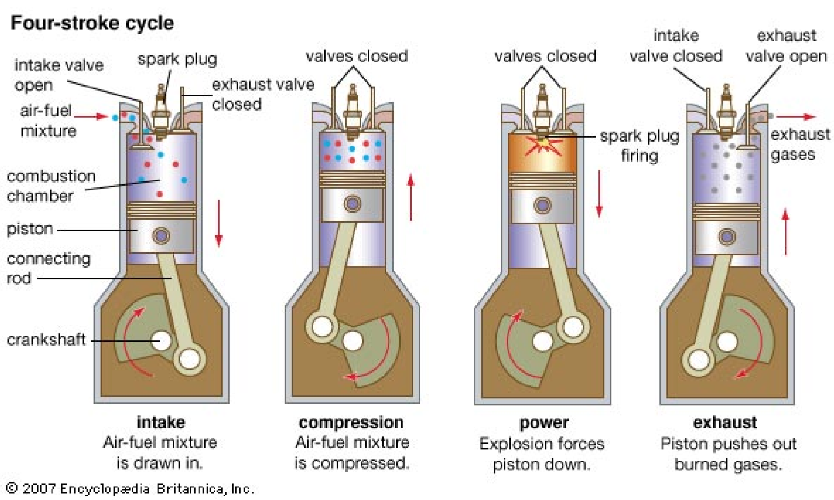


Heat engines must operate cyclically --take in heat, convert some heat to work, return to the original state and repeat the process. In a cyclic heat engine, the working substance, e.g., the gas, is always returned exactly to its original state at the end of the cycle, $U_f = U_i$. Thermodynamically this means that $\Delta U = 0$ in a cyclic engine. Examples of two heat engines

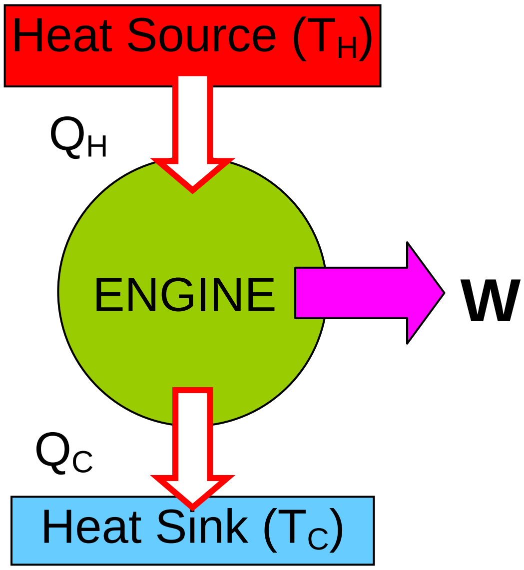
1. steam engine



2. internal combustion engine



IV. Analysis of the Generic Heat Engine



- The heat source may use gas, oil, coal, wood, or nuclear energy to make steam
- The heat enters the engine and increases its internal energy
- Some of the internal energy is used to do work
- The excess heat is discarded to the heat sink, bringing the system back to its original state.

Apply the 1st law:

$$\Delta U = 0 = Q - W = (Q_H - Q_C) - W$$

$$\rightarrow W = Q_H - Q_C$$

Engine efficiency:

$$e \equiv \frac{\text{useful output}}{\text{what must go in}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

V. The Second Law of Thermodynamics (Kelvin Statement)

It is impossible to construct an engine whose sole effect is to transform heat from a source at one temperature into work.

This says in effect that a heat engine with e = 100% is impossible; some of the heat extracted from the high temperature source must be discarded to a low temperature sink.

VI. The Carnot Engine

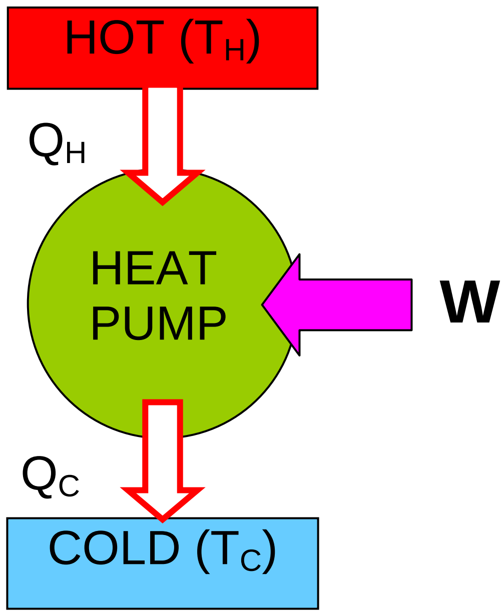
One might ask, how should a heat engine be operated so that for a given T_H and T_C the efficiency is as large as possible. This question was addressed and answered by S. Carnot in 1824. Carnot discovered that the most efficient heat engine is one in which all of the processes are carried out *reversibly*. A reversible process is one in which at any point in the process, the process can be reversed and the system returned to its pervious state. Practically speaking, it means that the processes (compression and expansion of the gas) are carried out in such a way that the system is always very close to equilibrium. For example, we imaging a gas in a container with a lid and a pile of sand is placed on the lid. The gas is allowed to expand by removing one grain of sand at a time. The concept of a reversible process is an ideal one, no real processes are truly reversible. Further, Carnot found that an engine run with only reversible processes, will have an efficiency that depends only on T_H and T_C, and furthermore, all engines operating between the same T_H and T_C will have the same efficiency independent of the working substance of the engine. Since the efficiency depends on Q_C/Q_H, This means that for a Carnot engine: $Q_C/Q_H = T_C/T_H$, so that the efficiency of a Carnot engine is: $e_{Carnot} = 1 - T_C/T_H$.

VII. Other Statements of the Second Law of Thermodynamics

There are a number of alternate statements of the 2nd law that contain essentially the same physical content.

[1] The efficiency of a Carnot engine is larger than the efficiency of any other engine operating between the same temperatures $e < e_{Carnot}$, where e is the efficiency of an engine not using exclusively reversible processes.

[2] Clausius statement: ***Heat flows spontaneously from a body at a high temperature to one at a lower temperature.***



Heat can be made to flow "backwards" but this requires that work must be done on the system.

This is what occurs in a refrigerator or air conditioner. Refrigerators and air conditioners are *heat pumps*, that transfer heat from inside the refrigerator (cold) to outside the refrigerator (warm).This does not occur spontaneously, but requires the input of electrical energy.

[3] ***Spontaneous processes proceed from more ordered to less ordered states***

e.g., ice $\rightarrow$ water $\rightarrow$ steam. Ice is a more ordered state than water which is more ordered than the gaseous state. As a system evolves spontaneously, there are many fewer ways in which a more ordered state can be achieved as compared to an ordered state. The more ways there are to get to a particular state, the more likely it is that the system will be found in that state.

For example, there is only one way to get 100 heads to appear when 100 coins are tossed, but many more ways to get to the state with roughly a 50:50 head to tail ratio. In the demonstration shown in class, a collection of 20 white ping pong balls and 20 orange ping pong balls are arranged neatly in 4 rows—white, orange, white orange. This is an ordered state. The box containing the ping pong balls is then shaken and the white and orange balls are mixed up. The mixed up state is less ordered than the initial state. If the box is continued to be shake, is it possible that the original ordered state may reoccur at some time? It is possible, but very unlikely, because the ways in which the balls can get back to the ordered state is far less that the ways in which the balls can get to a disordered state. *The second law of thermodynamics tells us that spontaneous processes always proceed from order to disorder.*