Heat engines and the second law of thermodynamics

**Thermodynamic cycles**

A thermodynamic cycle is a series of processes which change the volume, temperature and pressure of a gas, but which at the end return to the same conditions as at the start. Thermodynamic cycles are important because if we can find one that does something useful for us, it can be repeated indefinitely. Understanding of thermodynamic cycles was extremely important to the industrial revolution and they remain key to most large scale manufacturing processes, to most engines, refrigerators and air conditioners.

**Heat engines and refrigerators**

The basic principles which enable heat engines and refrigerators to work are as follows: (i) (heat engine) If you allow a gas to expand by moving a piston, then the gas does work on the piston. In this way the kinetic energy in the gas is converted into useful work (moving the piston). When the gas expands, it cools down so at the end of the expansion, we have to heat the gas up again. This is achieved by burning some kind of fuel, e.g. gasoline, coal, nuclear fuel, hydrogen etc. (ii) (refrigerator or heat pump) If you want to take heat from a house and pump it outside, you have to take heat from a colder region and move it to a hotter region. This is achieved by using evaporation of a “coolant” liquid. Evaporation of the coolant requires energy (latent heat of vaporization) and this energy is taken from the inside of the object (or rooms) which we want to cool. Once the coolant has evaporated, it is pumped to the compressor, which liquifies the coolant again to complete the cycle. In a refrigerator, the compressor is inside the house, while for an air conditioner, the compressor is outside the house. In designing a heat engine or heat pump many decisions have to be made, e.g. what is the fuel?, what is the working gas?, what is the nature of the thermodynamic cycle?. Heat engines, such as electrical generators and gasoline engines, use an expanding gas to drive a piston or turbine. In a gasoline engine the expanding gas is a mixture of the products of burning air and gasoline. In a turbine steam is usually used. In a refrigerator or air conditioner evaporation of a coolant gas is used (e.g. Freon, Ammonia, FR-12 etc.).

Heat engines work on a cycle where an incoming gas at low temperature $T_c$ is heated to a higher temperature $T_h$ causing expansion of the gas, which in turn does the mechanical work on the piston or turbine. At the end of
the expansion, the working gas still has some heat which is typically lost as waste heat. We define the heat which is added to the gas to cause expansion to be $|Q_h|$, while the heat lost is $|Q_c|$. The efficiency of the engine is defined to be,

$$ e = \frac{W}{|Q_h|} \quad (1) $$

Since the working gas at the end of the cycle is at the same temperature at which it started, the internal energy is the same at the beginning and at the end. The work done by the engine is then $W_{eng} = |Q_h| - |Q_c|$, so the efficiency of the heat engine is given by,

$$ e = \frac{W}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} \quad (2) $$

The efficiency is in the range $0 \leq e \leq 1$. E.g. for gasoline engines typical efficiencies are of order 0.25 or 25 percent. A refrigerator is a heat engine in reverse, so that work is done to extract heat from a cold reservoir. This is achieved by evaporating a gas, which extracts heat from its surroundings. For a refrigerator or air conditioner, the coefficient of performance is,

$$ COP = \frac{|Q_c|}{W} \quad (3) $$

The COP can be greater than one, e.g. 3 is a typical number for a house air conditioner. The Carnot cycle produces the most efficient heat engine possible. The four steps in a Carnot cycle are: Isothermal expansion; Adiabatic expansion; Isothermal compression; Adiabatic compression. For the Carnot cycle, the efficiency is given by,

$$ e_C = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h} \quad (4) $$

It is quite hard to prove that the Carnot cycle is the most efficient cycle possible. By reversing the cycle, the Carnot cycle can act as a refrigerator or air conditioner, and in that case, the Carnot coefficient of performance is given by,

$$ COP_C = \frac{|Q_c|}{|Q_h| - |Q_c|} = \frac{T_c}{T_h - T_c} \quad (5) $$
Human metabolism

The average metabolic rate for people in the age range 20-30 is $40 \text{kcal/m}^2\text{hr}$ hr for males and $37 \text{kcal/m}^2\text{hr}$ for females. Note that multiplying this by 24 hours and an average surface area($1.9\text{m}^2$ for adult men and $1.6\text{m}^2$ for adult women) gives the target consumption of an adult. The metabolic rate of a person can be measured quite easily by measuring the amount of oxygen which is consumed per unit time. The relation is,

$$\frac{\Delta U}{\Delta t} = 4.8\frac{\Delta V_{\text{oxygen}}}{\Delta t}$$

where the result is in $\text{kcal/s}$ and the oxygen volume if is $\text{liters/s}$. Many performance enhancing drugs aim at increasing the oxygen transport rate through the blood system in order to increase metabolic rate. Typical metabolic rates for some tasks are: sleeping ($80\text{W}$), walking ($450\text{W}$), extreme sport ($1600\text{W}$). A person’s fitness can be measured though his/her ability to use oxygen, with a couch potato having a peak oxygen consumption rate of $28\text{mL/minkg}$ and Lance Armstrong having a peak consumption rate of $70\text{mL/minkg}$. Since by the equation above this translates directly into the energy available to the human body, a high oxygen consumption rate is essential to high activity. The metabolic rate is the amount of power available to the human body. The efficiency of our metabolism is the rate at which mechanical work is done divided by the metabolic rate for the task, ie.

$$e = \frac{W}{\Delta t}/\frac{\Delta U}{\Delta t}$$

The efficiency of humans at some tasks are approximately: shovelling (0.03), bike riding (0.19). This means that the $1600\text{W}$ available for an extreme sportsperson translates into roughly $0.19 * 1600\text{W} = 304\text{W}$ of mechanical work for a cyclist.

Entropy

Entropy is a very important concept in thermodynamics and is also important in philosophical and religious discussions about whether life could possibly have originated spontaneously on our planet.
Entropy is a measure of the amount of disorder in a system. If a system has a lot of different possible configurations, it has high entropy. For example if 100 particles of an ideal gas move randomly in a volume $V$, then the gas has entropy $S$. If the same 100 particles are given the same kinetic energy and are placed in volume $2V$, then when the gas in the larger volume has higher entropy because it has a much larger number of possible configurations. Boltzmann introduced a quantity $\Omega$, which is the total number of “states” which are available to the gas. It is evident that if the kinetic energy of a gas is fixed, then $\Omega(V,T) < \Omega(2V,T)$. In fact, Boltzmann was able to prove a general relation, that the entropy is given by,

$$S = k_B \ln(\Omega)$$ \hspace{1cm} (8)

where $S$ is the entropy, $k_B$ is Boltzmann’s constant and $\Omega$ is the number of states available to the system.

The second law of thermodynamics: In an isolated system, the entropy either stays the same or it increases.

The second law means that in an isolated system the disorder can either stay the same or increase. If we consider that our universe is an isolated system, then the amount of order in our universe can only decrease or stay the same. So how can life, which is very ordered, arise?? They key issue is that parts of our universe can become more ordered provided other parts become more disordered, provided that the net effect does not violate the second law. Note also that disorder does not imply high temperatures. Gas particles in interstellar space (which is at $2.3K$) have very high entropy because they have a lot of volume to move in.

When does entropy stay the same? An important observation is that when heat is added to a system at fixed temperature, the system must expand. This expansion leads to an increase in volume and hence an increase in entropy. In fact the increase in entropy of an equilibrium process at temperature $T$ is given by,

$$\Delta S = \frac{Q_{\text{rev}}}{T} \hspace{1cm} (\text{equilibrium process})$$ \hspace{1cm} (9)

Equilibrium processes are also called reversible processes. The discussion of thermodynamic cycles given above are all based on the assumption of
equilibrium. If equilibrium does not occur, then the efficiency is reduced further.

An example of a non-equilibrium process is the free expansion of a gas in a thermodynamically isolated system. This is called an adiabatic expansion as no heat enters or leaves the gas. In this system, the gas particles have the same kinetic energy before and after the expansion. Therefore the temperature is the same before and after. Since no work is done and no heat is added, the internal energy does not change. However the entropy is larger due to the larger volume. This is an example of a process in which \( \Delta S > 0 \) and is used as an simple example of an expanding universe. Of course our universe is influenced by a gravitational potential which needs to be considered in a complete discussion.