

Thermodynamics

Thermodynamic variable: A thermodynamic variable is a system property whose *change* for any process depends *only* on the *initial and final states* of a system. Another term for this could be *state variable*. One example is temperature T . Consider ΔT for a cup of coffee that is initially very hot (the initial state). You can let it sit on your desk for a few hours, at which point it will be at room temperature (our final state). Or, you could sometime in the morning decide to put it back in the microwave and heat it back up, but subsequently forget about it a second time, allowing it to cool to room temperature. The path by which the cup reached its final temperature is different in the two cases, but ΔT is exactly the same, thus T is a thermodynamic quantity. Variables that do depend on path are known as (not surprisingly) *path variables*.

Internal Energy U : Internal energy is a state variable that can be thought of as the energy of the system (sensible, latent, chemical bond, nuclear etc.). It's not obvious how to define it, and thus it's much easier to discuss changes in internal energy rather than absolute values (which is true of many state variables).

Enthalpy H : Enthalpy is a state variable that is most easily thought of as heat energy, although strictly speaking it's only heat energy in a system that is at constant pressure and which experiences no other work (other than constant pressure expansion).

Entropy S : Entropy has many definitions, many of which are applicable under specific circumstances. We'll think of S as a measure of disorder, i.e. higher values of S are systems with greater disorder. A similar but slightly different view is that S represents the number of possible states for a system. This latter view explains why my bedroom is rarely neat. There are very few ways in which my bedroom, with all the clothes, books, etc. can be considered tidy. There are many configurations in which it would be considered messy. A spontaneous change is unlikely to result in a more orderly room (it's uncommon for a thrown t-shirt to end up folded and in the right drawer of my dresser), thus over time things get messy.

Gibbs Free Energy G : $G = H - TS$, or equivalently, $\Delta G = \Delta H - \Delta(TS)$. G can be thought of as the energy relevant to chemical reactions, and thus involves both enthalpy and entropy. A reaction is *spontaneous* if $\Delta G < 0$ for a reaction, i.e. it can occur without the input of energy. To satisfy this requirement, a reaction can either stabilize molecules (leading to $\Delta H < 0$) or it can create greater disorder ($\Delta S > 0$), or both.

Heat energy Q : The heat exchanged between a system and its environment for some change in state is a path variable. We'll define positive Q as the heat added to a system. Note that we don't write ΔQ since it is a path variable. We could use some notation like $Q_{||path}$ to emphasize that Q is a path variable, but we usually dispense with the clumsy notation and just write Q .

Work W : The work exchanged between a system and its environment for some change in state is a path variable. We'll define positive W as the work done on a system.

Example: If I drive from home to my office, the gravitational potential energy of the system (car + me) is a state variable. However, the amount of work the system does (i.e. how much gasoline is consumed) to create this change in state depends on the path, i.e. if I drive via San

Francisco, or take a direct route. These two paths also differ in how much heat is released by the system. Thus, work and heat released must be path variables.

First Law of Thermodynamics

The first law says that:

$$\Delta U = Q + W \tag{1}$$

which is simply a statement of conservation of energy, with the subtlety that it also expresses the equivalence of work and heat as forms of energy. To re-word this law, the sum of all work and heat added to the system must be conserved, and is thus taken up as internal energy of the system. So for the example we're using, driving to campus via San Francisco causes more work on the system (large positive W), but also leads to a large release of heat to the environment (large negative Q). The sum of these two will be slightly positive due to the positive change in potential energy ($PE_{final} - PE_{initial}$).

The first law, however, does not necessarily tell us which direction a *spontaneous* change will occur. While in many cases systems will tend towards energy minima, this isn't always the case. An ice cube at a temperature above freezing will spontaneously melt, this this melting requires energy to be added to the system. The molecules in Francis' aftershave will spontaneously spread throughout a room even though there is no energy change. Many spontaneous chemical reactions are *endothermic* (require heat energy, i.e. $Q > 0$, as opposed to *exothermic*), which again is going away from minimum energy. We need to invoke the second law to understand some of these problems.

Second Law of Thermodynamics

To understand the second law, we need to know a bit about entropy, which is defined as:

$$\Delta S = \frac{Q_{rev}}{T} \tag{2}$$

where the subscript "rev" indicates a reversible addition or removal of heat from the system. This is an idealized transfer of heat, in essence one that occurs infinitesimally slowly such that at any moment, a tiny change can reverse the direction of heat transfer. The odd thing about the definition of entropy is that it appears to depend on a path variable. But the fact that the heat transfer isn't just any type of heat transfer, but only along a special kind of path, allows it to be a state variable. Put another way, calculating changes in entropy from one state to another, we must construct a special kind of path between these two states, one where the heat is transferred reversibly. Since all paths are equivalent for a state variable like entropy, we're permitted to do this.

The second law of thermodynamics can be stated in lots of different and equivalent ways. Here's one common way:

$$\text{For an isolated system, } \Delta S \geq \frac{Q}{T} \tag{3}$$

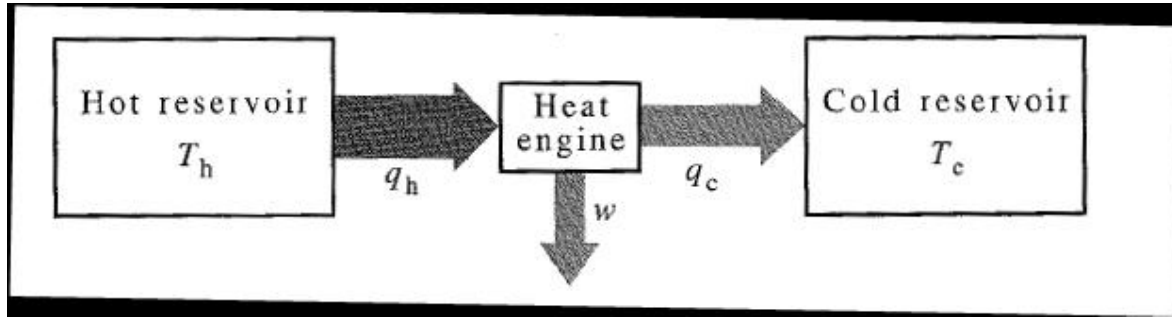


Figure 1: Carnot heat engine

which says that the entropy change in any isolated system (which is defined as one that can not exchange either mass or heat with its surroundings) will either stay the same or increase. The equality is true only if Q is reversible for any changes to this isolated system, otherwise the inequality must be used.

Carnot Engine

A Carnot engine is an idealized engine which produces work by extracting energy from a hot reservoir, and releasing heat to a cold reservoir in a cyclic manner. The difference in these energies is the work that can be done. The maximum efficiency of such an engine occurs when no entropy is generated, which means that the heat transferred must be reversible.

Because the process is cyclic and reversible, it is true that:

$$\Delta U_{engine} = W + Q_{h,rev} - Q_{c,rev} = 0 \quad (4)$$

and

$$\Delta S_{engine} = \frac{Q_{h,rev}}{T_h} - \frac{Q_{c,rev}}{T_c} = 0 \quad (5)$$

We will define efficiency as:

$$\text{efficiency} = \frac{-W}{Q_{h,rev}} \quad (6)$$

(Recall that we defined W as work done on a system, so to get work done by the system, we take the negative). If we take Eq. 4 and substitute W from this equation into Eq. 6, we get:

$$\text{maximum efficiency} = -\frac{W}{Q_{h,rev}} = \frac{Q_{h,rev} - Q_{c,rev}}{Q_{h,rev}} \quad (7)$$

Now if we substitute for $Q_{c,rev}$ using Eq. 5, we get:

$$\text{maximum efficiency} = \frac{Q_{h,rev} - Q_{c,rev}}{Q_{h,rev}} = \frac{Q_{h,rev} - Q_{h,rev} \left(\frac{T_c}{T_h} \right)}{Q_{h,rev}} = \frac{T_h - T_c}{T_h} \quad (8)$$

This is an amazing result, since it is a general result that doesn't depend on the nature of the engine! Note that living creatures don't qualify as Carnot engines, which is probably a good thing (see examples). We can probably convince ourselves of this in a simple way: if humans were Carnot engines, and the cold reservoir to which we dump heat is the surrounding air, then we would completely fail to be able to do work if the temperature rises above our body temperatures!

Examples: Hurricanes; a human climbing a mountain if we were Carnot engines.