

Chapter N

Entropy and the Second Law of Thermodynamics

Entropy

Definition of Entropy

Entropy S is a measure of disorder. One is not used to thinking of disorder as a precise notion that can be quantified, but it turns out that we can give it a precise definition. Doing so is beyond the scope of this course.

If we add heat to a system then we increase its disorder. For example, water at 0°C is a more disordered state than ice at 0°C ; to go from ice to water requires only heat. We define entropy as the state function whose exact differential is given by

$$dS = \frac{dQ}{T}.$$

Equivalently, we can define it as an integral

$$\Delta S = \int \frac{dQ}{T}.$$

When heat is added to a system its entropy increases. When it is removed ($Q < 0$) it decreases.

Constant Temperature and Latent Heats

If the temperature T is a constant then we can take it out of the integral and since $Q = \int dQ$ we get.

$$\Delta S = \frac{Q}{T}.$$

When some substance changes phase, its temperature stays constant. In that case the heat can be written in terms of the latent heat and mass.

$$Q = \pm mL$$

Temperature Change and Specific Heats

We may now more precisely relate heat and specific heat using inexact differentials. An infinitesimal temperature change dT requires the infinitesimal quantity of heat dQ .

$$\begin{aligned} dQ &= mc dT \\ \Delta S &= \int \frac{dQ}{T} = mc \int_{T_i}^{T_f} \frac{dT}{T}. \end{aligned}$$

The integral gives the natural log and we get

$$\Delta S = mc \ln \frac{T_f}{T_i}.$$

The Second Law of Thermodynamics

Statement of the Second Law

A thermally isolated system is one with no heat entering or leaving it. This could consist of smaller systems exchanging heat between them but no heat is allowed to leave or enter the larger system. The total change in entropy for a system is written as ΔS_{tot} .

For a thermally isolated system the total change in entropy cannot be negative.

$$\Delta S_{\text{tot}} \geq 0$$

Heat Reservoirs

In thermodynamics we define a reservoir to be something sufficiently large to maintain a constant temperature given whatever amount of heat exchange as is relevant. If the amount of heat transferred is sufficiently small then a reservoir could be as small as a glass of water. If the amount of heat is large then we must consider reservoirs that are very large.

The Second Law and the Direction of Heat Flow

In any spontaneous process, heat flows from hot to cold. This is an immediate consequence of the second law. Consider an amount of heat Q flowing from a reservoir at temperature T_1 to a second reservoir at temperature T_2 . Since heat is leaving T_1 its entropy decreases, while the entropy of T_2 increases. The total change in entropy is the sum of these two; by the second law it must be nonnegative.

$$\begin{aligned} 0 \leq \Delta S_{\text{tot}} &= \Delta S_1 + \Delta S_2 = \frac{-Q}{T_1} + \frac{Q}{T_2} \\ \implies \frac{1}{T_1} &\leq \frac{1}{T_2} \end{aligned}$$

Cross-multiplying and remembering that absolute temperatures are always positive gives

$$T_2 \leq T_1.$$

Thus, heat flows from a higher to a lower temperature.

Refrigerators, Air Conditioners and Heat Pumps

It is possible however, to have a situation where heat is taken from a cold reservoir and vented to a hotter reservoir. The key phrase in the above discussion is *spontaneous process*. A refrigerator removes heat from a cold interior and vents it to the warm coils behind. The crucial point is that more heat is vented to the back than is removed from the interior. The additional energy is provided by some motor (a compressor) doing work; it pumps the coolant around some cycle.

Consider a cold reservoir at temperature T_C and a hot reservoir at T_H . Q_C is removed from T_C and Q_H then is vented to T_H . The conservation of energy implies that

$$Q_H = Q_C + W.$$

This says that the additional energy comes from the work done by the motor. The change in the total entropy is

$$\Delta S_{\text{tot}} = \Delta S_C + \Delta S_H = \frac{-Q_C}{T_C} + \frac{Q_H}{T_H}.$$

It should be clear that if W is large enough that the Q_H may be sufficiently large to cancel any negative ΔS_C . Heat is moved from cold to hot.

An air conditioner is simply a refrigerator operating between the cold interior of a house and the warmer exterior. A heat pump is an air conditioner running in reverse on a cold winter day. The outdoors is air conditioned! Heat Q_C is removed from the cold

exterior and more heat Q_H is vented inside. The amount of electrical energy that is used is determined by the work W . The heat vented inside is larger than the amount of electrical energy that is used. The Q_C is essentially a bonus.

Heat Engines

Heat Engines and Efficiency

A heat engine is essentially an air conditioner running in reverse. Some fuel is burned creating an input heat of Q_H . The point of the engine is to convert this heat to work W . We will define the efficiency of a heat engine to be the energy output of the engine, the work, divided by the energy input, Q_H .

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

A perfect heat engine would be 100% efficient. Unfortunately this is, because of the second law, impossible. There is a decrease in entropy without any increase to cancel it.

With a heat engine we have a hot reservoir at temperature T_H producing the input heat Q_H . Some of that heat is converted to work W , but necessarily some of it must be vented to the environment. Take the environment to be a cold reservoir at T_C receiving the vented heat Q_C .

Conservation of energy gives

$$Q_H = Q_C + W.$$

With this we can rewrite the efficiency

$$e = 1 - \frac{Q_C}{Q_H}.$$

The Second Law and Efficiency

The second law has the following form

$$\Delta S_{\text{tot}} = \Delta S_C + \Delta S_H = \frac{Q_C}{T_C} + \frac{-Q_H}{T_H} \geq 0.$$

This gives a fundamental upper limit on the efficiency of a heat engine.

$$\frac{Q_C}{T_C} + \frac{-Q_H}{T_H} \geq 0 \implies \frac{Q_C}{Q_H} \geq \frac{T_C}{T_H} \implies 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

It follows that

$$e \leq e_{\text{max}} \quad \text{where} \quad e_{\text{max}} = 1 - \frac{T_C}{T_H}.$$

A Carnot Engine

A Carnot engine is a theoretical heat engine of maximum efficiency. Its efficiency e_c is then given by

$$e_c = e_{\text{max}} = 1 - \frac{T_C}{T_H}.$$