

Chapter 0

Entropy and the Second Law of Thermodynamics

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O.1 - Entropy

Irreversibility and Reversible Processes

Thermodynamics puts an arrow on time. Take a video of dropping an egg on the floor and run it in reverse. Clearly, the reversed video would show itself as unphysical. All real-world physical processes are irreversible but we can consider idealized reversible processes.

A quasi-static process is *reversible*. As we saw last chapter a quasi-static process is one where we have an equilibrium state for each intermediate state in a process; they are given by clear paths in PV -diagrams. By following backward along the path in a PV -diagram we can restore the system and its surroundings to their original state. A thermodynamic system undergoing an irreversible process can always be returned to its original state but in both the process and return, a net quantity of heat will flow to the environment; this cannot be undone. Whenever heat flows spontaneously across a temperature gradient we have an irreversible process. The free expansion of a gas, as discussed earlier is not quasi-static and thus not reversible. This chapter will discuss entropy and the second law of thermodynamics. For a system and its environment, a reversible process has zero change in the total entropy and an irreversible process has a net increase in entropy.

A reversible (quasi-static) process is an idealization. When the state of a system is changed by a small amount it moves slightly away from equilibrium, but if done sufficiently slowly the deviations from equilibrium can be negligible and the process can be arbitrarily close to being reversible.

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

$$dS = \frac{\delta Q}{T}.$$

Equivalently, we can define it as an integral

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

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 $Q = \int \delta Q$ 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.

$$Q = \pm m L$$

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 δQ .

$$\delta Q = m c dT$$

$$\Delta S = \int \frac{\delta Q}{T} = m c \int_{T_i}^{T_f} \frac{dT}{T}.$$

The integral gives the natural log and we get

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

Example 0.1 - Making Ice Cubes

(a) A tray of water is put in the freezer. What is the change in entropy of an ice tray when 0.45-kg of water initially at 22 °C is frozen to ice at -18 °C?

Solution

The relevant data are the mass, and the temperatures. The constants needed are the specific heats of water and ice and the latent heat of fusion for water.

$$m = 0.45 \text{ kg}, \quad 22 \text{ }^\circ\text{C} = 295 \text{ K}, \quad 0 \text{ }^\circ\text{C} = 273 \text{ K}, \quad -18 \text{ }^\circ\text{C} = 255 \text{ K},$$

$$c_W = 4186 \frac{\text{J}}{\text{kg K}}, \quad c_I = 2100 \frac{\text{J}}{\text{kg K}} \quad \text{and} \quad L_f = 3.34 \times 10^5 \frac{\text{J}}{\text{kg}}$$

There are three steps we need to consider.

$$\text{Water at } 22 \text{ }^\circ\text{C} \xrightarrow{1} \text{Water at } 0 \text{ }^\circ\text{C} \xrightarrow{2} \text{Ice at } 0 \text{ }^\circ\text{C} \xrightarrow{3} \text{Ice at } -18 \text{ }^\circ\text{C}$$

The total change in entropy will be the sum of the changes for each of the three steps. In each step, heat is being removed so the changes must be negative.

$$\Delta S_1 = m c \ln \frac{T_f}{T_i} = m c_W \ln \frac{273 \text{ K}}{295 \text{ K}} = -146.99 \frac{\text{J}}{\text{K}}$$

$$\Delta S_2 = \frac{\pm m L}{T} = \frac{-m L_f}{273 \text{ K}} = -550.55 \frac{\text{J}}{\text{K}}$$

$$\Delta S_3 = m c \ln \frac{T_f}{T_i} = m c_I \ln \frac{255 \text{ K}}{273 \text{ K}} = -64.46 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{ice tray}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -761.0 \frac{\text{J}}{\text{K}}$$

0.2 - 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.

Example 0.2 - Making Ice Cubes (Continued)

(b) The heat that flows out of the ice tray flows into the freezer. What is the total change in entropy of the system consisting of the freezer ice and the ice tray in the “Making Ice Cubes” example above?

Solution

Take the freezer to be a heat reservoir at $-18^\circ\text{C} = 255\text{ K}$. The total change in entropy of the freezer-ice system is the the ΔS from the the previous part, which we will now refer to as ΔS_{ice} , added to the change in entropy of the freezer, $\Delta S_{\text{freezer}}$. The (positive) heat that flows into the freezer Q_{freezer} is the heat flowing out of the ice. Using our convention that Q is the heat added to a system, take the Q_{ice} to be negative.

$$0 = Q_{\text{tot}} = Q_{\text{freezer}} + Q_{\text{ice tray}} \implies Q_{\text{freezer}} = -Q_{\text{ice}}$$

The constants and values used in part (a) are also needed here.

$$m = 0.45\text{ kg}, \quad 22^\circ\text{C} = 295\text{ K}, \quad 0^\circ\text{C} = 273\text{ K}, \quad -18^\circ\text{C} = 255\text{ K},$$

$$c_W = 4186 \frac{\text{J}}{\text{kg K}}, \quad c_I = 2100 \frac{\text{J}}{\text{kg K}} \quad \text{and} \quad L_f = 3.34 \times 10^5 \frac{\text{J}}{\text{kg}}$$

Before finding the entropy change of the freezer $\Delta S_{\text{freezer}}$ we must first find Q_{freezer} and for that we need to sum the heats for each of the three steps referred to in part (a).

$$Q_1 = m c_W \Delta T_W = -14441\text{ J}$$

$$Q_2 = \pm m L = -m L_f = -150300\text{ J}$$

$$Q_3 = m c_I \Delta T_I = -170010\text{ J}$$

$$Q_{\text{ice}} = Q_1 + Q_2 + Q_3 = -208751\text{ J}$$

Since the freezer is a reservoir, its entropy change is

$$Q_{\text{freezer}} = -Q_{\text{ice}} \quad \text{and} \quad \Delta S_{\text{freezer}} = \frac{Q}{T} = \frac{Q_{\text{freezer}}}{255\text{ K}} = -\frac{Q_{\text{ice}}}{255\text{ K}} = 818.6 \frac{\text{J}}{\text{K}}$$

The change in entropy of the freezer is positive since heat flows into it. The total change in entropy of the ice tray and freezer combined is the sum of Q_{freezer} with the change in the entropy of the ice, found in part (a) $\Delta S_{\text{ice tray}} = -761.0\text{ J/K}$.

$$\Delta S_{\text{total}} = \Delta S_{\text{freezer}} + \Delta S_{\text{ice tray}} = 57.6 \frac{\text{J}}{\text{K}}$$

Since this larger system is thermally isolated, no heat flows out of it or into it, then by the second law our answer had to be positive.

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.

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

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

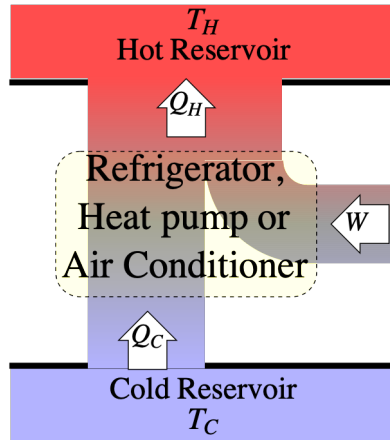
$$T_2 \leq T_1.$$

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

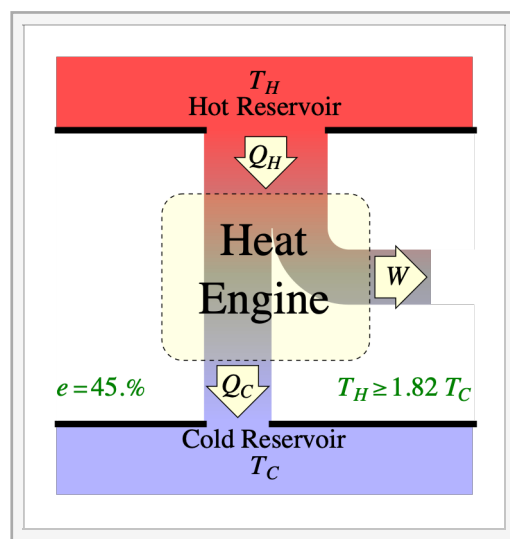
$$\Delta S_{\text{tot}} = \Delta S_C + \Delta S_H = \frac{-Q_C}{T_C} + \frac{Q_H}{T_H}.$$

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.

0.3 - Heat Engines

Heat Engines and Efficiency



Interactive Figure

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

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

A Carnot Engine

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

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

Example 0.3 - Heat Engine

A heat engine takes 3800 kcal of heat from a hot reservoir at 350 °C and vents 2400 kcal of heat to the environment at 40 °C.

(a) What is the efficiency of this heat engine?

Solution

First list what is given, remembering that temperatures must be in Kelvin.

$$Q_H = 3800 \text{ kcal}, \quad Q_C = 2400 \text{ kcal}, \quad T_H = 350 \text{ °C} = 623 \text{ K} \quad \text{and} \quad T_C = 40 \text{ °C} = 313 \text{ K}$$

The efficiency involves only the heats.

$$e = 1 - \frac{Q_C}{Q_H} = 0.368 = 36.8 \%$$

(b) What is the total change in the entropy for this process?

Solution

We are removing Q_H from T_H and adding Q_C to T_C . The total change in entropy is the sum of the negative change in the hot reservoir's entropy and the positive change in the cold reservoir.

$$\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = -6.0996 \frac{\text{kcal}}{\text{K}} + 7.6673 \frac{\text{kcal}}{\text{K}} = +1.568 \frac{\text{kcal}}{\text{K}}$$

(c) What is the maximum efficiency a heat engine could have when operating between these two reservoirs?

Solution

The maximum efficiency will depend only on the temperatures.

$$e_{\text{max}} = 1 - \frac{T_C}{T_H} = 0.498 = 49.8 \%$$