Chapter 20

The Second Law of Thermodynamics

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1. Some basic concepts

Thermodynamic process — a process in which the state variables of a thermodynamic system are changed. (Examples: pressure changed, or temperature changed, or both changed but with some other condition satisfied, etc.)

Reversible processes — thermodynamic processes which can also be run backward in time. (Running backward in time is like what you see when a movie is run backward in time.) Reversible processes are equilibrium processes. That is, the system is in an equilibrium state at any moment during the process. This is impossible in practice, and is an idealization.

Irreversible processes — thermodynamic processes which can only be run forward in time but not backward in time. Irreversible processes are non-equilibrium processes, meaning that except for its beginning and ending states, and perhaps (but unlikely) a few other intermediate states, the system is not in an equilibrium state. One obvious example is an explosion. During an explosion, after it has started and before it ends, the exploding gas cannot be described by a single temperature, pressure, and density, so it is not in an equilibrium state. The different parts of the exploding gas are not at thermal or mechanical equilibrium.

Quasi-equilibrium processes (also known as quasi-static processes) — changing from a first equilibrium state to a second equilibrium state that is only infinitesimally different from the first one, then to a third equilibrium state that is only infinitesimally different from the second one, and so on. Thus at any moment in time during such a process, the system is very close to some equilibrium state. The change is very slow, and hard to detect, and yet after some finite time, the total change can be sizable. A quasi-equilibrium process is very nearly a reversible process.

A quasi-equilibrium process can be represented by a continuous curve in the space of state variables, called the state space, such as in the $P$-$V$ space. A non-equilibrium process often can not be so represented. But if a continuous curve in a state-space is traced rapidly, it is still irreversible. So even a continuous curve in the state space can still represent a non-equilibrium process, if it is not traced very slowly.
2. Heat Engines

It is very easy to convert all forms of energy other than heat into heat. Friction can convert both translational and rotational kinetic energy into heat. Other forms of energy can be converted to kinetic energy with 100% efficiency, which can then be converted to heat via friction, with 100% efficiency. Thus one can say that it is possible, at least in principle, to convert any other form of energy into heat with 100% efficiency.

But the reverse, namely converting heat into any other form of energy, is not so easy, and is in fact far from being near 100% efficiency. Any machine or device of which the main function is to convert some percentage of available heat into useful work is called a heat engine. It should always run in cycles so it can be repeated many many times, in order to act practically as a continuous operation (as in an automobile engine).

This heat engine in each cycle will take in a certain amount of heat, $Q_H$, from a hot reservoir (i.e., a large source or sink of heat), converts a fraction $f$ of it into useful work, (which can then be converted into any other form of energy with, in principle at least, 100% efficiency,) and dump the remaining heat into a colder reservoir (such as the air, or the water in a lake or river, or ocean, etc.). If $f$ were unity, there would be no remaining heat to dump out to a cold reservoir. Then the conversion of heat to work would have 100% efficiency. Unfortunately, we shall see that this is impossible. We shall see that this fraction $f$ can not be made larger than a certain number less than unity. This number will depend on the absolute temperatures of the hot and cold reservoirs. We can represent a heat engine by the following schematic diagram:
By energy conservation, we must have \[ |Q_H| = |Q_C| + |W|. \]

Generally, we define the efficiency \( e \) of a heat engine as:

\[
e = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}.
\]

(All the absolute signs merely indicate that they do not carry their signs, but it is important to know that the heat \( |Q_H| \) is taken out of the hot reservoir by the engine, where as the heat \( |Q_C| \) is dumped into the cold reservoir by the engine, and finally the work \( |W| \) is done by the engine. Thus from the point of view of the working substance of the engine, \( Q_H \) should be positive, \( Q_C \) should actually be negative, and \( W \) should be positive, since any heat flowing into a system is positive, and any work done by the system is positive.)

The highest possible value for \( e \) is unity. But if \( e \) were unity, we would have \( |Q_C| = 0 \), with \( |Q_H| > 0 \), and there would be no heat dumped into any cold reservoir, or \( |Q_H| = \infty \), with \( |Q_C| \) zero or finite. We shall see that these situations are impossible. As a matter of fact, we shall see that the highest possible value for \( e \) is the Carnot efficiency \((1 - T_C/T_H)\), which is less than unity, unless \( T_C \) is absolute zero, or \( T_H \) is infinity, or both, but they are impossible!

3. **Clausius Statement of the Second law of thermodynamics**

This statement is that heat will never flow spontaneously (that is, by itself, without assistance) from a cold reservoir to a hot reservoir, thus making the colder reservoir even colder, and the hot reservoir even hotter.

An important consequence of this statement of the law is that one has to run a properly designed device (called a refrigerator, or an air conditioner, or a heat pump) in order to make heat flow from a cold reservoir to a hot reservoir. To run this device, you have to supply a certain amount of energy to the device. This energy will be converted to heat after you run the device. Thus more heat will have to be dumped into the hot reservoir, than the amount of heat you can extract from the cold reservoir. In fact, there will be a law governing this ratio of heat output divided by heat input, so this ratio can not be made arbitrary close to unity by however way to improve the design of the device!

In another word, no matter how well you design the device, this ratio can not be made to drop below a certain number larger than unity. We shall see that
this minimum ratio is equal to $T_H / T_C$.

4. Kelvin-Planck statement of the second law of thermodynamics

This statement is that it is impossible to make a device which can convert any given amount of heat completely into work without causing any other effect to itself or anything else in the universe. This conversion would be the sole consequence of running the device if it could be made, but it can not be made! Clearly, this statement is true because the efficiency $e$ of any engine cannot be unity (barring $T_H = \infty$, or $T_C = 0$, or both, which are impossible to reach). (Note that in order for the device to not cause any effect to itself, it must be run in complete cycles, so that the device can return to its original state.)

The left figure below illustrates the impossible device in the Clausius statement. The right figure below illustrates the impossible device in the Kelvin-Planck statement.

5. Equivalence of the two statements

Actually the above two statements of the second law of thermodynamics are equivalent. In another word, they imply each other. The following figures explain why this is the case:
Should the device in the Clausius statement exist, then running it (the left part of the following figure) and an ordinary engine (the right part of the following figure) together, so that no net $|Q|$ were to flow into or out of the cold reservoir, one would get a device in the Kelvin-Planck statement:

\[
|Q| - |Q| = |W| = |Q_1| - |Q|
\]

On the other hand, should the device in the Kelvin-Planck statement exist, then running it (the left part of the following figure) and an ordinary refrigerator (the right part of the following figure) together, so that the work $|W|$ output by the Kelvin-Planck device is completely used up by the refrigerator, then one would get a device in the Clausius statement:

\[
|Q| - |Q| = |W| = |Q_1| - |Q|
\]
6. Refrigerator, air conditioner, and heat pump

A refrigerator or air conditioner or heat pump is simply a heat engine running in reverse, with all arrows in the energy flow reversed. That is, work \( |W| \) would be going into the device, \( |Q_C| \) would be taken out of the cold reservoir, and \( |Q_H| (= |Q_C| + |W|) \) would be dumped into the hot reservoir. The coefficient of performance of a refrigerator or air conditioner is defined to be:

\[
K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}.
\]

The main purpose of a refrigerator or air conditioner is to remove heat from a cold reservoir, such as the food inside a refrigerator, or the air inside a house, whereas the main purpose of a heat pump is to pump heat into a hot reservoir (from a cold reservoir), but they work on the same principle. It should be clear that \( K \) should be the larger the better. That is, you would like to spend the smallest \( |W| \) to pump the largest amount of \( |Q_C| \) out of the cold reservoir or region. This is why \( |W| \) is in the denominator, and \( |Q_C| \) is in the numerator of \( K \). Note that \( K \) can be larger than, equal to, or less than unity.

7. Carnot engine

A Carnot engine is an idealized engine composed of four reversible processes executed by a system containing some fixed amount of a working substance. These four reversible processes form a cycle called a Carnot cycle. A Carnot cycle can be executed with all kinds of substances, but we shall assume that the substance here is a gas. As a matter of fact, we shall approximate the gas by an ideal gas. The state space can then be taken as the \( P-V \) space. The four reversible processes forming a Carnot cycle are:

- An adiabatic process
- An isothermal process
- An adiabatic process
- An isothermal process

Since this is a cycle, one can call any one of these four processes as the first process. For example, if one begins with isothermal process on the left of the diagram, then it is followed by the adiabatic process on the top of the diagram, which is then followed by the isothermal process on the right of the diagram, which is then followed by the adiabatic process on the bottom of the diagram. This last process brings the system back to the state it has started in, so the cycle can repeat itself.
If the system is made of a fixed amount of a gas, then the four processes forming a Carnot cycle are indicated by the following four sections forming a closed loop in the $p$-$V$ space:

![Diagram of p-V space with sections labeled a, b, c, d, and T_H, T_C.]

The section ab is an isothermal expansion at temperature $T_H$. The section bc is an adiabatic expansion, which cools the system from the higher temperature $T_H$ to a lower temperature $T_C$. The section cd is an isothermal compression at temperature $T_C$. Finally, the section da is an adiabatic compression, which warms the system from $T_C$ back to $T_H$. (Expansion means that the volume increases, and compression means that the volume decreases. Since the total number $N$ of molecules in the gas is fixed, the density of the gas increases when the gas is compressed, and decreases when the gas expands.)

We now show that the efficiency of a Carnot engine is given by

$$e_{Carnot} = 1 - \frac{T_C}{T_H}.$$  \hspace{1cm} (*)

It follows easily from the general formula for efficiency: $e = |W|/|Q_H| = 1 - |Q_C|/|Q_H|$: The two adiabatic processes involve no heat flowing in or out of the system, and for the isothermal process ab (at temperature $T_H$), the heat intake is: $|Q_H| = U_b - U_a + W_{ab} = W_{ab} = nRT_H \ln(V_b/V_a)$, whereas the heat released by the process cd (at temperature $T_C$) is: $|Q_C| = -Q_C = -[(U_d - U_c) + W_{cd}] = -W_{cd} = -nRT_C \ln(V_d/V_c) = nRT_C \ln(V_c/V_d)$, because for $|Q_C|$ to be released, $Q_C$ itself must be negative. This can also be seen by the fact that $V_d$ is less than $V_c$, so $\ln(V_d/V_c)$ is actually negative, and we need to remove the sigh of $Q_C$ to get $|Q_C|$ for the efficiency formula. The Carnot efficiency formula (*) follows easily from these results if one notices that $V_b/V_a = V_c/V_d$. This is shown as follows: For any adiabatic process, we have $pV^\gamma = \text{constant}$. This is equivalent to $TV^{\gamma-1} = \text{constant}$. 
Thus for the process bc we have $T_H V_b \gamma^{-1} = T_C V_c \gamma^{-1}$, or $T_C / T_H = (V_b / V_c)\gamma^{-1}$.

Similarly, for the process da we have $T_C V_d \gamma^{-1} = T_H V_a \gamma^{-1}$, or $T_c / T_H = (V_a / V_d)\gamma^{-1}$. Combining the two expressions, one clearly obtains $V_b / V_c = V_a / V_d$, or $V_b / V_a = V_c / V_d$. This result implies $|Q_c| / |Q_H| = T_c / T_H$ and Eq. (*).

The Carnot efficiency is important because it is the highest possible efficiency any engine can reach if the highest possible temperature the working substance of the engine can reach is $T_H$, and the lowest possible temperature the working substance of the engine can reach is $T_C$. Thus if the hottest temperature the exploded gasoline in a car engine can reach is 500K, and outside air temperature is 300K, then the car engine can not have an efficiency higher than $1 - 300/500 = 40\%$! That is, at least 60\% of the available energy in this gasoline engine must be wasted as heat dumped into the air outside the car engine! This is called thermal pollution. It raises the temperature of the environment, and affects the ecology of the environment. Worse yet, this heat energy, now stored as internal energy in a lower temperature system, is now harder to utilize, since to use at least some of it, you need an even-lower-temperature system to absorb some unused part of this energy, which is then even harder to utilize, and so on. If the whole universe is at a single temperature, then no heat energy can be used to generate useful work. This is called heat death.

**Carnot theorem**: All reversible engines operating between the same two thermal reservoirs at temperatures $T_H$ and $T_C$ have the same Carnot efficiency $1 - T_C / T_H$. All irreversible engines operating between these two thermal reservoirs have efficiencies less than that of the Carnot engine running between these two reservoirs. All engines with heat intake at temperatures $T_H$ and below, and heat exhaust at temperatures $T_C$ and above, so that $T_H$ and $T_C$ are the highest and lowest temperatures involved, respectively, have efficiencies below that of a reversible Carnot engine operating between $T_H$ and $T_C$. This theorem is a direct consequence of either the Clausius or Kelvin-Planck statements of the second law of thermodynamics. The proof is actually very short, but we omit it here.

When can the Carnot efficiency be 100\%? Only when $T_H$ equals to infinity, or when $T_C$ equals to zero. But both are impossible to reach! Thus we again obtain the conclusion that no device can convert a given amount of heat completely into work, which would imply $|Q_C| = 0$, and $e = 100\%$. 
8. **Internal combustion engines**

These heat engines share the common property that the heat intake is derived from burning some combustible chemicals inside the engine.

8a. **The Otto cycle**

The internal combustion engine of an automobile running on a gasoline-air mixture can be approximated by this reversible cycle. This cycle is defined by two isochoric processes and two adiabatic processes, as shown by the following $P$-$V$ diagram:

![P-V diagram showing the Otto cycle with labeled points a, b, c, and d.](image)

The processes ab and cd are adiabatic, and involve no heat input or output. Thus the heat intake $|Q_H|$ is by the isochoric process da only, and the heat released $|Q_C|$ is by the isochoric process bc only. (For isochoric processes, $W = 0, Q = \Delta U$. It is easy to see that for process da, $\Delta U > 0$, and for the process bc, $\Delta U < 0$, by assuming that the substance is an ideal gas.) However, $Q_H$ does not occur at a single higher temperature, and $Q_C$ does not occur at a single lower temperature. The working substance reaches its highest temperature at the point a, and its lowest temperature at the point c. But the engine efficiency is lower than $1 - T_c/T_a$, because $Q_H$ does not all occur at $T_a$, but rather occurs at all temperatures between $T_a$ and $T_d < T_a$, and $Q_C$ does not all occur at $T_c$, but rather occurs at all temperatures between $T_c$ and $T_b > T_c$). Note that $T_b$ is necessarily less than $T_a$, and $T_c$ is necessarily less than $T_d$, because the processes ab and cd are adiabatic. These observations confirm that $T_a$ is the highest temperature reached in the cycle, and $T_c$ is the lowest temperature reached in the cycle.

In the process cd, there is a fuel-air mixture in the cylinder. The piston is moving inward to compress the mixture adiabatically. The fuel is ignited by firing spark plugs at point d, converting chemical energy into heat, causing the pressure and temperature of the gas mixture in the cylinder to rise rapidly...
at practically constant volume (process da). When heating stops, the piston begins to move outward, expanding the gas mixture in the cylinder adiabatically (process ab). At point b, the exhaust valve is opened, releasing the mixture to the outside world, causing the pressure inside the cylinder to drop rapidly at essentially constant volume (process bc). A certain amount of heat \( Q_c \) is also dumped into the outside world during this process. At the point c fresh fuel-air mixture is introduced into the cylinder at this low pressure, and the piston begins to move inward to compress the mixture adiabatically again. So the cycle repeats.

An analysis similar to that done for a Carnot cycle gives the efficiency of the Otto engine to be:

\[
e = 1 - \left( \frac{V_b}{V_a} \right)^{1-\gamma} = 1 - \left( \frac{V_a}{V_b} \right)^{\gamma-1}.
\]

(The second expression is better because \( \gamma > 1 \), and \( V_a < V_b \).) The detailed derivation of this formula is omitted here, because this cycle is not as fundamental as the Carnot cycle, but it is practically important. The theoretical limit of the efficiency of this engine is about 50 to 60\%. (\( \gamma \) is 1.4 for diatomic air. The ratio \( V_b / V_a \) is around 10 or less.) The efficiency of actual Otto engines are much smaller than this theoretical value due to the existence of friction, imperfect combustion, timing error, heat leak, etc. So an efficiency of around 40\% is already a good auto engine in practice!

8b. The Diesel cycle

An idealized Diesel engine runs in this cycle. The cycle is made of the following four processes:

- An adiabatic process
- An isobaric process
- An isochoric process
- An adiabatic process

It is represented by the diagram shown:

Air in the cylinder is compressed adiabatically by the piston in the step cd. Shortly before reaching d, Diesel fuel is injected
into the cylinder. The compression continues to raises the temperature of the
air in the cylinder. At the point d the temperature becomes so high that the
fuel inside the cylinder ignites spontaneously. Heat is generated by the
burning of the fuel, (which is injected into the cylinder continuously,) heating up the air in the cylinder, causing the air in the cylinder to expand at
essentially constant pressure (process da). After burning stops, the cylinder
continue to expand, but adiabatically, so the temperature in the cylinder
drops (process ab). The piston of the cylinder is moving outward during
these two processes. At point b, with the volume staying essentially fixed,
the exhaust valve is opened to let out the exhaust gas, so the pressure in the
cylinder drops (process bc). Some heat \((Q_c)\) is dumped into the outside air
during this process. Fresh air in the cylinder is then compressed adiabatically
again because the piston is now moving inward (process cd) to repeat the
cycle.

Theoretical limit of the efficiency of this engine is about 65 to 70\%. The ef-
ficiencies of actual Diesel engines are much smaller than this theoretical
limit, for the same reasons as given for an Otto engine.

**General remarks about how to calculate the efficiency of an engine:** If
you use the formula \(e = \left| \frac{W}{Q_H} \right|\) to calculate the efficiency of an engine,
you need to know that \(W\) is the net work done by whatever cycle involved.
That is to say, if the cycle is made of sections \(ab, bc, cd,\) and \(da,\) then
\[ W = W_{ab} + W_{bc} + W_{cd} + W_{da}, \]
(with some of them negative and the others positive,) and this net work better be positive, otherwise this cycle is not an engine. [This condition requires that the cycle runs clockwise in the \(P-V\) dia-
gram. Then the area enclosed by the cycle, in the unit of work (the unit of \(P\)
times the unit of \(V\), is this net work.] On the other hand, if \(Q_{ab}\) and \(Q_{bc}\) are
positive, and \(Q_{cd}\) and \(Q_{da}\) are negative, then \(Q_H = Q_{ab} + Q_{bc},\) and \(Q_C = |Q_{cd}| + |Q_{da}|.\) That is, \(|Q_H|\) is the sum of all positive ones in \(Q_{ab}, Q_{bc}, Q_{cd},\) and \(Q_{da},\) and \(|Q_C|\) is the sum of all negative ones in them, with the overall
minus sign removed. Some times it is more convenient to use the formula
\[ e = 1 - \frac{|Q_C|}{Q_H} \] to calculate the efficiency. The two formulas should
give the same result. If the sign of \(Q_C\) is not removed, then the formula
becomes \(e = 1 + \frac{Q_C}{Q_H},\) because \(Q_C\) itself is negative, and \(Q_H\) is positive.
It makes \(e < 1.\)

Neither the Clausius statement nor the Kelvin-Planck statement of the second law of thermodynamics are sufficiently general. That is, there are processes which do not violate these statements which still can not occur in nature. A general statement of the second law of thermodynamics should let one find all situations that are impossible to occur in nature. This general statement can be made only after the concept of entropy has been defined.

If an infinitesimal amount of heat $dQ$ flows into a system at the absolute temperature $T$ in a reversible process, the system's total entropy $S$ increases by the infinitesimal amount $dS$ given by:

$$dS = \frac{dQ}{T}. \quad \text{(for any infinitesimal reversible process)} \quad (†)$$

(If $dQ$ is negative, it means that heat is flowing out of the system. Then $dS$ is also negative, meaning that the entropy $S$ of the system has decreased by $|dS|$.) For a general reversible process, represented by a continuous curve in the state space, one must integrate both sides in order to obtain a finite change of $S$ in the system. (For an irreversible process, the entropy change is larger than is given by this integration.) However, in an isothermal process, the temperature $T$ of the working substance does not change. Then when a finite amount of heat $\Delta Q$ flows into a system, a finite change $\Delta S$ of the total entropy $S$ of the system can be simply calculated as:

$$\Delta S = \frac{\Delta Q}{T} \quad \text{(valid for reversible isothermal processes only).}$$

Note that in Eq. (†), we have d-bar $Q$, but we have $dS$. This is because there is a state function $S$, and its differential is $dS$. But there is no such state function $Q$, and d-bar $Q$ is not the differential of any $Q$. Rather, we often denote $\Delta Q$ simply as $Q$. In spite of this simpler notation, we must understand that $Q$ is not a state function, but $S$ is. An important conclusion is then that integrating $dS$ along any path in the state space (such as the $P$-$V$ space for a gas) from an initial state $i$ to a final state $f$ will simply give the same path-independent result $S_f - S_i$. This would not be true if you integrate d-bar $Q$. That is, integrating d-bar $Q$ from an initial state $i$ to a final state $f$ along a path $\Gamma$ will produce a path-dependent result. It will not simply be $Q_f - Q_i$. As a matter of fact, there are no such quantities as $Q_f$ and $Q_i$, as $Q$ is associated with a process, not a point in the state space, which would mean a par-
ticular state of the working substance. For the Carnot cycle, only the two isothermal processes involve $Q$. Since they are isothermal processes, it is easy to calculate the change of $S$ of the universe due to a Carnot cycle: It arises from these two isothermal processes only, and is simply given by:

$$\Delta S_{\text{Carnot}} = -\frac{|Q_H|}{T_H} + \frac{|Q_C|}{T_C} = 0,$$

(The second equality is true because we have previously shown that $|Q_C|/|Q_H| = -Q_C/Q_H = T_C/T_H$ for a Carnot cycle.) The first term $(-|Q_H|/T_H)$ is the negative entropy change of the hot reservoir which gives out heat. The second term $(+|Q_C|/T_C)$, with $Q_C$ itself actually negative, (as it is defined from the point of view of the working substance,) is the positive entropy change of the cold reservoir, which receives a certain amount of heat equal to $|Q_C|$. We do not need to figure out the entropy change of the working substance, since it has gone through a cycle, so its initial state must be the same as its final state. Thus its net change of entropy must be zero. (If you do calculate the net change of entropy of the working substance, you will get the negative of the above expression, which is zero.) Combining all three contributions, and in view of the second equality in the above equation, we conclude that the net change of entropy of the universe is zero for a Carnot cycle. This is why the Carnot cycle is reversible.

Actually, it can be shown that $\Delta S_{\text{universe}} = 0$ for all reversible processes, and $\Delta S_{\text{universe}} > 0$ for all irreversible processes, thus we have the following

**General statement of the second law of thermodynamics:**

No process can lower the total entropy of the universe. (Here the universe means everything that is involved.) A reversible process will not change the total entropy of the universe, and an irreversible process will make the total entropy of the universe increase. Thus entropy is an **arrow of time**. It can distinguish between the future and the past.

This general statement tells you the common feature of all impossible processes (forbidden by the second law of thermodynamics).

If a system is isolated from the rest of the universe, then no process happening in the system can lower the total entropy of this system. A reversible process in the system will not change the total entropy of this system, and an irreversible process in the system will make the total entropy of this system
increase. This is because the rest of the universe is not involved, and therefore its entropy can not be changed by the processes happening in the system.

**How to calculate entropy change by doing an integration**

You already know how to calculate $\Delta S$ for a reversible isothermal process. No integration is needed. What about other reversible processes? For an isochoric process, we have $dW = 0$, and therefore $\Delta Q = dU = nC_V dT$. Then

$$\Delta S = nC_V \int_i^f \frac{dT}{T} = nC_V \ln \frac{T_f}{T_i} \quad \text{(for an isochoric process if } C_V \text{ is a constant.)}$$

For an isobaric process, you can use $dQ = nC_P dT$. So

$$\Delta S = nC_P \int_i^f \frac{dT}{T} = nC_P \ln \frac{T_f}{T_i} \quad \text{(for an isobaric process if } C_P \text{ is a constant.)}$$

For an adiabatic process, we must have $\Delta S = 0$, since no heat flow is involved.

(For a gas, $C_P = C_V + R$. For a solid or liquid, the two molar specific heats are practically equal to each other, and can simply be denoted as $C$.)

For a metal bar conducting heat of amount $Q$ between a hotter reservoir of temperature $T_H$ and a colder reservoir of temperature $T_C$, it is easy to see that

$$\Delta S_{\text{universe}} = \frac{-Q}{T_H} + \frac{Q}{T_C} > 0$$

where the first term is the negative entropy change of the hotter reservoir, because heat $Q$ has flown out of it at the constant hotter temperature $T_H$, and the second term is the positive entropy change of the colder reservoir, because heat $Q$ has flown into it at the constant colder temperature $T_C$. No integrations are involved here because the temperatures of the reservoirs are assumed to not change when a finite amount of heat flows out of the hotter reservoir and into the colder reservoir via the thermal conductor. We do not need to calculate the change of entropy of the thermal conductor, since in a steady state the state of the thermal conductor does not change, so its contribution to $\Delta S_{\text{universe}}$ must vanish. However, note that this calculation is correct only if $Q$ is not very large, so $T_H$ and $T_C$ are practically not changed after the heat flow. This would not be true if $Q$ is sufficiently large. $T_H$ would decrease and $T_C$ would increase due to the heat flow. One would then have to do integrals in order to calculate $\Delta S_{\text{universe}}$ (See below for an example.)
In a phase change of a substance, such as the melting of ice, the temperature is a constant. So the entropy change $\Delta S$ of the substance is simply $Q/T$, where $Q$ is positive if heat is flowing into the substance, as in melting, and is negative if heat is flowing out of the substance, as in freezing.

An important process to understand is an adiabatic free expansion. It is not the same thing as an adiabatic process. The key word is free. It means to let a gas zoom out of a hole, into essentially vacuum (or into a region of much lower pressure, so the very dilute gas in there can be neglected). The gas is initially in a volume $V_1$. After it zooms out, the gas becomes occupying a larger volume $V_2$. Actually, the gas in $V_1$ will not all come out. So one should consider $V_1$ as part of $V_2$. The following figure illustrates the situation:

This adiabatic free expansion of a gas from volume $V_1$ to $V_2$ is not a reversible process, so one cannot directly integrate the formula $dS = dQ/T$ to calculate the change of $S$. Instead, one must find a reversible path that has the same initial and final states, and use it to calculate the change of $S$. Free expansion of a gas means expansion into vacuum, so it cannot do any work, implying $W = 0$. Being adiabatic, no heat flow is involved, implying $Q = 0$. So $U$ cannot change either, implying that the temperature of the gas is fixed. (We approximately treat the gas as an ideal gas). Thus the reversible process we are looking for is an isothermal expansion of the volume of the gas from $V_1$ to $V_2$. The entropy change is then given by

$$\Delta S = Q/T = W/T = (1/T) \int_{V_1}^{V_2} PdV = nR \int_{V_1}^{V_2} dV / V = nR \ln(V_2/V_1).$$

(It has been explained before how to find $Q$ for an isothermal process.)

If you mix something of higher temperature with something of lower temperature, the entropy of the universe will increase as the mixture reaches a new equilibrium temperature. It can be calculated as follows:

Consider the problem of 50kg of water at 20°C mixed with 50kg of water at 24°C. Clearly, the final state is 100kg of water at 22°C.
The negative entropy change of the hot water is (with \(m = 50\text{kg}\)):

\[
\Delta S_1 = \int_i^f \frac{dQ}{T} = mc_\text{water} \int_{22^\circ\text{C}}^{24^\circ\text{C}} \frac{dT}{T} = mc_\text{water} \ln \frac{295}{297}.
\]

(Remember that \(T\) should be Kelvin temperature.) Similarly, the positive entropy change of the cold water is:

\[
\Delta S_2 = mc_\text{water} \int_{20^\circ\text{C}}^{22^\circ\text{C}} \frac{dT}{T} = mc_\text{water} \ln \frac{295}{293}.
\]

Their sum is the net change of entropy of the universe, and is equal to:

\[
\Delta S_{\text{universe}} = mc_\text{water} \ln \left(\frac{(295)^2}{293 \cdot 297}\right) = 50\text{kg} \times 1\text{ kcal \cdot kg}^{-1} \cdot K^{-1} \times 4.60 \times 10^{-5} = 2.30 \frac{\text{cal}}{K}.
\]

This change is indeed positive, as is required by the second law of thermodynamics. When the starting temperature difference is larger, the entropy increase will be larger. So heat flowing from high to low temperature will cause the total entropy of the universe to increase! In other words, as two systems reach thermal equilibrium, the entropy of the universe will increase.

10. Order to disorder

Why the entropy of the universe can only increase? Because entropy is a scientific measure of disorder, which is the opposite of order. Temperature involves uncontrolled random motion, so higher temperature generally means higher disorder. At \(T = 0\), all random motion stops, so \(S = 0\) at \(T = 0\). This is called the third law of thermodynamics. (Ideal gas does not obey this law, since ideal-gas behavior is a consequence of classical mechanics, after neglecting the interactions between molecules, but this third law of thermodynamics is actually a consequence of quantum mechanics and interaction between the molecules.) It is difficult to convert heat to work because heat involves random motion and disorder, whereas work does not. To turn some heat completely into work, without any other effects to the universe, the entropy of the universe would have to decrease, which is impossible. The second law of thermodynamics can also be stated as:

Natural processes tend to move toward a state of greater disorder (i.e., higher entropy).
Here “natural processes” means processes which can happen by itself spontaneously, such as the breaking of a glass, or the spreading of a drop of ink inside a glass of water.

Whenever there are a hotter region and a colder region in the universe, it is at least theoretically possible to put a heat engine between them and extract some heat from the hotter region and convert part of that heat to work. (This work can also be stored as kinetic or potential energy which can then be utilized fully later.) Every time this happens, the temperature of the hotter region will be lowered and the temperature of the colder region will be raised, maybe by just a little bit if those regions are very large. (Their total heat capacity would then be very large.) No matter, eventually we expect that the whole universe will reach thermal equilibrium at a single temperature. Furthermore, all order would have disappeared, and replaced by a state made of a uniform mixture of everything, with no structure of any sort remains. (If any reaction can occur it would also have occurred, so no nuclear or chemical energy is still available.) When that happens (far, far in the future), it will no longer be possible to get any useful work. There will be no energy left except the internal energy of this uniform mixture, which can not come out as heat and be at least partially used, since there will be no more regions of the universe with a lower temperature. This ultimate state of the universe is called heat death. It is also the ultimate fate of the universe. But this whole discussion is based on the assumption that the universe is finite in size, and containing a finite amount of matter. If this is not true, then it will take infinite length of time to reach heat death. We don’t know whether the universe is finite or infinite: When you look at a very far point in space, you are also looking back in time. Since the age of the universe is finite, there is also a farthest point about which you can learn something.

11. Statistical interpretation of entropy and the second law of thermodynamics

So far, the connection between entropy and disorder is vague and qualitative. It has been made very precise and quantitative by the creation of a new branch of physics called statistical mechanics. If statistical mechanics is based on classical mechanics it is called classical statistical mechanics. If statistical mechanics is based on quantum mechanics it is called quantum statistical mechanics. (Classical Statistical mechanics works only at high temperatures. Otherwise, one has to use quantum statistical mechanics.) The new principles added are the same:
**Ludwig Boltzmann** introduced the concepts of **macrostate** and **microstate**. They are what are regarded as a state from the macroscopic and microscopic points of view. A simple but artificial example may be given in terms of $N$ identical coins all lying on a flat table. A macrostate would refer to a given number of heads $N_h$, and the corresponding number of tails, $N_t = N - N_h$, but not paying attention to which coin has head and which coin has tail. A microstate would refer to a full and precise description on which coin has head, and which coin has tail. Another example is $N$ dice on a flat table. A macrostate would be described by six numbers $N_1, N_2, N_3, N_4, N_5, N_6$, with their sum equal to $N$, so that $N_i$ would give the number of dice with one dot facing upward, etc., whereas a microstate would be fixed by the full and precise information of exactly which dice have each of the six faces facing up. But the two terms are mainly introduced for describing a physical system. For example, a gas with given values of pressure, volume, temperature, and the molecular number of each species of molecules in the gas, is considered to be a macrostate. (There are similar definitions for a liquid or a solid.) From the microscopic (i.e., molecular) point of view, this is not one state at all. If one looks at it from the classical microscopic point of view, (i.e., based on the Newton's laws,) then a single microstate should have the positions and velocities of all molecules specified. Clearly, there are a very large number of such microstates in each macrostate. Let this number be denoted as $W$ (script-W). An important fundamental principle in statistical mechanics is that each of these microstates is equally probable in being realized in a given macrostate, and the system is actually rapidly switching between these different microstates due to the interactions and collisions of the molecules. (The coin and dice examples are bad examples because the coins or dice do not rapidly switch between its microstates, unlike a gas, for example.) Boltzmann showed that if the entropy of a given macrostate is defined as:

**Boltzmann's definition of entropy:**

\[ S = k \ln W, \]

then it is actually consistent with

**Clausius' definition of entropy:**

\[ \mathrm{d}S = \frac{\mathrm{d}Q}{T}. \]

(Thus, if $W$ is equal to $2^N$, then Boltzmann's formula would give $S = Nk \ln 2$.) Boltzmann’s formula has the important property that if a composite system is made of two subsystems that are not interacting with each other, such as when they are separated by a large distance, then clearly $W = W_1 W_2$, which
gives \( S = k \ln (\mathcal{W}_1 \mathcal{W}_2) = k \ln \mathcal{W}_1 + k \ln \mathcal{W}_2 = S_1 + S_2 \), as it should be. Now you see why logarithm should be involved in the definition, if only \( \mathcal{W} \) is involved. Note that \( \mathcal{W} \) is also the relative probability that a macrostate is realized, since all microstates are equally probable to appear. So the equilibrium state always corresponds to the macrostate of maximum possible \( S \), after satisfying some constraints, such as a given total internal energy, volume, number of particles, etc.

A general proof of the consistency between the above two definitions of \( S \) is difficult, so only a simple example is given to demonstrate this consistency. This example is an adiabatic free expansion of an ideal gas from a volume \( V \) to a volume \( 2V \). Clausius definition would give:

\[
\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{dW}{P} = \int_i^f \frac{PdV}{T} = nR \int_V^{2V} \frac{dV}{V} = nR \ln 2 = N k \ln 2,
\]

where the detailed justification of each step has been given before. [The expression after the first equal sign particularly needs explanation: The integral is not really about the original process of adiabatic free expansion, which is an irreversible process, and therefore is not even represented by a continuous path in the state space (i.e., the \( P-V \) space), but is about a reversible process with the same initial and final states. Why? Because \( \Delta S \) should only depend on the initial and final states, and therefore you can pick any path to do the integration, as long as the path links up the given initial and final states of the free expansion. It has then been shown that this process can be taken as an isothermal process, for which \( \Delta U = 0 \), so \( dQ = dW = PdV \). The rest is easy to understand.]

Next, we use the Boltzmann definition to calculate the same change of entropy: Since each molecule now has twice as big a volume to choose its location, its number of ways to choose a location must have doubled. With \( N \) molecules in the gas, \( \mathcal{W} \) must have gained a multiplicative factor \( 2^N \). That is, as \( V \to 2V \), we must have \( \mathcal{W} \to 2^N \mathcal{W} \). Since \( \ln (2^N \mathcal{W}) = \ln 2^N + \ln \mathcal{W} \), it then follows that \( \Delta S = k \ln 2^N = N k \ln 2 \), which is the same result. (You might say that so far we have considered the positions of the molecules, but what about their velocities? The answer is that since the temperature does not change in an adiabatic free expansion, (see explanation given before,) the velocity distribution can not change. Thus there is no contribution to \( \Delta S \) from the velocities of the molecules in an adiabatic free expansion. This is
not true for other processes. Then it will be much harder to calculate \( \Delta S \). The Clausius definition will then be more convenient for this purpose. Nevertheless, the Boltzmann formula is the starting point of a whole new branch of physics called **statistical mechanics**, which is extremely useful for explaining and even predicting the properties of all kinds of materials.

12. **Thermodynamic Temperature scale, absolute zero, and the third law of thermodynamics**

The Carnot engine can be realized with all kinds of working substances. The only condition is that the cycle is made of two reversible adiabatic processes and two reversible isothermal processes. Then the efficiency will be the same (for a given \( T_H \) and \( T_C \)) and be given by the Carnot formula. Furthermore, we will have:

\[
\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}.
\]

Thus if one chooses one of the two temperatures to be the triple-point temperature \( T_{tp} \) of water, say, then a Carnot cycle can be used as a definition of the absolute temperature scale:

\[
T = (273.16 K) \left( \frac{|Q|}{|Q_{tp}|} \right),
\]

where \( |Q| \) is measured at temperature \( T \), and \( |Q_{tp}| \) is measured at the triple-point temperature of water, \( T_{tp} \). (One of the \( Q \)'s is positive, then the other one must be negative before the absolute sign. But it doesn't matter which one is positive, and which one is negative. After all, a Carnot cycle can be run in reverse anyway. Then the signs of both \( Q \)'s will be reversed.) This way of defining the absolute temperature is called the **Kelvin** or **thermodynamic temperature scale**. Its advantage is that it can be carried out with all kinds of working substances. Its disadvantage is that it is very difficult to carry out reversible processes (infinitely slow, etc.). Nevertheless, it is a very good definition in principle. [Equation (*) was derived previously for ideal gas only, but Kelvin has been able to show that it is also true with any other working substance, if the \( T \)'s in there are in the ideal gas temperature scale, implying that all kinds of working substances can be used for this purpose, and the same \( T \) will be obtained, and in agreement with the ideal gas temperature scale. (The ideal gas temperature scale is useful above about 1K only, since below it no gas exists.)}
The best coefficient of performance of a refrigerator, $CP_{\text{Carnot}} = \frac{T_C}{T_H - T_C}$, becomes worse and worse as $T_C$ becomes lower and lower. So it becomes harder and harder to lower the temperature of any substance further if it is already close to absolute zero. In fact, it is infinitely difficult to reach the absolutely zero temperature, meaning that it would take infinite number of processes and therefore infinite length of time to reach the absolute zero temperature. The absolute zero temperature is therefore a unique temperature which cannot actually be reached. As the absolute zero temperature is approached, the entropy of practically any substance will drop to zero. All of these underlined statements in this paragraph are alternate statements of the third law of thermodynamics.

So you have now learned four laws of thermodynamics. The zeroth law (about thermal equilibrium and temperature), the first law (about energy conservation including heat), the second law (about entropy as an arrow of time, and limitations on converting heat into work), and the third law (about the absolute zero temperature).