

Contents

20 Entropy and the Second law of Thermodynamics	1
20.1 Reversible and Irreversible Processes	2
20.2 Heat Engines and the Second Law	5
20.2.1 Efficiency of a Heat Engine	6
20.2.2 Kelvin-Planck form for the second law:	6
20.3 Refrigerators and the Second Law	6
20.3.1 The Coefficient of Performance	7
20.3.2 Clausius form for the second law:	7
20.3.3 Equivalence of Clausius and Kelvin-Planck Statements	8
20.4 The Carnot engine	9
20.4.1 Efficiency of a Carnot engine	10
20.4.2 Coefficient of Performance of a Carnot Refrigerator . .	11
20.4.3 Carnot's Theorem and the Second Law	11
20.5 Entropy: Reversible Processes	13
20.5.1 Carnot engine in $T - S$ diagram	16
20.6 Entropy: Irreversible Processes	18
20.7 Entropy and The Second Law of Thermodynamics	20
20.7.1 Free Compression	20
20.7.2 The Kelvin-Planck Form of the Second Law	21
20.7.3 The Clausius Form of the Second Law	21
20.7.4 The Arrow of Time	21
20.8 A Statistical View of Entropy	21
20.8.1 Probability and Entropy	23

20 Entropy and the Second law of Thermodynamics

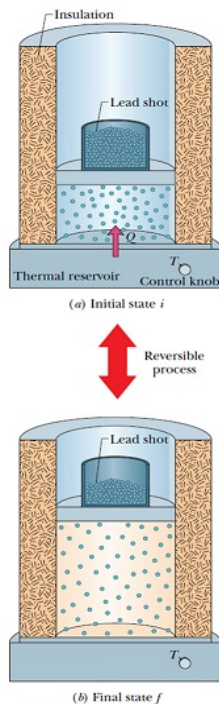
In this chapter we will introduce the second law of thermodynamics. The following topics will be covered:

Reversible processes. Entropy. The Carnot Engine. Refrigerators. Real engines.

20.1 Reversible and Irreversible Processes

Consider a typical system in thermodynamic equilibrium, say n moles of a (real) gas confined in a cylinder-piston arrangement of volume V , the gas having a pressure p and a temperature T . In an equilibrium state, these thermodynamic variables remain constant with time. Suppose that the cylinder, whose walls are insulating but whose base conducts heat, is placed on a large reservoir maintained at this same temperature T . Now let us take the system to another equilibrium state in which the temperature T is the same but the volume V is reduced by one-half. Of the many ways in which we could do this, we discuss two extreme cases.

1. We depress the piston very rapidly, we then wait for equilibrium with the reservoir to be re-established. During this process, the gas is turbulent, and its pressure and temperature are not well defined. We cannot plot the process as a continuous line on a $p - V$ diagram because we would not know what value of pressure (or temperature) to associate with a given volume. The system passes from one equilibrium state i to another f through a series of non-equilibrium states.
2. We depress the piston (assumed to be frictionless) extremely slowly—perhaps by gradually adding sand to the top of the piston—so that the pressure, volume, and temperature of the gas are, at all times, well-defined quantities.



We first drop a few grains of sand on the piston. This will reduce the volume of the system a little, and the temperature will tend to rise; the system will depart from equilibrium, but only slightly. A small amount of heat will be transferred to the reservoir, and in a short time the system will reach a new equilibrium state, its temperature again being that of the reservoir. Then we drop a few more grains of sand on the piston, reducing the volume further. Again we wait for a new equilibrium state to be established, and so on. By many repetitions of this entire process the system is always in a state differing only slightly from an equilibrium with still smaller successive increases in pressure, the intermediate states will depart from equilibrium even less. By indefinitely increasing the number of changes and correspondingly decreasing the size of each change, we arrive at an ideal process in which the system passes through a continuous succession of equilibrium states, which we can plot as a continuous line on a $p - V$ diagram. During this process a certain amount of heat Q is transferred from the system to the reservoir.

Processes of type 1 are called irreversible, and those of type 2 are called reversible. A reversible process is one that by a differential change in the environment, can be made to retrace its path. That is, if we add a few grains of sand to the piston when the system is in a particular state A, the

volume decreases by dV and a small amount of heat is transferred to the reservoir. If we next remove those few grains of sand (a differential change in the environment), the volume increases by dV and an equal amount of heat is transferred from the reservoir, thereby returning both the system and the environment to the original state A. In practice all processes are irreversible, but we can approach reversibility arbitrarily closely by making appropriate experimental refinements. The strictly reversible process is a simple and useful abstraction that bears a similar relation to real processes that the ideal gas abstraction does to real gases.

Not all processes carried out very slowly are reversible. For example, if the piston on our example exerted a friction force on the cylinder walls, it would not return to its previous state when we remove a few grains of sand. If we added sand slowly to the piston, the system would still evolve through a series of equilibrium states, but it would not do so reversibly. The word quasi-static is used to describe processes that are carried out slowly enough so that the system passes through a continuous sequence of equilibrium states; a quasi-static process may or may not be reversible.

The process described in 2 is not only reversible but isothermal, because we have assumed that the temperature of the gas differs at all times by only a differential amount dT from the (constant) temperature of the reservoir on which the cylinder rests.

We could also reduce the volume adiabatically by removing the cylinder from the thermal reservoir and putting it on a non-conducting stand. In an adiabatic process, no heat is allowed to enter or to leave the system. An adiabatic process can be either reversible or irreversible; the definition does not exclude either. In a reversible adiabatic process, we move the piston extremely, perhaps using the sand-loading technique; in an irreversible adiabatic process, we shove the piston down quickly.

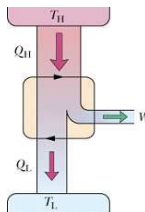
The temperature of the gas will rise during an adiabatic compression because, from the first law with $Q = 0$, the work W done on the system by the environment in pushing down the piston must appear as an increase ΔE_{int} in the internal energy of the system. The work has different values for different rates of pushing down the piston, being given by $-\int p dV$ only for reversible processes, for which p has a well-defined value. Thus ΔE_{int} and the corresponding temperature change ΔT are not the same for reversible and irreversible processes.

On the other hand, for a transformation from a given initial point i to a given final point f , the internal energy change depends only on the ther-

thermodynamic coordinates (p , V , and T , perhaps) of i and f . Although W and Q depend on the path, ΔE_{int} does not. In particular, if we are able to calculate ΔE_{int} from one particular reversible path, it has the same value for all other paths, including irreversible ones. Entropy, as we shall see, is also a state variable like E_{int} whose change in any irreversible process can be found from a suitably chosen reversible process connecting the same initial and final states.

20.2 Heat Engines and the Second Law

A heat engine is a device that extracts heat from its environment and does work. Every engine has a working substance. In a steam engine the working substance is water. In a car engine the working substance is an air - gasoline mixture. The engine operates on a cycle; it passes through a series of thermodynamic processes and returns again and again to each state in the cycle. An engine may be schematically represented by the following.



The input heat, which may be transferred in several steps, is represented simply as Q_H , and the exhaust heat is similarly represented as Q_L . It is helpful to keep in mind the sign conventions that we are using for heat and work:

Heat entering the system is considered to be positive; heat leaving a system is considered to be negative.

Work done by a system, corresponding to an increase in volume, is considered to be positive; work done on a system is the negative of work done by the system.

Accordingly, for the heat engine in the above diagram, $Q_H > 0$, $Q_L < 0$. From the first law for the cyclical process, if $|Q_H| > |Q_L|$

$$W = Q_H + Q_L > 0$$

and

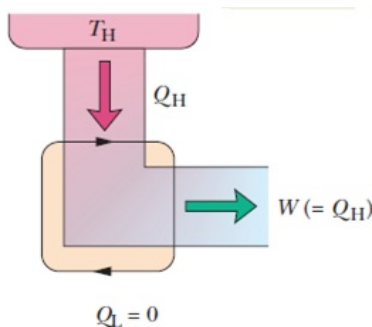
$$|W| = |Q_H| - |Q_L|$$

20.2.1 Efficiency of a Heat Engine

We define the efficiency e of any cycle to be the net amount of work done on the environment during the cycle divided by the input heat

$$\varepsilon = \frac{W}{Q_H} = \frac{|Q_H| - |Q_L|}{|Q_H|}$$

A perfect engine (see lower figure) would have $|Q_L| = 0$.



Such an engine would have $\varepsilon = 1$.

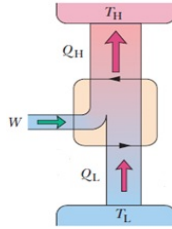
20.2.2 Kelvin-Planck form for the second law:

There are no perfect heat engines.

This form of the second law of thermodynamics asserts that the goal of making a perfectly efficient heat engine is impossible.

20.3 Refrigerators and the Second Law

A refrigerator is basically a heat engine running in reverse. Like a heat engine, a refrigerator operating in a cyclical process is an engine that uses work to transfer heat from a low temperature reservoir to a high temperature reservoir as the engine repeats a set series of thermodynamic processes.



In the refrigerator, heat is input from the low-temperature reservoir, so $Q_L > 0$, and is output to the high temperature reservoir, so $Q_H < 0$ as suggested in the above heat diagram. If $|Q_H| > |Q_L|$

$$W = Q_H + Q_L < 0$$

and

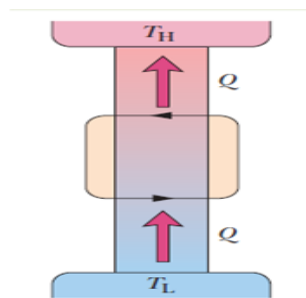
$$|W| = |Q_H| - |Q_L|$$

20.3.1 The Coefficient of Performance

We evaluate a refrigerator in terms of the coefficient of performance K , defined by

$$K = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

For a perfect refrigerator, $W = 0$ and $K = \infty$.



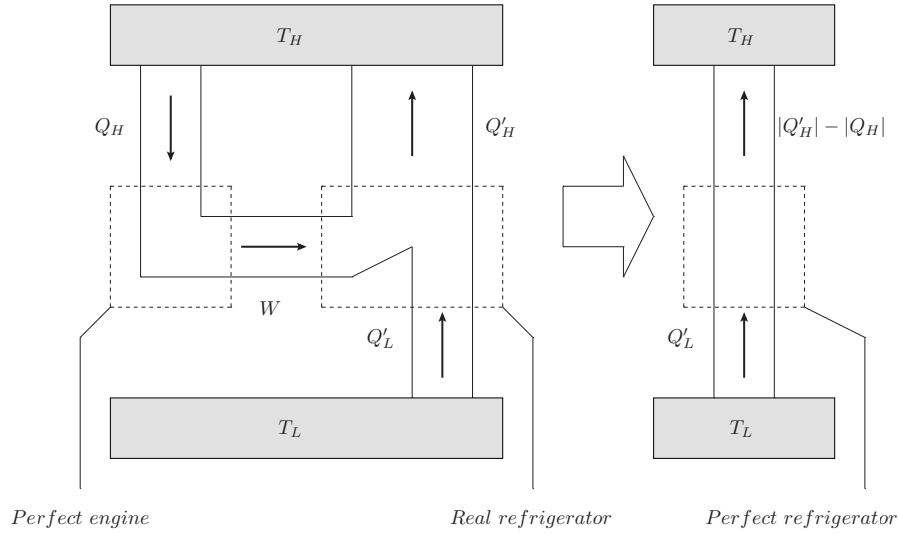
20.3.2 Clausius form for the second law:

An alternative statement of the second law of thermodynamics due to Clausius is:

There are no perfect refrigerators.

20.3.3 Equivalence of Clausius and Kelvin-Planck Statements

The two statements we have presented for the second law are not independent and we are, in fact, entirely equivalent. To show this, let us consider what would happen if Kelvin-Planck form were incorrect, and that we could build a perfect engine, converting heat Q_H entirely into work W . Let us use this work W to drive a real refrigerator, as shown below:



This refrigerator takes heat $|Q'_L|$ from the low-temperature reservoir and pumps heat $|Q'_H| = |Q'_L| + |W|$ to the high-temperature reservoir. Let us regard the combination of the perfect engine and the real refrigerator as a single device, as indicated in the above figure. The work W is an internal feature of this device and does not enter into any exchange of energy with the environment. This device takes heat $|Q'_L|$ from the low-temperature reservoir, and it transfers to the high-temperature reservoir a net amount of heat equal to $|Q'_H| - |Q_H|$. But $|Q_H| = |W|$, and so

$$|Q'_H| - |Q_H| = |Q'_H| - |W| = |Q'_L|$$

Thus our combined device acts like a perfect refrigerator, taking heat $|Q'_L|$ from the low-temperature reservoir and pumping heat $|Q'_L|$ to the high-temperature reservoir, with no external work performed.

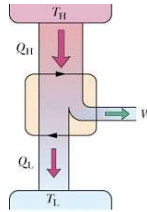
This example shows that, if we can build a perfect engine, then we can build a perfect refrigerator. That is, a violation of the Kelvin-Planck statement of the second law implies a violation of the Clausius statement. In a

similar manner, a perfect refrigerator allows us to turn a real engine into a perfect heat engine. Thus a violation of the Clausius statement implies a violation of the Kelvin-Planck statement. Because a violation of either statement implies a violation of the other, the two statements are logically equivalent.

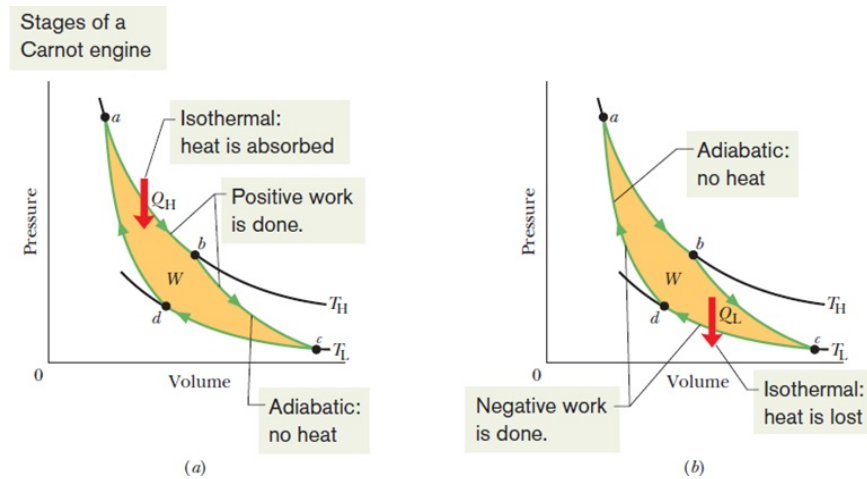
In what follows we will examine ideal engines in which the working substance is an ideal gas. Furthermore, all processes are reversible and there is no friction or turbulence.

20.4 The Carnot engine

One such ideal engine is the Carnot engine. It operates between two reservoirs. One at higher temperature T_H and the other at lower temperature T_L .



The Carnot engine cycle is shown in the following $P - V$ diagram.



The engine starts at point a and undergoes an isothermal expansion $a \rightarrow b$ at temperature T_H . During this process it absorbs an amount of heat Q_H at temperature T_H from the high temperature reservoir. The gas then undergoes an adiabatic expansion $b \rightarrow c$ and its temperature drops to T_L . The gas then is isothermally compressed from $c \rightarrow d$. During this process it delivers an amount of heat Q_L at temperature T_L to the low temperature reservoir. Finally the gas undergoes adiabatic compression $d \rightarrow a$ and its temperature rises back to T_H . During processes ab and bc the gas does positive work on its environment. During processes cd and da the environment does work on the gas. The net work W per cycle is equal to the area enclosed by the curve $abcda$.

20.4.1 Efficiency of a Carnot engine

Let us now calculate the efficiency of the Carnot engine. During isothermal expansion process ab , the work done on the environment is

$$W_{ab} = \int_{V_a}^{V_b} p dV = nRT_H \int_{V_a}^{V_b} \frac{dV}{V} = nRT_H \ln \frac{V_b}{V_a}$$

Since $\Delta E_{int}(a \rightarrow b) = 0$ for an ideal gas during an isothermal process, we have

$$\Delta E_{int}(a \rightarrow b) = Q_H - W_{ab} = 0$$

and

$$Q_H = W_{ab} = nRT_H \ln \frac{V_b}{V_a} \quad (1)$$

Similarly, for the isothermal process cd , we have

$$Q_L = W_{cd} = nRT_L \ln \frac{V_d}{V_c} \quad (2)$$

For the two adiabatic processes bc and da ,

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1} \text{ and } T_H V_a^{\gamma-1} = T_L V_d^{\gamma-1}$$

Dividing the above two equations results in

$$\frac{V_b^{\gamma-1}}{V_a^{\gamma-1}} = \frac{V_c^{\gamma-1}}{V_d^{\gamma-1}}$$

or

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} \quad (3)$$

Combining this with Eqs. (1) and (2) yields

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \quad (4)$$

or

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L}$$

Since $T_H > T_L \rightarrow |Q_H| > |Q_L|$, more energy is extracted from the high temperature reservoir than delivered to the low temperature reservoir. The efficiency ε of the Carnot engine is

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{W_{ab} + W_{cd}}{Q_H} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

20.4.2 Coefficient of Performance of a Carnot Refrigerator

A Carnot engine, because it is reversible, can be run backward to make a refrigerator. The coefficient of performance of a Carnot refrigerator is given by the equation:

$$K = \frac{\text{heat we want to transfer}}{\text{work we pay for}} = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

For a Carnot refrigerator we have:

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H} \rightarrow K = \frac{T_L}{T_H - T_L}$$

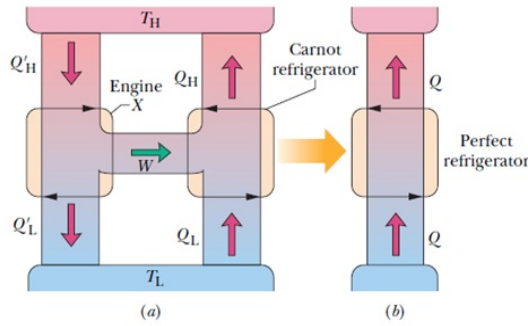
20.4.3 Carnot's Theorem and the Second Law

Based on his ideal reversible heat engine, Carnot developed a general theorem applicable to all heat engines.

Theorem 1 *The efficiency of any heat engine operating between two specific temperatures can never exceed the efficiency of a Carnot engine operating between the same two temperatures.*

That is, the Carnot efficiency is the upper limit for the performance of a heat engine. Clausius and Kelvin showed that the Carnot theorem was a necessary consequence of the second law of thermodynamics, but it is remarkable that Carnot's work was complete long before Clausius and Kelvin developed the statements of the second law. (Carnot's work on heat engines was published in 1824, the year of Kelvin's birth and two years after Clausius was born!)

To show that violating Carnot's theorem is also a violation of the second law, let us suppose we have an engine, which we call engine X . We will prove that the efficiency ε_X of a real engine X cannot be larger than the efficiency of a Carnot engine ε_C . Let's assume for a moment that $\varepsilon_X > \varepsilon_C$. We couple the engine X with a Carnot refrigerator C as shown in the following figure:



They both operate between the same high and low temperature reservoirs. The engine provides the work necessary to operate the refrigerator so that no net work is being used by the engine - refrigerator combination.

$$\varepsilon_X > \varepsilon_C \rightarrow \frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|} \rightarrow |Q_H| > |Q'_H|$$

Since

$$|W| = |Q_H| - |Q_L| = |Q'_H| - |Q'_L|,$$

we have

$$|Q_H| - |Q'_H| = |Q_L| - |Q'_L| = Q$$

By virtue of $|Q_H| > |Q'_H| \rightarrow Q > 0$ Thus the net result of the engine - refrigerator combination is to transfer heat Q from the low temperature to

the high temperature reservoir and thus it is a perfect refrigerator which violates the second law of thermodynamics. As a result

$$\varepsilon_X \leq \varepsilon_C. \quad (5)$$

On the other hand if the engine X is reversible, then the engine X may be reversed to function as refrigerator X . Following the exact argument in showing that $\varepsilon_X > \varepsilon_C$ cannot hold by making the interchange (Engine X , Carnot refrigerator) \Leftrightarrow (Carnot engine, Refrigerator X), we may also show that $\varepsilon_X < \varepsilon_C$ cannot hold and we must have

$$\varepsilon_X \succeq \varepsilon_C. \quad (6)$$

We can thus summarize Carnot's theorem, applied to the efficiency e of any engine, as follows:

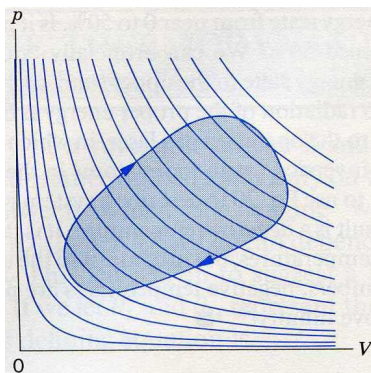
$$\begin{aligned} e &= e_{Carnot} && \text{(reversible)} \\ e &< e_{Carnot} && \text{(irreversible)} \end{aligned}$$

20.5 Entropy: Reversible Processes

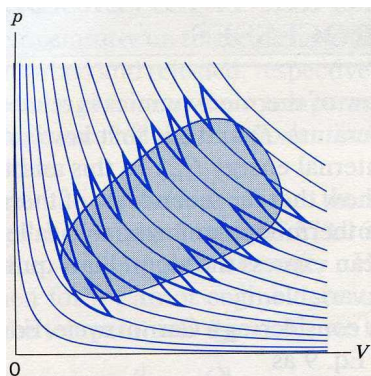
For a Carnot cycle, either as an engine or a refrigerator, Q_H and Q_L always have the opposite signs and

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \quad (7)$$

This equation states that the sum of the algebraic quantities $\frac{Q}{T}$ is zero for a Carnot cycle. As a next step, we want to generalize (7) to any reversible cycle, not just a Carnot cycle. To do this, we approximate any reversible cycle as an assembly of Carnot cycles. The following figure illustrates a reversible cycle superimposed on a family of isothermals.



We can approximate the actual cycle by connecting the isothermals by suitably chosen short segments of adiabatic lines, thus forming an assembly of thin Carnot cycles as demonstrated below.



Traversing the individual Carnot cycles in the above figure in sequence is exactly equivalent, in terms of heat transferred and work done, to traversing the jagged sequence of isotherms and adiabatic lines that approximates the actual cycle. This is so because adjacent Carnot cycles have a common isothermal, and the two traversals, in opposite directions, cancel each other in the region of overlap as far as heat transfer and work done are concerned. By making the temperature interval between the isotherms in the above figure small enough, we can approximate the actual cycle as closely as possible as we wish by an alternating sequence of isotherms and adiabatic lines. We can then write for the isothermal-adiabatic sequence of lines in the above figure,

$$\sum \frac{Q}{T} = 0$$

or, in the limit of infinitesimal temperature differences between the isothermals

$$\oint \frac{dQ}{T} = 0 \quad (8)$$

in which \oint indicates that the integral is evaluated for a complete traversal of the cycle, starting and ending at the same arbitrary point of the cycle. As we have already seen in the case of potential energy, if the integral of a variable around any closed path in a coordinate system is zero, then the value of that variable at a point depends only on the coordinates of the point and not at all on the path by which we arrived at that point. Such a variable is called a state variable, meaning that it has a value that is characteristic only of the state of the system, regardless of how that state was arrived at. (8) is such an integral, and therefore $\frac{dQ}{T}$ must be a differential change in a state variable. We call this new variable the **entropy** S , such that

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

and (8) becomes

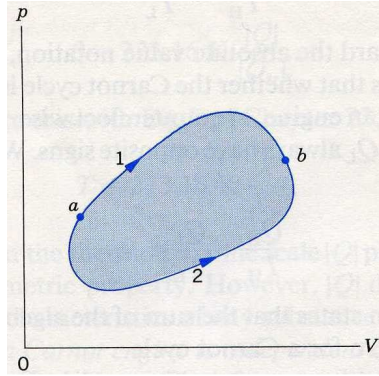
$$\oint dS = 0 \quad (9)$$

The SI unit for entropy is J/K .

The essential point of (9) is that, although dQ is not an exact differential, $\frac{dQ}{T}$ is. The property of a state variable expressed by $\oint dX = 0$ can also be expressed by saying that $\int dX$ between any two equilibrium states has the same value for all reversible paths connecting those states. Let us prove this for the state variable entropy. We can write (9) as

$$\int_{\substack{a \\ \text{path 1}}}^b dS + \int_{\substack{b \\ \text{path 2}}}^a dS = 0 \quad (10)$$

where a and b are two arbitrary points on the cycle, and 1 and 2 are reversible paths connecting them as shown in the following figure:



Since the cycle is reversible, we can traverse path 2 in the opposite direction. (10) can be written as

$$\int_{a}^{b} dS - \int_{a}^{b} dS = 0$$

path 1 path 2

or

$$\int_{a}^{b} dS = \int_{a}^{b} dS$$

path 1 path 2

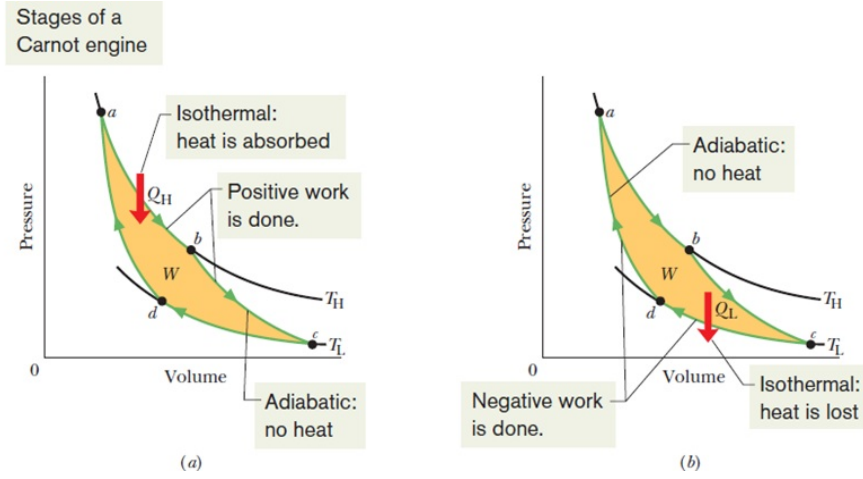
which tells us $\int_a^b dS$ that the quantity between any two equilibrium states of the system is independent of the path connecting those states. The change in entropy between any two states i and f is then

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dQ}{T} \text{ (reversible process)}$$

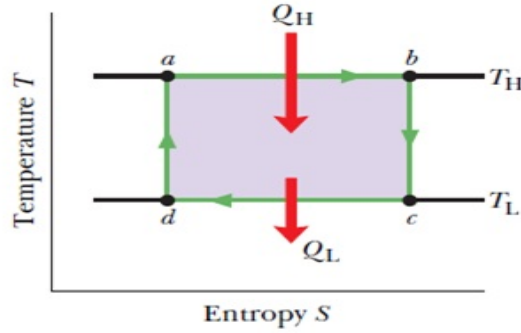
where the integral is evaluated over any reversible path connecting these two states.

20.5.1 Carnot engine in $T - S$ diagram

A Carnot cycle with the $p - V$ diagram,



can be expressed in the following $T-S$ diagram, in which the temperature is plotted as function of the entropy S during one cycle of the Carnot engine.



The net work W done by the engine can be determined from the first law of thermodynamics:

$$\Delta E_{int} = Q - W = 0$$

Since the working substance returns to its original state there is no change in its internal energy. Thus

$$W = Q = |Q_H| - |Q_L|$$

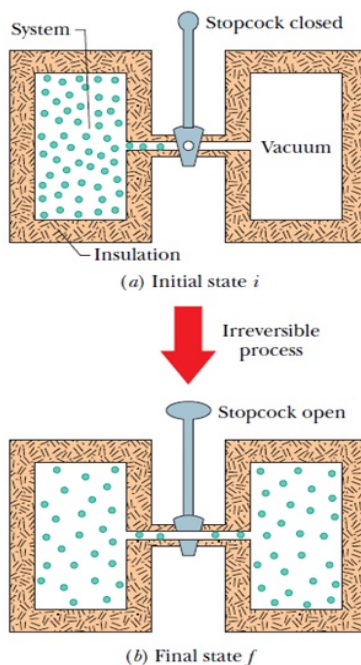
The change in entropy for a cycle is zero.

$$\Delta S = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L} = 0 \rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L} \rightarrow \frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$$

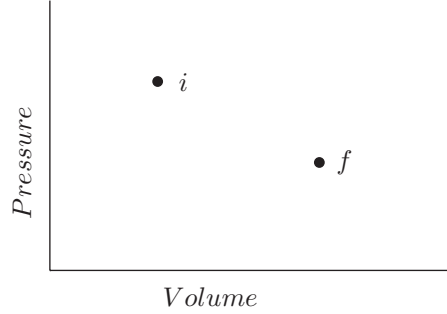
If $T_H > T_L \rightarrow |Q_H| > |Q_L|$, more energy is extracted from the high temperature reservoir than delivered to the low temperature reservoir.

20.6 Entropy: Irreversible Processes

To calculate the entropy change for an irreversible process, we take advantage of the fact that entropy is a state variable. The difference in entropy between states i and f is independent of the path we choose from i to f . We can choose any convenient reversible path for the calculation of the entropy change. Consider the free expansion of a gas shown in the figure.



The initial and final states (P_i, V_i) and (P_f, V_f) are shown on the $P - V$ diagram below.



Even though the initial and final states are well defined, we do not have intermediate equilibrium states that take us from (P_i, V_i) to (P_f, V_f) . During the free expansion the temperature does not change $T_i = T_f$. In order to define the entropy change ΔS for an irreversible process that takes us from an initial state i to a final state f of a system, we find a reversible process that connects states i and f . We then calculate:

$$\Delta S = S_i - S_f = \int_i^f \frac{dQ}{T}$$

In the free expansion of the example $T_i = T_f$. We thus replace the free expansion with an isothermal expansion that connects states (P_i, V_i) and (P_f, V_f) .

From the first law of thermodynamics we have:

$$dE_{int} = dQ - dW \rightarrow dQ = dE_{int} + dW = nC_V dT + PdV \rightarrow \frac{dQ}{T} = P \frac{dV}{T} + nC_V \frac{dT}{T}$$

From ideal gas law we have:

$$pV = nRT \rightarrow P \frac{dV}{T} = nR \frac{dV}{V}$$

$$\Delta S = \int_i^f \frac{dQ}{T} = nR \int_i^f \frac{dV}{V} + nC_V \int_i^f \frac{dT}{T} = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i} \quad (11)$$

The change in entropy depends only on the properties of the initial and final states. It does not depend on how the system changes from the initial to the final state.

20.7 Entropy and The Second Law of Thermodynamics

One - way processes than cannot be reversed by only small changes in their environment are called irreversible. Irreversible processes are so common that if they were to occur spontaneously in the opposite way (the wrong way) we would be astonished. Yet none of these events violate the first law of thermodynamics. As an example imagine that we put our hands around a hot cup of coffee. Experience tells us that our hands will get warmer. We would be astonished if our hands would get cooler even though such an event obeys the first law of thermodynamics. Thus changes in the energy of a closed system do not set the direction of an irreversible process. This is defined by what we will call the change in entropy (ΔS) of the system. We are now ready to express the second law in its most general form in terms of entropy:

In any thermodynamic process that proceeds from one equilibrium state to another, the entropy change of the system + environment either remains unchanged or increases.

For reversible processes, the entropy remains unchanged. For irreversible processes, the total entropy + environment must increase. It is possible that the entropy of the system might decrease, but the entropy of the environment always shows an increase of greater amplitude, so that the total change in entropy is always positive. No natural process can ever show a decrease in the total entropy of the system + environment. The second law, like the zeroth and first laws, is a generalization from experience. It cannot be proved, but we can test it in a variety of circumstances.

20.7.1 Free Compression

Eq. (11) shows that a free compression, in which $V_f < V_i$, would have a negative change of entropy for the system (with no change in entropy of the environment, as in the free expansion). The statement of the second law in terms of entropy thus forbids the free compression, and so it is unlikely that you will find all the air rushing to the opposite side of the room in which you are sitting.

20.7.2 The Kelvin-Planck Form of the Second Law

Because all engines operates in cycles, the entropy change for the system must be zero for one complete cycle of operation. In a perfect engine, the environment release heat Q at temperature T , and its entropy change is $\frac{Q}{T}$, a negative quantity. The total entropy change of system + environment is therefore negative for a perfect engine. The existence of a perfect engine would thus violate entropy statement of the second law.

20.7.3 The Clausius Form of the Second Law

In a perfect refrigerator, the system has no entropy change fin a complete cycle, but the environment release heat $-|Q|$ at temperature T_L and absorbs heat $|Q|$ at temperature T_H . The total entropy change of the environment is

$$\Delta S = \frac{|Q|}{T_H} - \frac{|Q|}{T_L} = |Q| \left(\frac{1}{T_H} - \frac{1}{T_L} \right) < 0$$

because $T_H > T_L$. A perfect refrigerator would thus violate entropy statement of the second law.

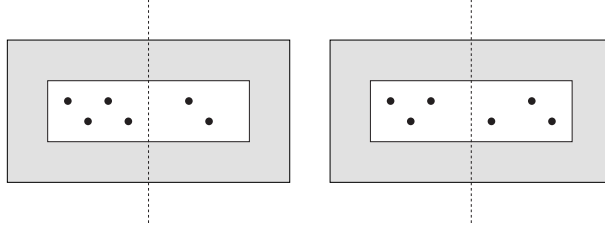
20.7.4 The Arrow of Time

It is the change in entropy that ultimately provides us with the answer to why systems will naturally evolve in one direction of time and not the other: systems always evolve in time in such a way that the total entropy of system + environment increases. If you observe a system in which the entropy appears to decrease, you can be sure that somewhere there is a change of entropy of the environment large enough to make the total entropy change positive.

20.8 A Statistical View of Entropy

We shall focus on the problem involving the distribution of gas molecules between the two halves of an insulated box. This problem is reasonably simple to analyze, and it allows us to use statistical mechanics to calculate the entropy change for the free expansion of an ideal gas.

For a box that contains 6 identical molecules of gas.



At any instant, a gas molecule will be in either the left or the right half of the box; because the two halves have equal volumes, the molecule has the same likelihood, or probability, of being in either half. The following table shows the 7 possible configurations of the 6 molecules.

<i>Configuration</i>	n_1	n_2	<i>Multiplicity</i> W	<i>Entropy</i> $10^{-23} J/K$
<i>I</i>	6	0	$\frac{6!}{6!0!} = 1$	0
<i>II</i>	5	1	$\frac{6!}{5!1!} = 6$	2.47
<i>III</i>	4	2	$\frac{6!}{4!2!} = 15$	3.74
<i>IV</i>	3	3	$\frac{6!}{3!3!} = 20$	4.13
<i>V</i>	2	4	$\frac{6!}{2!4!} = 15$	3.74
<i>VI</i>	1	5	$\frac{6!}{1!6!} = 6$	2.47
<i>VII</i>	0	6	$\frac{6!}{0!6!} = 1$	0

The number of microstates that correspond to a given configuration is called the multiplicity W of that configuration. In the case of $N = n_1 + n_2$ molecules with n_1 and n_2 being the number of molecules in the left and right compartments, the multiplicity W is

$$W = \frac{N!}{n_1!n_2!} \quad (12)$$

The basic assumption of statistical mechanics is:

All microstates are equally probable.

Because all microstates are equally probable but different configurations have different members of microstates, the configurations are not all equally probable.

For large values of N there are extremely large numbers of microstates, but nearly all the microstates belong to the configuration in which the molecules are divided equally between the two halves of the box.

20.8.1 Probability and Entropy

In 1877, Austrian physicist Ludwig Boltzmann derived a relationship between the entropy S of a configuration and the multiplicity W of that configuration. The relationship is

$$S = k \ln W \text{ (Boltzmann's entropy equation)}$$

This famous formula is engraved on Boltzmann's tombstone.

For free expansion, initially the (n_1, n_2) configuration is $(N, 0)$ which gives the multiplicity

$$W_{(N,0)} = \frac{N!}{N!0!} = 1$$

and

$$S_i = k \ln W_i = 0$$

With molecules spread through the full volume, the final (n_1, n_2) configuration is $(\frac{N}{2}, \frac{N}{2})$

$$\begin{aligned} S_f &= k \ln \frac{N!}{\left(\frac{N}{2}\right)^2} \simeq k \left(N \ln N - \frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} \ln \frac{N}{2} \right) \\ &= kN \left(\ln N - \ln \left(\frac{N}{2} \right) \right) = kN \ln 2 = nR \ln 2 \end{aligned}$$

note we have used

$$\ln N! \simeq N \ln N - N$$