

## 5 Second Law of Thermodynamics

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### Introduction

Thermodynamics is built on three laws we have met already, together with two important new ones.

1. Heat flows from a higher temperature body to a lower temperature one, thus allowing thermal equilibrium to be established.
2. For a substance or mixture in equilibrium there is an equation of state, giving, for example, density  $\rho$  as a function of pressure  $p$ , temperature  $T$ , and, possibly, other variables such as chemical composition (for a mixture), electric or magnetic fields, and so on.
3. Heat is a form of conserved energy (first law of thermodynamics).
4. Friction, viscosity, the creation of turbulence, heat conduction, etc., can be minimized in principle to get processes that change the state of a system in ways that are almost reversible.
5. You cannot get work out of heat without paying a price for it.

The last of these statements is a paraphrase of the Kelvin–Planck statement of the second law of thermodynamics, that it is not possible to convert heat entirely into work, with no other change taking place. The Clausius statement of the second law is that it is not possible to get heat to flow from a lower temperature to a higher temperature without other changes taking place; you cannot run a refrigerator without having a source of power.

From the second law it follows that you need a source of power, so thermal energy at uniform temperature does not enable you to do useful work, or to heat or cool one region at the expense of another. A lot of unexpected consequences also follow from this, and the concept of *entropy* and its usefulness are the most striking ones. Up to this point we have referred to a small quantity of heat as  $\delta Q$ , but have not been able to relate this to the change of anything. Once entropy  $S$  is defined we can write  $\delta Q = T\delta S$ , where  $S$  is the entropy, when we are talking about reversible processes.

The original analysis was done by Sadi Carnot in the 1820s, but was largely ignored for the next twenty years. Carnot analyzed the operation of a heat engine, something like a steam engine that produces power from the transfer

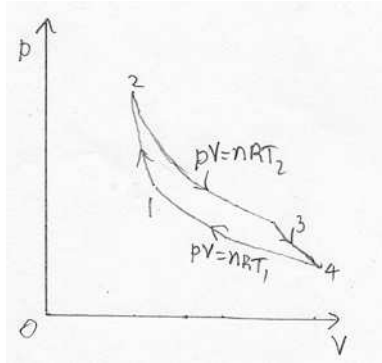


Figure 1: Carnot cycle shown in a  $pV$  diagram. The arrows show the direction in which the cycle is traversed when work is being obtained from a heat source at temperature  $T_2$ . For use as a heat pump cooling an object at temperature  $T_1$  the cycle should be traversed in the opposite direction

of heat from a hot body to a cold one. The hot body is the boiler or the furnace that heats it, and the cold body is the outside air or the condenser, which in Watt's design and in most subsequent useful engines, is separate from the hot cylinder. In a steam engine hot steam goes into a cylinder, causing it to drive the piston outwards. The inlet valve is then closed, the outlet valve opened, and steam driven out by the piston from the cylinder to the condenser. Water is cheap, so it is lost to the outside air in a steam engine, but the working substance could be recycled, as it is in a domestic refrigerator.

One of Carnot's important results was that the nature of the working substance is unimportant, so the analysis can be done for an ideal gas, and then the results applied to any material.

I will go through the Carnot analysis, and show how it leads to the concept of entropy. The analysis is independent of the model of heat that is used, but entropy can be related in a precise way to the degree of disorder in statistical mechanics. I conclude by discussing a few simple examples of the use of the concept of entropy. One of the simplest examples relates the slope of a vapor pressure curve or melting curve to the latent heat and change in density in a transition.

## 5.1 Carnot cycle and entropy

The Carnot engine is a cylinder containing an ideal gas, closed off by a piston which can do work or have work done on it. There are four steps which we will analyze in turn:

1. the gas is compressed adiabatically, so that no heat flows out of the cylinder during the process;
2. the gas expands at constant temperature;
3. the gas expands adiabatically until it returns to its original temperature;
4. the gas is compressed isothermally until it returns to its original pressure and volume.

This cycle is shown in fig. 1. Throughout this analysis it is assumed that no heat is generated by friction, viscosity, or other processes that generate heat irreversibly.

In this argument we make much use of the gas law,  $pV = nRT$ , and of the condition for an adiabatic change in an ideal gas

$$pV^\gamma = \text{constant} , \quad (1)$$

where  $\gamma$  is the ratio of specific heats  $c_p/c_V$ , which was derived in sec. 3.2..

For each of the four steps that takes the gas in the cylinder round back to its initial conditions we work out the work  $W$  done by the gas and the heat  $Q$  taken in. We start and end with  $n$  moles of gas at temperature  $T_1$  and volume  $V_1$ , so that the pressure is  $p_1 = nRT_1/V_1$ .

1. In the course of compressing adiabatically from  $T_1$  to  $T_2$ , with  $pV^\gamma = p_1V_1^\gamma$ , the work done by the gas is

$$W_{12} = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} p_1 V_1^\gamma \frac{dV}{V^\gamma} ,$$

but we do not have to bother to evaluate it, since it is just minus the increase in internal energy, from the first law. We therefore get that the work done by the gas is

$$W_{12} = -C_V(T_2 - T_1) .$$

2. For the isothermal expansion at temperature  $T_2$  from  $V_2$  to  $V_3$ , with  $p = nRT_2/V$ , the work done by the gas is

$$W_{23} = nRT_2 \int_{V_2}^{V_3} \frac{dV}{V} = nRT_2 \ln \frac{V_3}{V_2}. \quad (2)$$

Since the ideal gas maintains the same internal energy at constant temperature, the heat taken in at this temperature must be

$$Q_{23} = nRT_2 \ln \frac{V_3}{V_2}. \quad (3)$$

3. In the adiabatic expansion from  $T_2$  to  $T_1$  the change in internal energy is just the opposite of the change in the adiabatic compression, so the work done by the gas in this stage is just

$$W_{34} = -W_{12}.$$

4. In the final isothermal compression the work done by the gas is

$$W_{41} = nRT_1 \ln \frac{V_1}{V_4}, \quad (4)$$

and the heat emitted at temperature  $T_1$  is

$$-Q_{41} = nRT_1 \ln \frac{V_4}{V_1}. \quad (5)$$

A combination of the four relations

$$p_1 V_1^\gamma = p_2 V_2^\gamma, \quad p_3 V_3^\gamma = p_4 V_4^\gamma, \quad p_2 V_2 = p_3 V_3, \quad p_4 V_4 = p_1 V_1,$$

multiplied together in pairs gives

$$(p_1 p_3)(V_1 V_3)^\gamma = (p_2 p_4)(V_2 V_4)^\gamma, \quad (p_1 p_3)(V_1 V_3) = (p_2 p_4)(V_2 V_4).$$

This leads to  $V_1 V_3 = V_2 V_4$ , and so Eqs. (2) and (3) can be combined as

$$W_{23} = Q_{23} = nRT_2 \ln \frac{V_4}{V_1}. \quad (6)$$

These equations give the total work done in the cycle as

$$W = W_{12} + W_{23} + W_{34} + W_{41} = nR(T_2 - T_1) \ln \frac{V_4}{V_1}. \quad (7)$$

For an engine, converting heat into work, we are interested in the ratio of the net work output  $W$  to the heat  $Q_{23}$  put in at the higher temperature  $T_2$ , since it is the heat put in that is paid for in fuel bills. This ratio is naturally called the *efficiency* of this ideal heat engine, and Eqs. (7) and (6) show that this ideal efficiency is

$$e = \frac{W}{Q_{23}} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}. \quad (8)$$

The cooling is done at whatever temperature the surroundings have, probably a little below 300 K, since that is where cooling can be done at no cost, so the higher the operating temperature  $T_2$  is the more efficient the engine can be. With a boiler operating at 373 K and a condenser at 293 K the maximum possible efficiency is  $80/373 = 21\%$ . This is the way that steam engines were made in the early days of James Watt and Robert Stephenson, but in Stephenson's time some engineers were making engines whose boilers were under pressure. At 200 C the maximum possible efficiency goes up to  $180/473 = 38\%$ , but the vapor pressure of water at that temperature is more than 15 atm., so boilers have to be well made to avoid an explosion.

We can also write the very important result for the ideal Carnot cycle

$$\frac{Q_{41}}{T_1} + \frac{Q_{23}}{T_2} = 0. \quad (9)$$

As we show in section 5.6, this result leads to the concept of entropy.

## 5.2 Refrigerators and heat pumps

The Carnot cycle can be run in reverse, so that work is done on the system, and heat is pumped from a low temperature to a high temperature. The most familiar devices that work this way are a refrigerator, which pumps heat out of the refrigerator into the room, and an air conditioner, that pumps heat from a house into the warmer outside air. Under these conditions Eq. (7) is modified to give

$$W = W_{14} + W_{43} + W_{32} + W_{21} = -nR(T_2 - T_1) \ln \frac{V_4}{V_1}, \quad (10)$$

while the heat absorbed by the engine at  $T_1$  and emitted at  $T_2$  are, from Eqs. (3) and (5) respectively

$$Q_{14} = nRT_1 \ln \frac{V_4}{V_1}, \quad -Q_{32} = nRT_2 \ln \frac{V_4}{V_1}. \quad (11)$$

For a refrigerator or air conditioner, one is interested in the ratio of the heat removed from the lower temperature to the work done by an outside power source on the heat pump. This gives the *coefficient of performance* of the ideal heat pump as

$$CP = \frac{Q_{14}}{|W|} = \frac{T_1}{T_2 - T_1} . \quad (12)$$

This coefficient of performance can be greater than unity, so that the heat taken out of the refrigerator can be greater than the work that is put into it. For a deep freeze kept at -20 C in a room at +20 C we get  $CP=253/40=632\%$  Both of these forms of energy are ejected into the room, so a refrigerator is a considerable source of heat. If a refrigerator is in a place where this heat is not dispersed quickly, the temperature  $T_2$  rises, the coefficient of performance drops, and the pump has to work even harder to keep the refrigerator cool.

One is warned not only to ventilate the back of the refrigerator, where the heat is usually emitted, properly, but also not to keep it in too cold a room. Why is this?

Kelvin looked at these equations and decided he could not lose by using a heat pump to pump heat from the outside into his house. In this case, the performance is determined by the heat that is delivered to the higher temperature, not by the heat that is taken from the lower temperature. This gives a different measure of the coefficient of performance

$$CP' = \frac{|Q_{32}|}{|W|} = \frac{T_2}{T_2 - T_1} , \quad (13)$$

and this is always greater than unity, and can be very large. You can guess from the fact that we do not all have our houses heated by heat pumps that the actual performance is considerably less than the possible performance, and that good equipment can be quite costly to buy and maintain. There can also be a problem of the heat intake getting covered with cold ice in winter, so that its temperature drops well below the ambient temperature.

### 5.3 Irreversibility

It is obvious that friction acting on the piston will reduce the amount of force it will deliver when it is doing work on an expansion stroke, and increase the amount of force that must be applied on compression, thus reducing the amount of work done by the engine. Similarly, in a heat pump more power

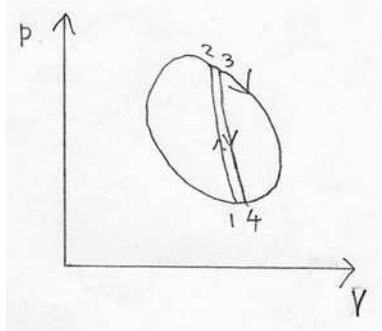


Figure 2: A general cycle shown in a  $pV$  diagram. At any point on the cycle an adiabatic curve can be found which intersects the closed loop again at another point. Two such lines, close to one another, are shown in the diagram.

must be delivered on compression, and less is given back on expansion, so  $|W|$  is increased and the coefficient of performance is reduced.

A similar analysis can be done for other sources of irreversibility. If the engine operates too rapidly, so that the gas in the system does not come to equilibrium, but has nonuniform temperature, the temperature, and hence the pressure, will be too low on the supposedly isothermal expansion, and too high on the supposedly isothermal compression, so less work is done by the engine. For the engine run in reverse as a heat pump the temperature will be too high on the high-temperature isothermal compression stroke, and too low on the low-temperature expansion stroke, so more work will be done, in relation to the heat transferred from the low-temperature side. Similar effects are produced if some of the internal energy is stored as turbulent motion, rather than as completely disordered thermal motion. Less work is done by the engine in its expansion strokes, and more work has to be done on it in the compression strokes.

#### 5.4 Other engines

The Carnot engine is highly idealized, and would be of little interest, except that it can be shown how the second law of thermodynamics can be applied to any engine or heat pump. Figure 2 shows a schematic cycle in the  $pV$  diagram of some real substance that might be used as the working substance of a heat engine or heat pump. If we pick one point on the cycle,

at temperature  $T_1$ , we can draw an adiabatic line through that, using the equation given by the first law of thermodynamics in the absence of heat flow,  $\delta U + p\delta V = 0$ , or

$$\frac{d}{dV}U(p, V) + p = \left(\frac{\partial U}{\partial p}\right)_V \frac{dp}{dV} + \left(\frac{\partial U}{\partial V}\right)_p + p = 0, \quad (14)$$

which can be used to track out an adiabatic curve on the  $pV$  diagram. This curve cuts the cycle at two points, with temperatures we call  $T_1, T_2$ . I have drawn a second adiabatic curve close to the first. We can imagine a new reversible heat engine or heat pump which goes around the long narrow loop enclosed by the two long segments of adiabatic curves, and the two short segments of the original cycle which are at temperatures close to  $T_2, T_1$  respectively. Although the short segments are not along isotherms the variation of temperature is small and does not affect the analysis; the area enclosed by this long narrow loop does not depend significantly on the two short end segments.

We can regard this as a new sort of Carnot cycle, operating with a real substance instead of with an ideal gas. The second law of thermodynamics can now be used to show that the efficiency of the ideal Carnot engine applies to all engines operating between temperatures  $T_2$  and  $T_1$ . It does not matter what the working substance is, but if the substance at temperature  $T_1$  is compressed adiabatically until it reaches temperature  $T_2$ , heat  $Q_2$  is put in it at temperature  $T_2$ , the working substance is allowed to expand adiabatically until it has temperature  $T_1$ , and finally heat  $-Q_1$  is removed at temperature  $T_1$ , the efficiency must be the same as that of the Carnot engine if it is reversible. If its efficiency  $e$  were greater than  $e_C = 1 - T_1/T_2$ , then we could use the work  $W$  it generated to run a Carnot engine in reverse, and return an amount of heat

$$Q = \frac{W}{e_C} > \frac{W}{e}$$

back to the heat source. Thus a net heat  $Q = W/e_C - W/e$  would be absorbed from the low temperature end and delivered back to the high temperature end, in contradiction to the Clausius statement of the second law of thermodynamics. Similarly, if  $e < e_C$  for some reversible engine, it will have a higher coefficient of performance in reverse than the Carnot engine, and you can use power from the Carnot engine to drive this lower efficiency engine in reverse, to get heat  $Q = W/e - W/e_C$  raised from temperature  $T_1$  to temperature  $T_2$ . Thus all reversible engines have the same efficiency

as the Carnot engine when operating with the same temperature difference, and irreversible engines have lower efficiency.

This shows that Eq. (9) applies to this generalized Carnot cycle as

$$\frac{\delta Q(T_2)}{T_2} + \frac{\delta Q(T_1)}{T_1} = 0 .$$

We can imagine the whole area inside the loop of fig. 2 divided into such narrow strips by a set of closely spaced adiabatic curves, and this equation should hold for each of them. We can add up such equations to get the result

$$\oint \frac{dQ_{\text{rev}}(T)}{T} = 0 , \quad (15)$$

for the integral round the closed loop, denoted in the usual way by  $\oint$ . Here  $\int dQ$  is the heat flowing into the working substance. This is the analog of Eq. (9) for the Carnot cycle, and is forced on us by the second law of thermodynamics.

In a real engine irreversible processes occur, such as the generation of heat by the friction between the pistons and cylinders, or by creation of turbulence in the gas, which is eventually dissipated as heat rather than as useful work. The result of such processes is to increase the amount of heat  $-dQ$  flowing out of the engine into the environment, so that the integral in Eq. (15) becomes negative, and the equation must be replaced by the inequality

$$\oint \frac{dQ(T)}{T} \leq 0 . \quad (16)$$

Similar effects are produced by departures from ideality, such as the failure of the gas in the cylinder to remain as hot as the heat source during the expansion, and to get as cold as the environment which cools it during the supposedly isothermal compression.

## 5.5 Thermodynamic temperature

In various parts of this course we have reexamined temperature. Initially temperature scales were dependent on how one constructed the thermometer, and all that we demanded was that heat should flow from warmer to cooler bodies. Then we showed that the gas laws provided a temperature scale that can use any dilute gas and give the same result. The zero of temperature is an absolute minimum, and only one fixed point has to be defined to define the scale. Then, on the basis of kinetic theory and the equipartition of energy we showed that the temperature as defined for the ideal gas

is proportional to the average translational kinetic energy of a molecule. It occurs in the denominator of the exponent in the Boltzmann distribution. Finally, we have shown that this temperature scale has general significance in thermodynamics, since the maximum possible efficiency of any engine depends in a simple manner on the temperature as we have already defined it. Therefore we can refer to the Kelvin scale as the *thermodynamic temperature* without any reference to the properties of an ideal gas.

## 5.6 Heat and entropy

Equation (15) shows that heat is not only a part of the conserved energy, according to the first law of thermodynamics, but that the quantity

$$\int \frac{dQ_{\text{rev}}}{T}$$

depends only on the end points of the integral, not on its path in  $pV$  space (or in any other appropriate space, such as  $VT$  space). Therefore we can define a new function of the equilibrium state of the system by

$$S(p, V) - S(p_0, V_0) = \int_{p_0, V_0}^{p, V} \frac{dQ_{\text{rev}}}{T}. \quad (17)$$

This argument is very similar to the argument that allows an electric potential function to be constructed in the theory of electricity whenever the integral of the electric field round a closed loop is zero. There would seem to be an arbitrary constant in the entropy, that depends on what values we choose for  $p_0, V_0$ , but the third law of thermodynamics, or Nernst's law, says that the entropy is zero at zero temperature. This law is based both on statistical mechanics and on experiment, and will be discussed later.

Entropy is conserved in reversible processes, but when heat is created from heat irreversibly, by friction or viscosity, or flows irreversibly by conduction or convection from a hot body to a colder body, entropy increases, and the amount of energy available for useful work becomes less available. This leads to the idea of *free energy* which is discussed in sec. 6.6.

The first law of thermodynamics allows the energy conservation condition to be written for small, reversible, changes of a substance as

$$dQ_{\text{rev}} = dU + p dV .$$

Equation (17) allows us to rewrite this in the form

$$dU = -p dV + T dS . \quad (18)$$

The identification of heat transferred as

$$\delta Q = T\delta S$$

allows us to rewrite the constant volume heat capacity as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V ,$$

and we can also write the constant pressure heat capacity as

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_p ,$$

since  $T dS$  is the heat. If the heat capacities are known, these can be used to determine the entropy of a substance, by

$$S(p, V) = S(p_0, V_0) + \int_{p_0, V_0}^{p, V_0} \frac{C_v}{T} dT + \int_{p, V_0}^{p, V} \frac{C_p}{T} dT . \quad (19)$$

Similarly the latent heat can be written in terms of the entropy change between two phases, in the forms

$$L_{\text{fus}} = T(S_{\text{liq}} - S_{\text{sol}}) , \quad L_{\text{boil}} = T(S_{\text{gas}} - S_{\text{liq}}) , \quad (20)$$

where the entropy changes are discontinuities of the entropy across the phase coexistence lines.

Equation (18) can be compared with the defining equation for partial derivatives, which in this case can be written as

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS . \quad (21)$$

This immediately allow us to write

$$\left(\frac{\partial U}{\partial V}\right)_S = -p , \quad \left(\frac{\partial U}{\partial S}\right)_V = T . \quad (22)$$

We can go one step further by using the mathematical result that for the second partial derivative with respect to two different variables, the order in which the derivatives are taken is unimportant. The equality of  $\partial^2 U / \partial S \partial V$  and  $\partial^2 U / \partial V \partial S$  gives the *Maxwell relation*

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S . \quad (23)$$

This equation gives an unobvious relation between the change of pressure when heat is supplied at constant volume, and the change in temperature in an adiabatic expansion.