

Chapter 2

Carnot Principle

2.1 Temperature

2.1.1 *Isothermal Process*

When two bodies are placed in thermal contact, the hotter body gives off heat to the colder body. As long as the temperatures are different, there will be a flow of heat between them. After a while, the temperature becomes equal and the heat flow ceases. From that moment on the bodies are in thermal equilibrium.

Once a body is in thermal equilibrium its temperature does not change anymore, unless it is disturbed. To verify possible changes in temperature, we used a tool comprising a substance having a thermometric property, that is, a property which varies with temperature. We call this instrument thermoscope and not thermometer, considering that we did not introduce a temperature scale yet.

Consider a gas confined in a cylindrical container whose base allows the exchange of heat and whose top can move freely. Over the top we place a certain amount of sand. Starting from a certain pressure adjusted by the quantity of sand on the top, we lead the gas through a process along which the temperature remains constant by monitoring the temperature of the gas by means of the thermoscope. We place the gas in the initial state and mark the value of the thermometric property. Then we allow the gas to expand by introducing a small amount of heat. If the temperature has changed, we vary the pressure by the removal of sand, until the temperature returns to the same value. This operation is then repeated many times. If the amount of heat introduced into each stage is small enough, the procedure approaches a quasi-static process carried out at constant temperature, or an isothermal process. The corresponding trajectory is an isotherm.

Another way to achieve an isothermal process is as follows. It is an experimental fact that can be verified by the use of thermoscope that a pure substance, such as pure water, has its temperature unchanged while it boils at constant pressure. If we place the cylinder containing the gas in contact with boiling water, the gas

temperature remains constant. Removing sand from the top in small quantities, we will be conducting an isothermal process.

The above procedures allow a system to go through an isothermal process. However, we do not know the temperature of the system since we have not defined a temperature scale. In the following we define a temperature scale, called absolute temperature T , which allows us to determine the temperature of equilibrium systems.

2.1.2 Carnot Cycle

Suppose that a system, comprising a fluid contained in a vessel, runs a cycle consisting of two isothermal processes and two adiabatic process. Starting from a state **A**, the system undergoes an isothermal expansion to a state **B**, then an adiabatic expansion to a state **C**, after an isothermal compression to a state **D** and finally an adiabatic compression back to the initial state **A**. This cycle, shown in Fig. 2.1, is referred to as the Carnot cycle. In the isothermal expansion, the system receives an amount of heat Q_1 from a heat reservoir at a temperature T_1 and, in the isothermal compression, gives off an amount of heat Q_2 to a heat reservoir at temperature T_2 . The Carnot principle states that *the ratio of the work and heat received by a system which operates according to a Carnot cycle depends only on the temperature of the reservoirs*. Denoting by W the work done by the Carnot cycle then W/Q_1 depends only on T_1 and T_2 . This principle is universal and is therefore independent of the substance that comprises the system that undergoes the cycle.

By the principle of conservation of energy, the work done in a closed cycle equals the heat received minus the heat given off, $W = Q_1 - |Q_2|$, so $W/Q_1 = 1 - |Q_2|/Q_1$. We conclude from the Carnot principle that the ratio of heat given off $|Q_2|$ and the heat received Q_1 depends only on the temperatures of the reservoirs, that is

$$\frac{|Q_2|}{Q_1} = f(T_1, T_2). \quad (2.1)$$

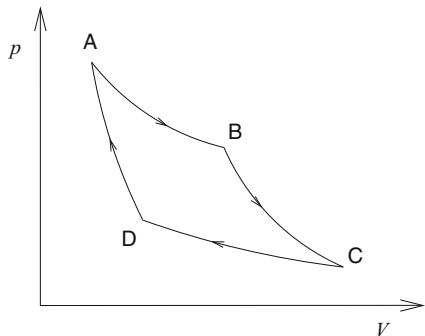
If now we use another system which runs a Carnot cycle whose isotherms correspond to temperatures T_2 and T_3 then

$$\frac{|Q_3|}{Q_2} = f(T_2, T_3), \quad (2.2)$$

where Q_2' is the heat received and $|Q_3|$ is the heat given off by the system running this second cycle. We conveniently choose the second cycle so that the heat given off by the first system is received by the second system so that $Q_2' = |Q_2|$. Multiplying the two equations (2.1) and (2.2) and taking into account that $Q_2' = |Q_2|$, we get

$$\frac{|Q_3|}{Q_1} = f(T_1, T_2)f(T_2, T_3). \quad (2.3)$$

Fig. 2.1 Representation of the Carnot cycle in the Clapeyron diagram. AB represents an isothermal expansion, BC an adiabatic expansion, CD an isothermal compression and DA an adiabatic compression



But Q_1 and Q_3 , appearing on the left side, can be considered respectively as the heat received and heat given off by a Carnot cycle operating between the temperatures T_1 and T_3 . Therefore,

$$\frac{|Q_3|}{Q_1} = f(T_1, T_3), \quad (2.4)$$

so that

$$f(T_1, T_2)f(T_2, T_3) = f(T_1, T_3). \quad (2.5)$$

A function that satisfies this equation is of the form

$$f(T, T') = \frac{\phi(T')}{\phi(T)}, \quad (2.6)$$

from which we conclude that

$$\frac{|Q_2|}{Q_1} = \frac{\phi(T_2)}{\phi(T_1)}, \quad (2.7)$$

where $\phi(T)$ is a function to be defined but which is independent of the substances which is used to run the cycle.

Next we use the Carnot principle, in the form given by equation (2.7), to define the absolute scale of temperature. Following the prescription of Kelvin, we define absolute temperature T as the quantity such that $\phi(T) \propto T$ or, equivalently,

$$\frac{|Q_2|}{Q_1} = \frac{T_2}{T_1}. \quad (2.8)$$

Thus, to construct an absolute temperature scale, it suffices to assign a numerical value to the temperature of a reference state. Any other temperature is determined

in accordance with (2.8). For the Kelvin scale (K) one uses the triple point of water as a reference state whose temperature we assign the exact value

$$T_0 = 273.16 \text{ K.} \quad (2.9)$$

It is worth mentioning that in the Kelvin scale the temperature of the melting of ice at a pressure of 1 atm is $T_{sl} = 273.15 \text{ K}$ and that the temperature of boiling water at the same pressure of 1 atm is $T_{lv} = 373.15 \text{ K}$.

The Celsius scale ($^{\circ}\text{C}$) of temperature θ is defined by

$$\theta = T - 273.15 \text{ }^{\circ}\text{C}, \quad (2.10)$$

where T is given in kelvins. In the Celsius scale, the temperature of the triple point of water is $\theta_0 = 0.01 \text{ }^{\circ}\text{C}$, whereas the temperature of the melting ice and boiling water at the pressure of 1 atm are $\theta_{sl} = 0 \text{ }^{\circ}\text{C}$ and $\theta_{lv} = 100 \text{ }^{\circ}\text{C}$, respectively.

2.2 Entropy

2.2.1 Definition of Entropy

The definition of temperature allowed us to determine the temperature of a gas for any values of p and volume V . Thus, to each point of the Clapeyron diagram is associated a temperature. The points having the same temperature form an isotherm. The isotherms are a set of lines that never intersect, as can be seen in Fig. 2.2.

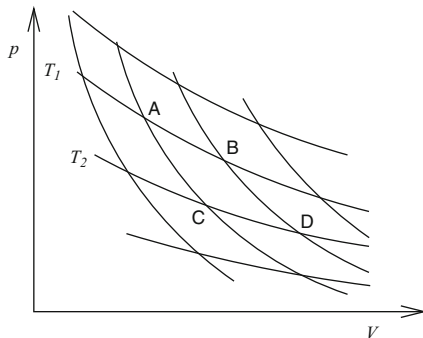
We can also plot on the same Clapeyron diagram, adiabatic lines corresponding to the same gas. To set up an adiabatic line, we confine the gas in a cylindrical container with adiabatic walls and slowly raise the top of the cylinder, while measuring the volume and pressure. Repeating this procedure several times, we get several adiabatic lines. The adiabatic lines form a set of lines which do not intersect, as can be seen in Fig. 2.2.

Just as there is a thermodynamic quantity associated with the isotherms, which is the temperature, already defined, we also associate to the adiabatic lines a thermodynamic quantity. This quantity should be invariant along an adiabatic line, but this is not sufficient to establish its value for each adiabatic line. To set this quantity, called entropy, we proceed as follows.

Consider any two adiabatic lines constructed in the manner shown above. Consider a point A on the first adiabatic line and a point B on the second adiabatic line such that A and B are in the same isotherm, corresponding to a temperature T_1 , as shown in Fig. 2.2. If S_A is the entropy of the first adiabatic line, then the entropy S_B of the second adiabatic line is defined by

$$S_B = S_A + \frac{Q_1}{T_1}, \quad (2.11)$$

Fig. 2.2 Set of isotherms and adiabatic lines in the Clapeyron diagram. The lines AB and CD are isotherms corresponding to temperatures T_1 and T_2 , respectively. The lines AC and BD are adiabatic lines



where Q_1 is the amount of heat received by the system from A to B along the isotherm T_1 .

Suppose that another pair of points C and D are chosen on the two adiabatic lines, C over the first adiabatic and D over the second, but belonging to another isotherm, corresponding to a temperature T_2 , as shown in Fig. 2.2. Using the same definition we also have

$$S_B = S_A + \frac{Q_2}{T_2}, \quad (2.12)$$

where Q_2 is the amount of heat received by the system from C to D along the isotherm T_2 . At first sight, expressions (2.11) and (2.12) seem to be inconsistent. But by the Carnot principle $Q_1/T_1 = Q_2/T_2$ so that (2.11) and (2.12) are in fact consistent and the entropy of the second adiabatic line becomes independent of the choice of the isotherms.

Thus, taking an adiabatic line as reference for entropy, all other adiabatic lines will be associated with well defined values of entropy. To each point of the Clapeyron diagram is associated a certain value of entropy. As the adiabatic lines connect points with the same entropy value, they are also called isentropic lines. The quasi-static adiabatic processes may equivalently be called isentropic processes.

2.2.2 Clausius Integral

Next we show that the entropy difference between any two points A and B in the Clapeyron diagram is given by the Clausius integral

$$S_B - S_A = \int \frac{dQ}{T}, \quad (2.13)$$

which extends over *any path* connecting the points A and B. This integral should be understood as follows. A path chosen from A to B is partitioned into a number of segments. For each segment, we determine the ratio Q_i/T_i between the heat

exchanged and the temperature at which the system is found along the segment. However, as the segment is not necessarily an isotherm, the temperature may vary along the segment. To avoid ambiguity we set T_i as the temperature of the system at the beginning of the segment. Thus, we calculate the sum

$$\sum_i \frac{Q_i}{T_i} \quad (2.14)$$

over all segments of the path. The integral in (2.13) should then be understood as the limit of this sum when the number of segments grows without bound.

Let us demonstrate now that the sum in (2.14) is an approximation to the difference in entropy $S_B - S_A$, while the number of sections is finite, but which becomes exact in the limit as the number of segments becomes infinite. To this end, we chose a smooth and monotonic decreasing path. In the extreme points of the segments, we draw adiabatic curves. We focus next in a segment between two consecutive adiabatic lines as the one shown in Fig. 2.3. The initial and final point of the segment are I and F. The curves IG and HF are the two adiabatic lines and GH is the isotherm built in such a way that the work W_{IGHF} done by the system along the path IGHF equals the work W_{IF} along the path IF. Thus, the heat Q_{IGHF} received by the system along the path IGHF equals the heat Q_{IF} received along the segment IF. Indeed, from the energy difference between the states F and I,

$$U_F - U_I = Q_{IF} - W_{IF} = Q_{IGHF} - W_{IGHF}, \quad (2.15)$$

calculated along the paths IF and IGHF, we conclude that $Q_{IGHF} = Q_{IF}$ because $W_{IF} = W_{IGHF}$. But $Q_{IGHF} = Q_{GH}$, since IG and HF are adiabatic lines, so that

$$Q_{GH} = Q_{IF}. \quad (2.16)$$

From the definition of entropy, we see that the difference $S_F - S_I$ between the points F and I is given by

$$S_F - S_I = \frac{Q_{GH}}{T_G}, \quad (2.17)$$

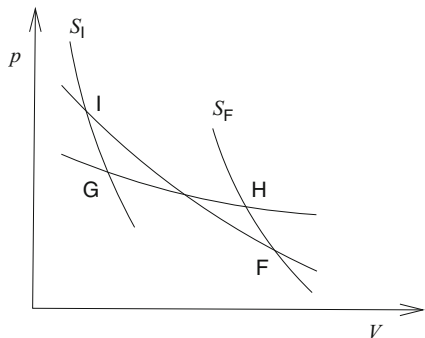
where T_G is the temperature corresponding to the isotherm GH. Therefore,

$$S_F - S_I = \frac{Q_{IF}}{T_G}. \quad (2.18)$$

Thus the entropy difference $S_B - S_A$ will be

$$S_B - S_A = \sum_i (S_F^i - S_I^i) = \sum_i \frac{Q_{IF}^i}{T_G^i}, \quad (2.19)$$

Fig. 2.3 The curve IF is a segment of a path in the Clapeyron diagram. The curves IG and HF are the adiabatic lines corresponding to the entropies S_I and S_F , respectively. The curve GH is an isotherm built in such a way that the works done by the system along the paths IGHF and IF are equal



where the summation is over all segments and the index i indicates that the quantities refer to the i -th segment. By construction, the expression (2.19) is exact, even for a finite number of segments. However, it cannot be identified with (2.14) because T_G^i and T_i are not equal, although $Q_{IF}^i = Q_i$. However, in the limit in which the number of segments increase indefinitely and the size of the segments decreases, T_G^i approaches T_i , and the two summations become equal in this limit and they are identified as the integral of expression (2.13).

2.2.3 Conservation of Energy in Differential Form

According to (2.18), the heat introduced along the segment IF is related to the entropy difference between the extreme points by

$$Q_{IF} = T_G(S_F - S_I). \quad (2.20)$$

The total heat Q introduced along the whole path is therefore given by

$$Q = \sum_i Q_{IF}^i = \sum_i T_G^i(S_F^i - S_I^i), \quad (2.21)$$

where the summation is over all segments of the path. In the limit where the number of segments grows without bounds, the summation becomes the integral

$$Q = \int TdS, \quad (2.22)$$

which extends along the path chosen between A and B. This equation says that the heat exchanged along a process is identified with the area under the corresponding trajectory in the T - S diagram.

Using (2.22) and (1.3), then the principle of conservation of energy can be written in integral form

$$\Delta U = \int TdS - \int pdV, \quad (2.23)$$

where ΔU is the internal energy difference between the points A and B, on the diagram S - V , and the integrals extends over any trajectory that connects these two points. Equivalently,

$$dU = TdS - pdV, \quad (2.24)$$

which is the equation of energy conservation in differential form. From this equation, we get

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad p = - \left(\frac{\partial U}{\partial V} \right)_S, \quad (2.25)$$

where the derivatives should be carried out keeping constant the variable that appears as an index.

2.3 Ideal Gas

2.3.1 Equation of State

All gases at sufficiently low densities behave similarly, irrespective of the type of molecules that they are composed. This behavior is called the ideal behavior and the gas is called an ideal gas. Therefore, an ideal gas must be understood as a shorthand for a gas in the regime of low densities.

If the temperature is kept constant, the pressure of an ideal gas is inversely proportional to the volume, that is,

$$p = \frac{A}{V}, \quad (2.26)$$

which is the Boyle law. Experimentally, one finds that the constant A is proportional to the temperature, which is the Gay-Lussac Law, so that we may write

$$p = \frac{BT}{V}. \quad (2.27)$$

The internal energy U of a gas which follows the law (2.27) is independent of the volume, depending only on the temperature. This independence on the volume was demonstrated experimentally by Joule by means of the free expansion of an ideal gas. In many cases the energy is linear with temperature, so that

$$U = CT, \quad (2.28)$$

where we arbitrarily set $U = 0$ for $T = 0$. If another behavior of the internal energy of an ideal gas is not explicitly stated, this means that we will be assuming the behavior given by (2.28).

To demonstrate that U depends only on the temperature, we use the equation (2.24) in the form

$$dS = \frac{1}{T}dU + \frac{p}{T}dV. \quad (2.29)$$

Since S is a state function, then dS is an exact differential and, therefore,

$$\frac{\partial}{\partial V} \left(\frac{1}{T} \right) = \frac{\partial}{\partial U} \left(\frac{p}{T} \right). \quad (2.30)$$

The right hand side of this equation vanishes because $p/T = B/V$ depends on V but not on U . Therefore, $1/T$ does not depend on V but only on U or, in other words, U depends on T but not on V .

Next, we examine the consequences of assuming that U depends only on temperature. This is to say that the left side of the equation (2.30) vanishes. Therefore, p/T depends only on V but not U . The equation of state (2.27) is therefore compatible with this result although not the most general equation.

2.3.2 Avogadro Hypothesis

Consider two vessels with distinct volumes containing different amounts of the same gas under the same temperature and pressure. Since the conditions are the same, then the ratio between the numbers of molecules in the containers must be equal to the ratio between the volumes. In other words, the number of molecules should be proportional to the volume. Bearing in mind that, from equation (2.27), B is proportional to the volume at T and p fixed, we then conclude that B is proportional to the number of molecules.

Using the standard for the number of molecules called mole, we may write $B = NR$ where N is the number of moles and R is the constant of proportionality. Therefore, for the gas we are considering, the following equation holds

$$p = \frac{NRT}{V}. \quad (2.31)$$

So far R is a constant which in principle should be different for each type of ideal gas. However, the Avogadro hypothesis implies that the constant R must be universal, that is, it must be the same for any gas at low densities. In fact, the Avogadro hypothesis states that equal volumes of distinct ideal gases under the same temperature and pressure contains the same number of molecules. This hypothesis implies, for instance, that the ratio NT/pV should be the same for any ideal gas.

But according to equation (2.31), this ratio is a constant R , which therefore, must be universal. It is called the universal gas constant and its value is

$$R = 8.314510 \text{ J/mol K.} \quad (2.32)$$

Under normal conditions of temperature and pressure, that is, under the pressure of 1 atm (101,325 Pa) and temperature of 0 °C, 1 mole of gas occupies a volume equal to 22.41410 dm³.

An argument similar to that used above leads us to conclude that the constant C that appears in equation (2.28) is also proportional to the number of moles, so that

$$U = NcT. \quad (2.33)$$

However, the constant c is not universal. For a monoatomic gas $c = (3/2)R$, for a diatomic gas $c = (5/2)R$.

An alternative form of presenting the internal energy of ideal gases that obey (2.33) is

$$U = \frac{c}{R}pV, \quad (2.34)$$

obtained from equations (2.31) and (2.33).

2.3.3 Adiabatic Curve

To determine the equation of an adiabatic curve, or isentropic line, in the Clapeyron diagram, we first calculate the differential dU from the equation (2.34),

$$dU = \frac{c}{R}(pdV + Vdp). \quad (2.35)$$

Substituting (2.35) in equation (2.29) we obtain

$$dS = \frac{c + R}{RT}pdV + \frac{c}{RT}Vdp, \quad (2.36)$$

or

$$dS = \frac{c}{RT}(\gamma pdV + Vdp), \quad (2.37)$$

where the constant γ is defined by

$$\gamma = \frac{c + R}{c}. \quad (2.38)$$

Along the isentropic line, S is constant so that

$$\gamma pdV + Vdp = 0. \quad (2.39)$$

Integrating this differential equation, we get

$$pV^\gamma = \text{const.}, \quad (2.40)$$

that gives the dependence of p on V along the adiabatic line of an ideal gas. The constant γ varies from one gas to another. For a monatomic gas, $\gamma = 5/3$ because $c = (3/2)R$ and for a diatomic gas, $\gamma = 7/5$ because $c = (5/2)R$.

2.3.4 Entropy

To determine the entropy of an ideal gas corresponding to a point in the Clapeyron diagram, we use the equation of state (2.31) to eliminate T in equation (2.37). Then we obtain the following equation

$$dS = Nc\left(\frac{\gamma}{V}dV + \frac{1}{p}dp\right). \quad (2.41)$$

Integrating this equation along a path formed by an isobaric line and by an isochoric line, starting from a reference point $O = (V_0, p_0)$, we find

$$S - S_0 = Nc\gamma \int_{V_0}^V \frac{1}{V}dV + Nc \int_{p_0}^p \frac{1}{p}dp, \quad (2.42)$$

or

$$S = S_0 + Nc\gamma \ln \frac{V}{V_0} + Nc \ln \frac{p}{p_0}, \quad (2.43)$$

where S_0 is the entropy of the reference point. But $V_0 = Nv_0$ and $S_0 = Ns_0$ are proportional to the number of moles N so that

$$S = Ns_0 + Nc\gamma \ln \frac{V}{Nv_0} + Nc \ln \frac{p}{p_0}, \quad (2.44)$$

equation that gives the entropy of an ideal gas as a function of volume, pressure and number of moles.

2.4 Cyclic Processes

2.4.1 Heat Engines

Consider a system composed of a fluid confined in a cylindrical vessel and suppose that initially it is a particular state. The fluid undergoes a process and returns to its

initial state. Suppose that the cyclic process is such that it performs some positive work, $W > 0$. In the Clapeyron diagram, this work corresponds to the area of the internal region of the cycle. As the fluid is back to the initial state, the change of internal energy is zero so that the work equals the total heat Q . This total heat is composed of the heat Q_R effectively received by the gas and the heat Q_C given away by the gas, that is, $Q = Q_R + Q_C$. But $Q_R > 0$ and $Q_C < 0$, so that $Q = Q_R - |Q_C|$. Therefore,

$$W = Q_R - |Q_C|. \quad (2.45)$$

Since $W > 0$, the heat received by the system is greater than the heat given away. Therefore, in this case, we can say that part of the heat received by the system becomes work and the other part is transferred to the outside. A heat engine works in this way, converting heat into useful work.

Because not all the heat effectively received by the system becomes work, it is important to know what fraction η of the heat received turns into work. This fraction is called the efficiency of the heat engine and is defined by

$$\eta = \frac{W}{Q_R}, \quad (2.46)$$

or

$$\eta = \frac{Q_R - |Q_C|}{Q_R} = 1 - \frac{|Q_C|}{Q_R}. \quad (2.47)$$

In general the efficiency is distinct for different cyclic processes and depends on the substance which runs the cyclic process.

The simplest heat engine is that operating according to a Carnot cycle. As we have seen, the Carnot cycle consists of four steps: (a) an isothermal expansion, at a temperature T_1 , in which the system receives a heat $Q_1 > 0$; (b) an adiabatic expansion; (c) an isothermal compression, at a temperature T_2 , in which the system yields a heat $Q_2 < 0$; and (d) an adiabatic compression. The system returns to its initial state, so that the work done $W = Q_1 + Q_2 = Q_1 - |Q_2|$. The temperature T_1 is greater than T_2 . Thus, in this cycle, the system receives an amount of heat Q_1 from a heat source at a higher temperature and gives off a smaller amount of heat to a heat sink at a lower temperature.

According to the Carnot principle, the ratio $|Q_2|/Q_1 = T_2/T_1$ is independent of the substance that undergoes the Carnot cycle. Therefore, the efficiency is

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}, \quad (2.48)$$

which is independent of the substance and depends only on the temperatures of the heat source and heat sink.

2.4.2 Otto Cycle

Let us examine a machine that operates with an ideal gas in a cycle called Otto cycle. It consists of four processes: (a) an isochoric compression from **A** to **B**, (b) an adiabatic expansion from **B** to **C**, (c) an isochoric decompression from **C** to **D**, and (d) an adiabatic contraction from **D** to the starting point **A**. In the calculations below we use the equation for the internal energy of an ideal gas in the form given by equation (2.34).

In the first process the gas receives an amount of heat Q_{AB} . As the gas does not perform work, then the heat is equal to the change of internal energy, that is,

$$Q_{AB} = U_B - U_A = \frac{c}{R} p_B V_B - \frac{c}{R} p_A V_A. \quad (2.49)$$

In the second process the gas performs a work W_{BC} . Because there is no heat exchange, then the work is equal to the decrease in energy, that is,

$$W_{BC} = U_B - U_C = \frac{c}{R} p_B V_B - \frac{c}{R} p_C V_C. \quad (2.50)$$

In the third process there is no work done, so that the heat in this process is given by

$$Q_{CD} = U_D - U_C = \frac{c}{R} p_D V_D - \frac{c}{R} p_C V_C. \quad (2.51)$$

Finally, in the last process there is no heat exchanged so that the work is

$$W_{DA} = U_D - U_A = \frac{c}{R} p_D V_D - \frac{c}{R} p_A V_A. \quad (2.52)$$

The efficiency will be then

$$\eta = \frac{W_{BC} + W_{DA}}{Q_{AB}} = \frac{p_B V_B - p_C V_C + p_D V_D - p_A V_A}{p_B V_B - p_A V_A}, \quad (2.53)$$

or

$$\eta = 1 - \frac{p_C V_C - p_D V_D}{p_B V_B - p_A V_A}. \quad (2.54)$$

Recalling that $V_B = V_A$ and $V_D = V_C$ then

$$\eta = 1 - \frac{V_C}{V_A} \frac{p_C - p_D}{p_B - p_A}. \quad (2.55)$$

Now, the points **A** and **D** are on the same adiabatic line so that $p_A V_A^\gamma = p_D V_D^\gamma$. Likewise, the points **B** and **C** are over the same adiabatic line so that $p_B V_B^\gamma = p_C V_C^\gamma$. Recalling that $V_B = V_A$ and $V_D = V_C$ and combining these two relations we get

$$\frac{p_D}{p_A} = \frac{p_C}{p_B} = \left(\frac{V_A}{V_C} \right)^\gamma. \quad (2.56)$$

Using these relations we obtain

$$\eta = 1 - \frac{V_C}{V_A} \frac{p_C}{p_B} = 1 - \left(\frac{V_A}{V_C} \right)^{\gamma-1}. \quad (2.57)$$

2.4.3 Refrigerators

If we run a heat engine in the reverse sense, then we are creating a refrigerator. For a better understanding, let us examine a Carnot cycle operated in the opposite direction. We start from a state corresponding to a temperature T_1 . First we perform an adiabatic expansion in which the system cools to a temperature T_2 smaller than T_1 . Then we go through an isothermal expansion at the temperature T_2 , the end of which the system will have received a heat $Q_2 > 0$. Then, the system is compressed adiabatically to the temperature T_1 . Finally, it is compressed isothermally at the temperature T_1 to the starting point. In this last stage it gives way a heat $Q_1 < 0$. The total work W is negative, which means that the system actually consumes work.

As the total energy change is zero, then $W = Q_1 + Q_2$, which can be written as

$$|W| = |Q_1| - Q_2, \quad (2.58)$$

so that the heat given way is greater than the heat received. However, the important point is that the system takes a certain amount of heat from a body at a lower temperature and reject a greater amount of heat to a body at a higher temperature.

The purpose of the refrigerator is to remove as much heat as possible for a given consumption of work. It is therefore convenient to define a performance coefficient ω of the refrigerator by

$$\omega = \frac{Q_2}{|W|} = \frac{Q_2}{|Q_1| - Q_2}, \quad (2.59)$$

where Q_2 is the heat extract from the colder body and W is the work consumed. Notice that Q_2 can be greater than $|W|$. Taking into account that for the Carnot cycle $|Q_1|/Q_2 = T_1/T_2$ then the performance coefficient for the cycle is

$$\omega = \frac{T_2}{T_1 - T_2}. \quad (2.60)$$

Paradoxically, a refrigerator may also function as a very efficient heater because the Q_1 rejected to the body at the higher temperature may be very large. It is at least greater than the work consumed.

Problems

2.1. Determine the work done, the absorbed heat, the energy variation and the change in entropy of an ideal gas undergoing the following processes. (a) Isothermal expansion at a temperature T between two states of volumes V_1 and V_2 . (b) adiabatic expansion from a state of volume V_1 and pressure p_1 to a state of volume V_2 . (c) Isobaric expansion at the pressure p between two states of volumes V_1 and V_2 . (d) Isochoric compression at the volume V between two states of pressures p_1 and p_2 .

2.2. An ideal gas goes from an initial state A whose pressure is p_0 and volume is V_0 to a final state B whose pressure is $2p_0$ and volume is $2V_0$, through two different processes comprising: (a) isothermal expansion to a point C followed by an isochoric increase of pressure, (b) an isothermal compression to a point D followed by an isobaric expansion. Represent the two processes in the Clapeyron diagram. Find the volume and the pressure of the point C and the point D. For each process, calculate for each section the work, the heat absorbed and the change in internal energy.

2.3. An ideal gas undergoes a Carnot cycle composed by (a) an isothermal expansion (AB) at a temperature T_1 , (b) an adiabatic expansion (BC), (c) an isothermal compression (CD) at a temperature T_2 and (d) an adiabatic compression (DA). Show that the volumes and the pressures of the four states A, B, C and D, satisfies the relations $V_C/V_D = V_B/V_A$ and $p_C/p_D = p_B/p_A$. Determine the work done and the heat exchanged in each section of the cycle. Show explicitly that the efficiency is given by $\eta = 1 - T_2/T_1$.

2.4. An ideal gas undergoes a cyclic process formed by an isobaric line (AB), an isochoric line (BC) and an isotherm (CA). Make a sketch of the possible cycles in the Clapeyron diagram. Determine the efficiency of a heat engine working according to the cycle such that the temperature T_B of state B is greater than the temperature T_A of state A, $T_B > T_A$.

2.5. Determine the efficiency of a heat engine that operates with an ideal gas in accordance with the Brayton-Joule cycle consisting of two adiabatic processes and two isobaric processes. Make a sketch of the cycle in the Clapeyron diagram.

2.6. Determine the efficiency of a heat engine that works with an ideal gas in accordance with the Diesel cycle composed by (a) an isobaric expansion, (b) an adiabatic expansion, (c) an isochoric decompression, and (d) an adiabatic compression. Make a sketch of the cycle in the Clapeyron diagram.

2.7. An ideal gas undergoes the cyclic transformation ABCA composed by an isochoric process (AB), an adiabatic process (BC) and an isobaric process (CA). Represent the cycle in the Clapeyron diagram given that the temperature T_B of B is greater than the temperature T_A of A, $T_B > T_A$. Show that the temperature T_C of C is related to T_A and T_B by

$$T_C^\gamma = T_B T_A^{\gamma-1}.$$

Determine the heat exchanged, the work done, the variation of the internal energy in each of the processes as well as the efficiency of a heat engine operating according to this cycle. Give the answers in terms of the temperatures of the three points.

2.8. An ideal gas undergoes a free expansion from a volume V_0 to a volume $2V_0$. Determine the variation of the entropy in this process.

2.9. Consider a straight line in the Clapeyron diagram passing through the point A and having a slope equal to $-\alpha < 0$. Suppose that an ideal gas undergoes an expansion along this straight line starting from point A. Determine the heat Q received by the gas as a function of the gas volume V . Plot Q versus V , indicating the interval in which the heat increases with volume and the interval in which it decreases with volume. Do the same with entropy.

2.10. In the Clapeyron diagram, consider the segment of a straight line connecting two points A and B found in the same adiabatic curve. The volume of A is smaller than the volume of B, that is, $V_A < V_B$. An ideal gas undergoes the cycle formed by the segment and the adiabatic curve. Initially, the gas expands from A to B along the straight line. Then, it is compressed adiabatically going back to the point A. Determine the efficiency of a heat engine operating according to this cycle.

2.11. Show that the efficiency of a heat engine working between two temperatures T_1 and T_2 in any cyclic quasi-static process is always smaller than the one operating according to a Carnot cycle between the same temperatures. The temperatures T_1 and T_2 must be understood as the maximum and minimum temperatures attained by the substances undergoing the cycle. Hint: plot the cycle in a T - S diagram and compare it with the Carnot cycle. Remember that in this diagram the heat exchanged is identified as the area under the trajectory and that the Carnot cycle is a rectangle.



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