9.2: The Carnot Cycle for an Ideal Gas and the Entropy Concept

Historically, the steam engine was the first machine for converting heat into work that could be exploited on a large scale. The steam engine played a major role in the industrial revolution and thus in the development of today's technology-intensive economy. It was important also in the development of the basic concepts of thermodynamics. A steam engine produces work when hot steam under pressure is introduced into a cylinder, driving a piston outward. A shaft connects the piston to a flywheel. When the connecting shaft reaches its greatest extension, the spent steam is vented to the atmosphere. Thereafter the flywheel drives the piston inward.

The economic viability of the steam engine derives, in part, from the fact that the spent steam can be vented to the atmosphere at the end of each cycle. However, this is not a necessary feature of heat engines. We can devise engines that alternately heat and cool a captive working fluid to convert heat energy into mechanical work. Stirling engines are practical devices of this type. A **Carnot engine** is a conceptual engine that exploits the response of a closed system to temperature changes. A Carnot engine extracts heat from one reservoir at a fixed high temperature and discharges a lesser amount of heat into a second reservoir at a fixed lower temperature. An amount of energy equal to the difference between these increments of heat energy appears in the surroundings as work.

For one cycle of the Carnot engine, let the heat transferred to the system from the hot and cold reservoirs be q_h and q_ℓ respectively. We have $q_h > 0$ and $q_\ell < 0$. Let the net work done on the system be w_{net} and the net work that appears in the surroundings be $\hat{w}_{net}$. We have

$\hat{w}_{net} > 0$, $\hat{w}_{net} = -w_{net}$, and $w_{net} < 0$. For one cycle of the engine, $\Delta E = 0$, and since

$$\Delta E = q_h + q_\ell + w_{net} = q_h + q_\ell - \hat{w}_{net},$$

it follows that $\hat{w}_{net} = q_h + q_\ell$. The energy input to the Carnot engine is q_h, and the useful work that appears in the surroundings is $\hat{w}_{net}$. (The heat accepted by the low-temperature reservoir, $\hat{q}_\ell = -q_\ell > 0$, is a waste product, in the sense that it represents energy that cannot be converted to mechanical work using this cycle. All feasible heat engines share this feature of the Carnot engine. In contrast, a perpetual motion machine of the second kind converts its entire heat intake to work; no portion of its heat intake goes unused.) The efficiency, ϵ, with which the Carnot engine converts the input energy, q_h, to *useful* output energy, $\hat{w}_{net}$, is therefore,

$$\epsilon = \frac{\hat{w}_{net}}{q_h} = \frac{q_h + q_\ell}{q_h} = 1 + \frac{q_\ell}{q_h}$$

We can generalize our consideration of heat engines to include any series of changes in which a closed system exchanges heat with its surroundings at more than one temperature, delivers a positive quantity of work to the surroundings, and returns to its original state. We use the Carnot cycle and the machine-based statement of the second law to analyze systems that deliver pressure–volume work to the surroundings. We consider both reversible and irreversible systems. We begin by considering reversible Carnot cycles. If any system reversibly traverses any closed path on a pressure–volume diagram, the area enclosed by the path represents the pressure–volume work exchanged between the system and its surroundings. If the area is not zero, the system temperature changes during the cycle. If the cycle is reversible, all of the heat transfers that occur must occur reversibly. **We can apply our reasoning about reversible cycles to any closed system containing any collection of chemical substances, so long as any phase changes or chemical reactions that occur do so reversibly**. This means that all phase and chemical changes that occur in the system must adjust rapidly to the new equilibrium positions that are imposed on them as a system traverses a Carnot cycle reversibly.

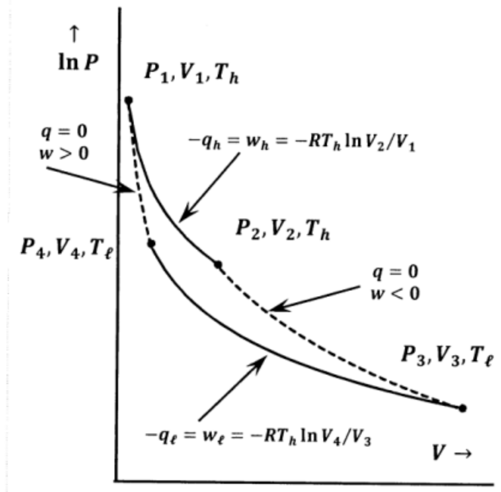

Figure 2. An ideal gas Carnot cycle. Note that the pressure axis is compressed: In *P* is plotted vs. *V*.

In Figure 2, we describe the operation of a reversible Carnot engine in which the working fluid is an ideal gas. We designate the system's initial pressure, volume, and temperature by P_1, V_1, and T_h. From this initial state, we cause the ideal gas to undergo a reversible isothermal expansion in which it absorbs a quantity of heat, q_h, from a high-temperature heat reservoir at $\hat{T}_h$. We designate the pressure, volume, and temperature at the end of this isothermal expansion as P_2, V_2, and T_h. In a second step, we reversibly and adiabatically expand the ideal gas until its temperature falls to that of the second, low-temperature, heat reservoir. We designate the pressure, volume, and temperature at the end of this adiabatic expansion as P_3, V_3, and T_ℓ. We begin the return portion of the cycle by reversibly and isothermally compressing the ideal gas at the temperature of the cold reservoir. We continue this reversible isothermal compression until the ideal gas reaches the pressure and volume from which an adiabatic compression will just return it to the initial state. We designate the pressure, volume, and temperature at the end of this isothermal compression by P_4, V_4, and T_ℓ. During this step, the ideal gas gives up a quantity of heat, $q_\ell < 0$, to the low-temperature reservoir. Finally, we reversibly and adiabatically compress the ideal gas to its original pressure, volume, and temperature.

For the high-temperature isothermal step, we have

$$-q_h = w_h = -RT_h \ln\left(\frac{V_2}{V_1}\right)$$

and for the low-temperature isothermal step, we have

$$-q_\ell = w_\ell = -RT_\ell \ln\left(\frac{V_4}{V_3}\right)$$

For the adiabatic expansion and compression, we have

$$q_{exp} = q_{comp} = 0$$

The corresponding energy and work terms are

$$\Delta_{exp} E = w_{exp} = \int_{T_h}^{T_\ell} C_V dT$$

for the adiabatic expansion and

$$\Delta_{comp} E = w_{comp} = \int_{T_\ell}^{T_h} C_V dT$$

for the adiabatic compression. The heat-capacity integrals are the same except for the direction of integration; they sum to zero, and we have $w_{exp} + w_{comp} = 0$. The net work done on the system is the sum of the work for these four steps, $w_{net} = w_h + w_{exp} + w_\ell + w_{comp} = w_h + w_\ell$. The heat input occurs at the high-temperature reservoir, so that $q_h > 0$. The heat discharge occurs at the low-temperature reservoir, so that $q_\ell < 0$.

For one cycle of the reversible, ideal-gas Carnot engine,

$$\epsilon = 1 + \frac{q_\ell}{q_h} = 1 + \frac{RT_\ell \ln(V_4/V_3)}{RT_h \ln\left(\frac{V_2}{V_1}\right)}$$

Because the two adiabatic steps involve the same limiting temperatures, the energy of an ideal gas depends only on temperature, and $dE = dw$ for both steps, we see from Section 9.7-9.20 that

$$\int_{T_h}^{T_\ell} \frac{C_V}{T} dT = -\int_{V_2}^{V_3} \frac{R}{V} dV = -R\ln\left(\frac{V_3}{V_2}\right)$$

and

$$\int_{T_\ell}^{T_h} \frac{C_V}{T} dT = -\int_{V_4}^{V_1} \frac{R}{V} dV = -R\ln\left(\frac{V_1}{V_4}\right)$$

The integrals over T are the same except for the direction of integration. They sum to zero, so that $-R\ln(V_3/V_2) - R\ln(V_1/V_4) = 0$ and

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Using this result, the second equation for the reversible Carnot engine efficiency becomes

$$\epsilon = 1 - \frac{T_\ell}{T_h}$$

Equating our expressions for the efficiency of the reversible Carnot engine, we find

$$\epsilon = 1 + \frac{q_\ell}{q_h} = 1 - \frac{T_\ell}{T_h}$$

from which we have

$$\frac{q_h}{T_h} + \frac{q_\ell}{T_\ell} = 0$$

Since there is no heat transfer in the adiabatic steps, $q_{exp} = q_{comp} = 0,$ and we can write this sum as

$$\sum_{cycle} \frac{q_i}{T_i} = 0$$

If we divide the path around the cycle into a large number of very short segments, the limit of this sum as the q_i become very small is

$$\oint \frac{dq^{rev}}{T} = 0$$

where the superscript "rev" serves as a reminder that the cycle must be traversed reversibly. Now, we can define a new function, S, by the differential expression

$$dS = \frac{dq^{rev}}{T}$$

In this expression, dS is the incremental change in S that occurs when the system reversibly absorbs a small of increment of heat, dq^{rev}, at a particular temperature, T. For an ideal gas traversing a Carnot cycle, we have shown that

$$\Delta S = \oint dS = \oint \frac{dq^{rev}}{T} = 0$$

S is, of course, the entropy function described in our entropy-based statement of the second law.

We now want to see what the machine-based statement of the second law enables us to deduce about the properties of S. Since the change in S is zero when an ideal gas goes around a complete Carnot cycle, we can conjecture that S is a state function. Of course, the fact that $\Delta S = 0$ around one particular cycle does not prove that S is a state function. If S is a state function, it must be true that $\Delta S = 0$ around any cycle whatsoever. We now prove this for any reversible cycle.

The proof has two steps. In the first, we show that $\oint dq^{rev}/T=0$ for a machine that uses any reversible system operating between two constant-temperature heat reservoirs to convert heat to work. In the second step, we show that $\oint dq^{rev}/T=0$ for any system that reversibly traverses any closed path.

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