

4.3: Concepts Developed with Carnot Engines

4.3.1 Carnot engines and Carnot cycles

Could the efficiency of the Carnot engine be different from the efficiency the heat pump would have when run in reverse as a Carnot engine? If so, either the supersystem is an impossible Clausius device as shown in Fig. 4.7(b), or the supersystem operated in reverse (with the engine and heat pump switching roles) is an impossible Clausius device as shown in Fig. 4.7(d). We conclude that *all Carnot engines operating between the same two temperatures have the same efficiency.*

This is a good place to pause and think about the meaning of this statement in light of the fact that the steps of a Carnot engine, being reversible changes, cannot take place in a real system (Sec. 3.2). How can an engine operate that is not real? The statement is an example of a common kind of thermodynamic shorthand. To express the same idea more accurately, one could say that all heat engines (real systems) operating between the same two temperatures have the same *limiting* efficiency, where the limit is the reversible limit approached as the steps of the cycle are carried out more and more slowly. You should interpret any statement involving a reversible process in a similar fashion: a reversible process is an idealized *limiting* process that can be approached but never quite reached by a real system.

Thus, the efficiency of a Carnot engine must depend only on the values of T_c and T_h and not on the properties of the working substance. Since the efficiency is given by $\epsilon = 1 + q_c/q_h$, the ratio q_c/q_h must be a unique function of T_c and T_h only. To find this function for temperatures on the ideal-gas temperature scale, it is simplest to choose as the working substance an ideal gas.

An ideal gas has the equation of state $pV = nRT$. Its internal energy change in a closed system is given by $dU = C_V dT$ (Eq. 3.5.3), where C_V (a function only of T) is the heat capacity at constant volume. Reversible expansion work is given by $\delta w = -p dV$, which for an ideal gas becomes $\delta w = -(nRT/V) dV$. Substituting these expressions for dU and δw in the first law, $dU = \delta q + \delta w$, and solving for δq , we obtain

$$\delta q = C_V dT + \frac{nRT}{V} dV \quad (4.3.4)$$

(ideal gas, reversible expansion work only)

Dividing both sides by T gives

$$\frac{\delta q}{T} = \frac{C_V dT}{T} + nR \frac{dV}{V} \quad (4.3.5)$$

(ideal gas, reversible expansion work only)

In the two adiabatic steps of the Carnot cycle, δq is zero. We obtain a relation among the volumes of the four labeled states shown in Fig. 4.3 by integrating Eq. 4.3.5 over these steps and setting the integrals equal to zero:

$$\text{Path B} \rightarrow \text{C}: \quad \int \frac{\delta q}{T} = \int_{T_h}^{T_c} \frac{C_V dT}{T} + nR \ln \frac{V_C}{V_B} = 0 \quad (4.3.6)$$

$$\text{Path D} \rightarrow \text{A}: \quad \int \frac{\delta q}{T} = \int_{T_c}^{T_h} \frac{C_V dT}{T} + nR \ln \frac{V_A}{V_D} = 0 \quad (4.3.7)$$

} Adding these two equations (the integrals shown with limits cancel) gives the relation

$$nR \ln \frac{V_A V_C}{V_B V_D} = 0 \quad (4.3.8)$$

which we can rearrange to

$$\ln(V_B/V_A) = -\ln(V_D/V_C) \quad (4.3.9)$$

(ideal gas, Carnot cycle)

We obtain expressions for the heat in the two isothermal steps by integrating Eq. 4.3.4 with dT set equal to 0.

$$\text{Path A} \rightarrow \text{B}: \quad q_h = nRT_h \ln(V_B/V_A) \quad (4.3.10)$$

$$\text{Path C} \rightarrow \text{D}: \quad q_c = nRT_c \ln(V_D/V_C) \quad (4.3.11)$$

The ratio of q_c and q_h obtained from these expressions is

$$\frac{q_c}{q_h} = \frac{T_c}{T_h} \times \frac{\ln(V_D/V_C)}{\ln(V_B/V_A)} \quad (4.3.12)$$

By means of Eq. 4.3.9, this ratio becomes

$$\frac{q_c}{q_h} = -\frac{T_c}{T_h} \quad (4.3.13)$$

(Carnot cycle)

Accordingly, the unique function of T_c and T_h we seek that is equal to q_c/q_h is the ratio $-T_c/T_h$. The efficiency, from Eq. 4.3.3, is then given by

$$\epsilon = 1 - \frac{T_c}{T_h} \quad (4.3.14)$$

(Carnot engine)

In Eqs. 4.3.13 and 4.3.14, T_c and T_h are temperatures on the ideal-gas scale. As we have seen, these equations must be valid for *any* working substance; it is not necessary to specify as a condition of validity that the system is an ideal gas.

The ratio T_c/T_h is positive but less than one, so the efficiency is less than one as deduced earlier. This conclusion is an illustration of the Kelvin–Planck statement of the second law: A heat engine cannot have an efficiency of unity—that is, it cannot in one cycle convert all of the energy transferred by heat from a single heat reservoir into work. The example shown in Fig. 4.5, with $\epsilon = 1/4$, must have $T_c/T_h = 3/4$ (e.g., $T_c = 300$ K and $T_h = 400$ K).

Keep in mind that a Carnot engine operates *reversibly* between two heat reservoirs. The expression of Eq. 4.3.14 gives the efficiency of this kind of idealized heat engine only. If any part of the cycle is carried out irreversibly, dissipation of mechanical energy will cause the efficiency to be *lower* than the theoretical value given by Eq. 4.3.14.

4.3.4 Thermodynamic temperature

The negative ratio q_c/q_h for a Carnot cycle depends only on the temperatures of the two heat reservoirs. Kelvin (1848) proposed that this ratio be used to establish an “absolute” temperature scale. The physical quantity now called **thermodynamic temperature** is defined by the relation

$$\frac{T_c}{T_h} = -\frac{q_c}{q_h} \quad (4.3.15)$$

(Carnot cycle)

That is, the ratio of the thermodynamic temperatures of two heat reservoirs is equal, by definition, to the ratio of the absolute quantities of heat transferred in the isothermal steps of a Carnot cycle operating between these two temperatures. In principle, a measurement of q_c/q_h during a Carnot cycle, combined with a defined value of the thermodynamic temperature of one of the heat reservoirs, can establish the thermodynamic temperature of the other heat reservoir. This defined value is provided by the triple point of H₂O; its thermodynamic temperature is defined as exactly 273.16 kelvins.

Just as measurements with a gas thermometer in the limit of zero pressure establish the ideal-gas temperature scale (Sec. 2.3.5), the behavior of a heat engine in the reversible limit establishes the thermodynamic temperature scale. Note, however, that a reversible Carnot engine used as a “thermometer” to measure thermodynamic temperature is only a theoretical concept and not a practical instrument, since a completely-reversible process cannot occur in practice.

It is now possible to justify the statement in Sec. 2.3.5 that the ideal-gas temperature scale is proportional to the thermodynamic temperature scale. Both Eq. 4.3.13 and Eq. 4.3.15 equate the ratio T_c/T_h to $-q_c/q_h$; but whereas T_c and T_h refer in Eq. 4.3.13 to the *ideal-gas* temperatures of the heat reservoirs, in Eq. 4.3.15 they refer to the *thermodynamic* temperatures. This means that the ratio of the ideal-gas temperatures of two bodies is equal to the ratio of the thermodynamic temperatures of the same bodies, and therefore the two scales are proportional to one another. The proportionality factor is arbitrary, but must be unity if the same unit (e.g., kelvins) is used in both scales. Thus, as stated in Sec. 2.3.5, the two scales expressed in kelvins are identical.

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