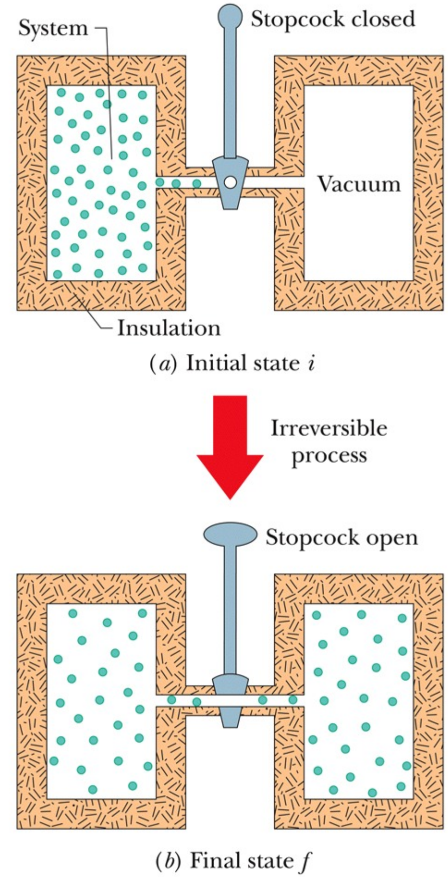
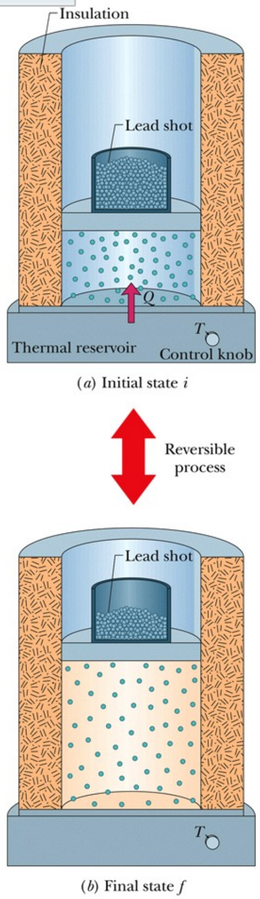
If a process occurs in a *closed* system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

The Second Law of Thermodynamics



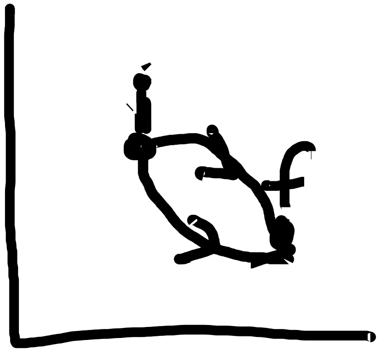
$$\Delta S \geq 0 \qquad \text{(second law of thermodynamics)},$$

where the greater-than sign applies to irreversible processes and the equals sign to reversible processes. Equation applies only to closed systems.



Entropy for ideal gas

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



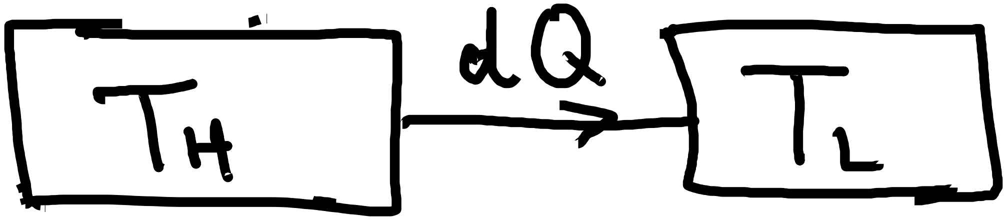
$$dQ = dE_{int} + PdV = nC_v dT + \frac{nRT}{V} dV$$

$$\frac{dQ}{T} = nC_v \frac{dT}{T} + nR\frac{dV}{V}$$

$$\Delta S = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$\boxed{S(T,V) = nC_v \ln T + nR \ln V + const}$$

Entropy change in heat transfer



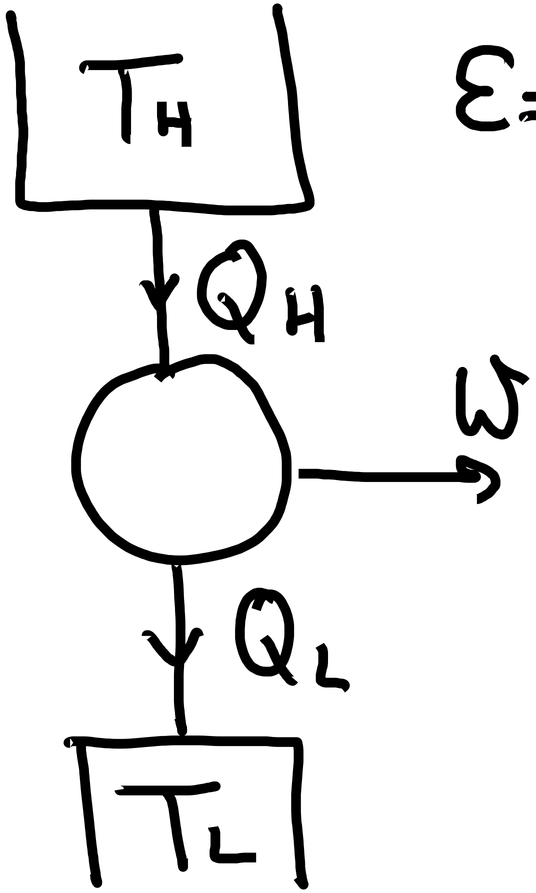
$$dS = -\frac{dQ}{T_H} + \frac{dQ}{T_L} = dQ\left(\frac{1}{T_L} - \frac{1}{T_H}\right) > 0$$

Heat engines

Learning Objectives

- **20.09** Identify that a heat engine is a device that extracts energy from its environment in the form of heat and does useful work.
- **20.10** Sketch a *p-V* diagram for the cycle of a Carnot engine, indicating the direction of cycling, the nature of the processes involved, the work done during each process , the net work done in the cycle, and the heat transferred during each process.
- **20.11** Sketch a Carnot cycle on a temperature–entropy diagram, indicating the heat transfers.
- **20.12** Determine the net entropy change around a Carnot cycle.
- **20.13** Calculate the efficiency ε_C of a Carnot engine in terms of the heat transfers and also in terms of the temperatures of the reservoirs.

Heat engine efficiency ε. Carnot engine



$$\varepsilon = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

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

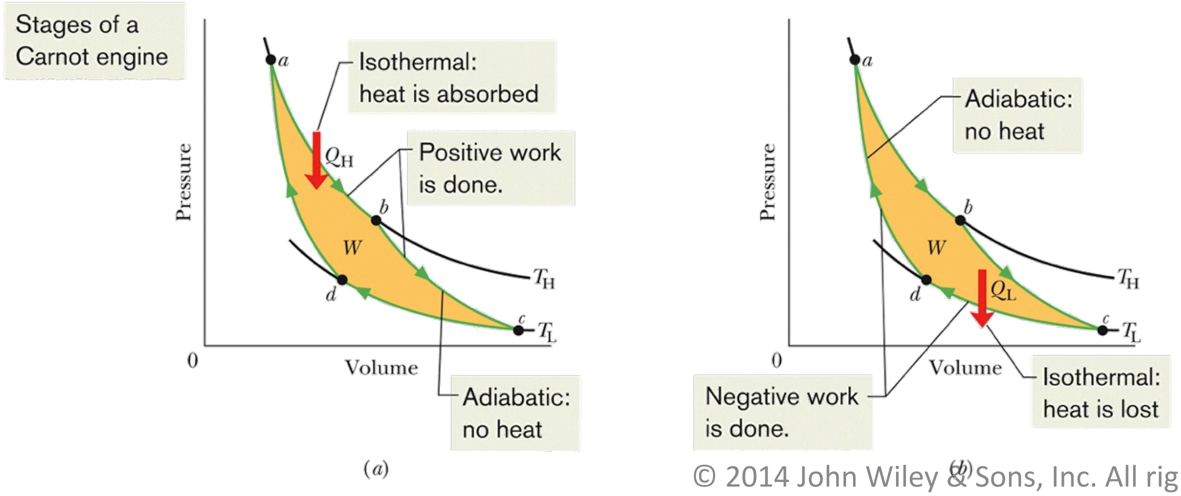
$$\Rightarrow \frac{|Q_L|}{|Q_H|} \geq \frac{T_L}{T_H}$$

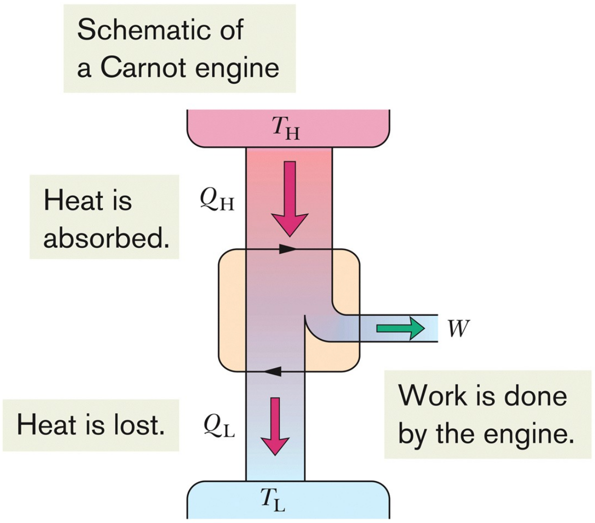
$$\Rightarrow \boxed{\varepsilon \leq 1 - \frac{T_L}{T_H}}$$

In an ideal engine, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence.

Carnot Engine

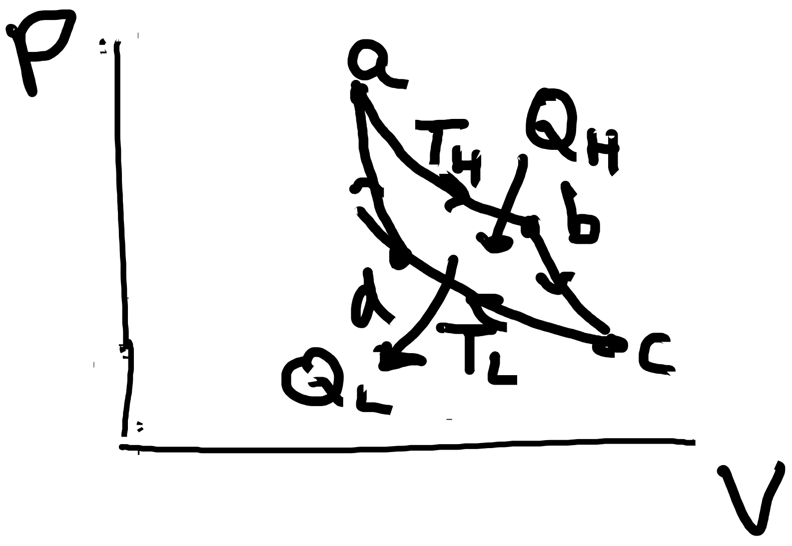
A pressure–volume plot (on the left) of the cycle followed by the working substance of the Carnot engine (on the right). The cycle consists of two isothermal (ab and cd) and two adiabatic processes (bc and da). The shaded area enclosed by the cycle is equal to the work W per cycle done by the Carnot engine.





The elements of a Carnot engine. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p-V plot.

Carnot cycle



$$Q_H = W_{ab} = nRT_H \ln \frac{V_b}{V_a}$$

$$Q_L = W_{dc} = nRT_L \ln \frac{V_c}{V_d}$$

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \frac{\ln V_b/V_a}{\ln V_c/V_d}$$

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$$

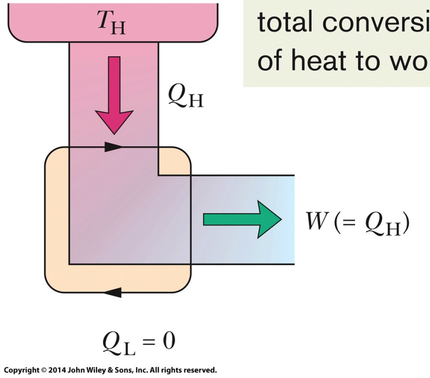
$$T_H V_a^{\gamma-1} = T_L V_d^{\gamma-1} \Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d} \Rightarrow$$

$$\Rightarrow \frac{\ln V_b/V_a}{\ln V_c/V_d} = 1 \Rightarrow \frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

No series of processes is possible whose sole result is the transfer of energy as heat from a thermal reservoir and the complete conversion of this energy to work.

fficiency of a Carnot Engine

Perfect engine: total conversion of heat to work



The elements of a perfect engine — that is, one that converts heat QH from a high-temperature reservoir directly to work W with 100% efficiency.

Efficiency of any engine:

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|}$$

Efficiency of Carnot engine:

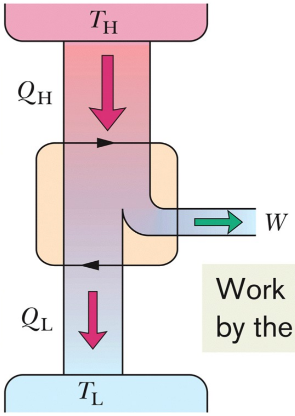
$$\varepsilon_C = 1 - \frac{T_L}{T_H}$$

Schematic of a Carnot engine

Heat is absorbed.

Heat is lost.

Work is done by the engine.



The elements of a Carnot engine. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p-V plot.

Learning Objectives (Continued)

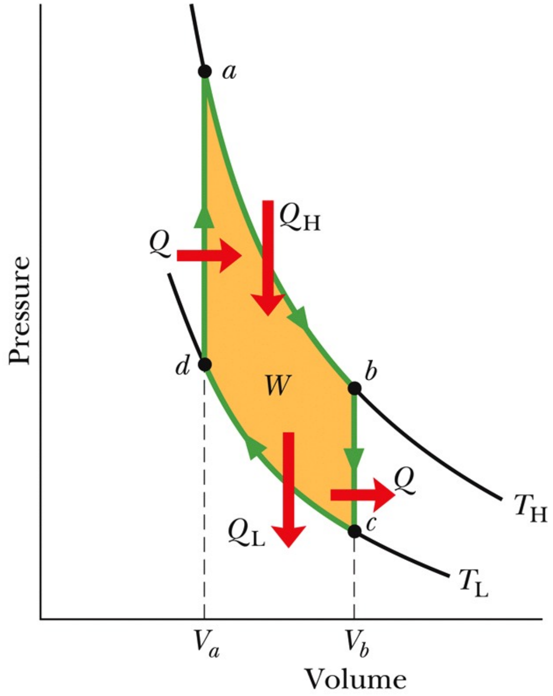
- **20.14** Identify that there are no perfect engines in which the energy transferred as heat Q from a high temperature reservoir goes entirely into the work *W* done by the engine.
- **20.15** Sketch a *p-V* diagram for the cycle of a Stirling engine, indicating the direction of cycling, the nature of the processes involved, the work done during each process (including algebraic sign), the net work done in the cycle, and the heat transfers during each process.

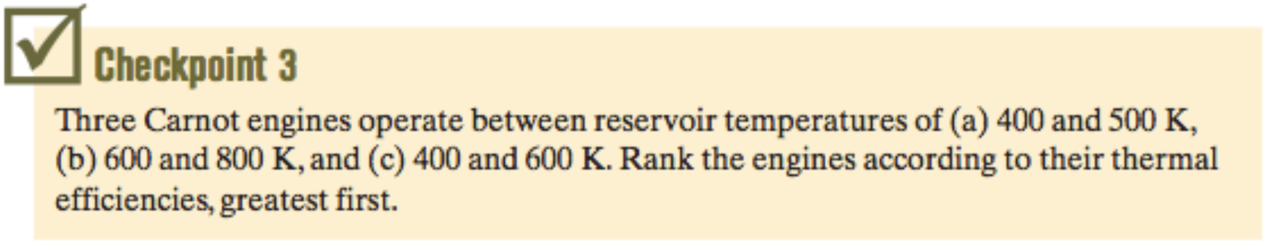
Stirling Engine

The Stirling engine was developed in 1816 by Robert Stirling. This engine, long neglected, is now being developed for use in automobiles and spacecraft.

Stages of a Stirling engine

A *p-V* plot for the working substance of an ideal Stirling engine, with the working substance assumed for convenience to be an ideal gas.





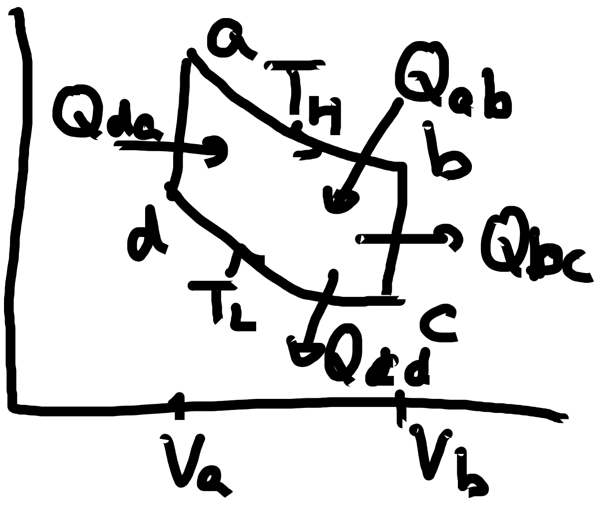
Checkpoint 3

Three Carnot engines operate between reservoir temperatures of (a) 400 and 500 K, (b) 600 and 800 K, and (c) 400 and 600 K. Rank the engines according to their thermal efficiencies, greatest first.

Answer: (c), (b), (a).

Stirling engine

$$\varepsilon = \frac{W}{Q_{abs}} = 1 - \frac{Q_{rel}}{Q_{abs}}$$



$$W = W_{ab} - W_{dc} = nR(T_H - T_L)\ln\frac{V_b}{V_a}$$

$$Q_{abs} = Q_{ab} + Q_{da} \ ; \quad Q_{ab} = W_{ab} = nRT_H \ln V_b/V_a$$

$$Q_{da} = nC_v(T_H - T_L) \Rightarrow Q_{abs} = nRT_H \ln\frac{V_b}{V_a} + nC_v(T_H - T_L)$$

$$\varepsilon = \frac{W}{Q_{abs}} = \frac{nR(T_H - T_L)\ln V_b/V_a}{nRT_H \ln V_b/V_a + C_v(T_H - T_L)}$$; dividing

$$\varepsilon = \frac{1 - T_H/T_L}{1 + C_v(T_H - T_L)/[T_H nR \ln V_b/V_a]} < 1 - \frac{T_H}{T_L}$$

Definition of Kelvin temperature scale

In a Carnot engine

$$\frac{Q_H}{Q_L} \equiv \frac{T_H}{T_L}$$

+ temp of triple point of water

$T = 273.16\ K$

defines Kelvin scale

Second law of thermodynamics

I. Can't have process that transfers heat from cold to hot and nothing else (no perfect refrigerator]

II. Can't convert heat to work using only one heat reservoir

$$\mathrm{I} \equiv \mathrm{II}$$

Refrigerators

Learning Objectives

- **20.16** Identify that a refrigerator is a device that uses work to transfer energy from a low-temperature reservoir to a high-temperature reservoir.
- **20.17** Sketch a *p*-*V* diagram for the cycle of a Carnot refrigerator, indicating the direction of cycling, the nature of the processes involved, the work done during each process, the net work done in the cycle, and the heat transferred during each process (including algebraic sign).
- **20.18** Apply the relationship between the coefficient of performance *K* and the heat exchanges with the reservoirs and the temperatures of the reservoirs.
- **20.19** Identify that there is no ideal refrigerator in which all of the energy extracted from the low-temperature reservoir is transferred to the high-temperature reservoir.
- **20.20** Identify that the efficiency of a real engine is less than that of the ideal Carnot

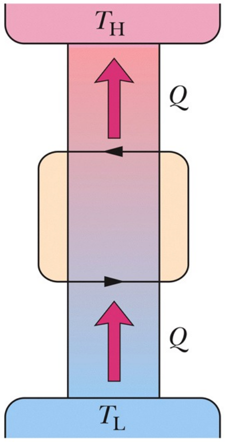
In an ideal refrigerator, all processes are reversible and no wasteful energy transfers occur as a result of, say, friction and turbulence.

Refrigerators

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|} \quad \text{(coefficient of performance, any refrigerator),}$$

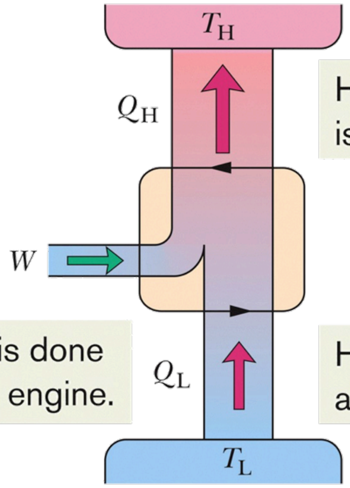
$$K_C = \frac{T_L}{T_H - T_L} \quad \text{(coefficient of performance, Carnot refrigerator).}$$

Perfect refrigerator: total transfer of heat from cold to hot without any work



The elements of a perfect refrigerator — that is, one that transfers energy from a low-temperature reservoir to a high-temperature reservoir without any input of work.

Schematic of a refrigerator



Heat is lost.

Work is done on the engine.

Heat is absorbed.

The elements of a refrigerator. Work W is done on the refrigerator (on the working substance) by something in the environment.